Aqueous methods for the cleaning of paintings

Richard C. Wolbers and Christopher Stavroudis, with revisions and additions by Matthew Cushman

30.1 Introduction

'Cleaning' a painting refers to the removal of any non-original material from the original paint surface created by the artist. Cleaning is most often undertaken to bring the appearance of the painting to a state visually appropriate and comparable to its appearance and effect when first created. This is often not fully possible due to irreversible changes in the paint itself on ageing and the nature of the interaction between soils, varnishes, or overpaints and the original paint surface. Cleaning is usually further complicated by the close solubilities of the materials used to create the painting with those used later in restoration campaigns. Cleaning often involves finding a means of dissolving or suspending one material without affecting the others by exploiting very subtle differences in chemistry, age, or arrangements within the materials.

Cleaning can be a difficult endeavour because most often the 'end point' is wholly visual and generally subjective; selective restraint is usually required in cleaning painted surfaces. Central concerns are efficacy and safety for the underlying film, but soil on a painted surface may be considered a valued visual aspect of the ageing process that appeals to aesthetic sensibilities. The complete removal of soiling materials may not be a desirable goal. The complete removal of varnish materials that have degraded (oxidised, discoloured) with age may also be problematic. The goal of discoloured varnish removal may be reduction rather than complete removal in some cases and in some geographical regions. (See also Chapter 27 on philosophical approaches to cleaning.)

Ethically and practically, painting conservators are constrained to employ cleaning methods and materials that are deemed consistent with professional guidelines for standards of practice; processes and materials should be 'reversible'. Removing old surface coatings cannot truly be 'reversible'; they cannot be replaced. However, 'reversibility' in cleaning can mean that cleaning, either with solvents or aqueous materials, should leave no residual material behind on the surface. Moreover, the process of cleaning must not damage or alter irreversibly the normal aged appearance of a painted surface; future treatment options should not be limited by present approaches. As in many areas of conservation, the materials and methods for carrying out these operations will constantly evolve as conservators and conservation scientists strive for more specificity and control.

Since the 1990s, more specifically 'engineered' aqueous cleaning methods have been developed, stemming from practical concerns such as: reducing toxicity, targeting certain soils, controlling processes, and providing greater safety for the underlying paint film. Few, if any, proprietary products have been manufactured

for this purpose. When aqueous cleaning materials are needed, the conservator usually prepares them on a case-by-case basis (Stavroudis, 2010). Shelf life, storage, and transportation are not major concerns; however, handling, formulation, and health and safety issues are important concerns regarding these aqueous cleaning materials that must be prepared by hand from stocks of acids, bases, buffers, and surfactants.

This chapter reviews the chemistry and properties of the most common aqueous materials currently in use in painting conservation for the removal of accrued soiling materials, degraded coatings (varnishes, etc), and more substantial materials such as restoration materials, retouchings, etc. Water can play a substantive role in all these activities. In the past, water-containing preparations were used almost exclusively to remove soils; however, since the 1990s, aqueous systems have been developed to aid in the removal of coatings, retouchings, and problematic materials such as highly oxidised varnish residues, drying-oil-based coatings, and other difficult materials. Technical language has concomitantly expanded to include the terms 'resin soaps', 'affinity surfactants', 'solvent-gels', etc. to describe these innovations.

30.2 Aqueous materials: removing soils

Removing soiling material adhered to the paint surface or 'surface cleaning' has probably been practised since antiquity. Historically, materials as wide-ranging as bread, spoiled wine, potatoes, garlic, simple soap preparations, chamber lye, and saliva have been used to reduce or remove accumulated soils on paint surfaces by combining mild abrasive materials with wet or water-containing substances, naturally occurring surfactants, and chelating materials.

All of these aqueous 'tools' together or separately form an effective array of materials to extend the possibility for soil removal under different conditions.

Critical factors in designing modern aqueous surface cleaning systems for painted surfaces

- Water purity (distilled, de-ionised, etc.)
- pH (acid, bases, buffers, etc.)
- Ionic species (specific ions, ionic strength)
- Surfactants (type and amount)
- Other 'adjuvant' materials (enzymes, 'redox' materials, preservatives etc.)
- Viscosity controlling materials (polymer type and amount)
- Solvents (water/oil (w/o), or oil/water (o/w) type emulsions, microemulsions)

30.2.1 Water quality, conductivity, pH, buffering

Water quality should be the highest possible. One should start with a 'blank slate' and add various other aqueous effects as needed for any given cleaning situation. One measure of purity is conductivity; conductivities as low as reasonably achievable (5–10 µS/cm) are usually possible even with low-cost lab- or studio-scale purification systems. Distillation, ion exchange systems, and reverse osmosis systems are all able to produce water of a quality that will be sufficiently pure for creating cleaning systems. The pH of pure water in air at standard temperature and pressure (20°C, 1 Atmosphere) might be close to 6.3 (a small amount of CO_2 usually dissolves in water under these conditions and forms carbonic acid H_2CO_3).

While water alone as a polar solvent (high hydrogen bonding and dipolar aspects) may solve some minor cleaning problems, it is often necessary to modify the chemistry and behaviour of water to successfully use it to best advantage in cleaning a painting. These modifications can involve adding ionic materials

and adjusting and regulating the pH through simple acid/base chemistry and buffering. Measuring and controlling both the pH and conductivity are easy, fundamental properties to manage, will limit swelling and damage to paint surfaces, and will allow other aqueous processes to work efficiently and predictably as well.

Ionic presence or strength is an intrinsic property of water that is a summing up of all of the ionic species in solution. Pure water has a very low ionic strength; the only ions in solution are 1×10^{-7} mol/L H^+ and 1×10^{-7} mol/L OH^- ions from the dissociation of water. As ionic materials (acids, bases, or salts) are dissolved in water, the dissociated ions are added into the mix of ions in the solution, and the ionic strength increases; its presence is often approximated (at least in dilute solutions) by measuring the electrical conductivity of the solution. Conductivity is the measurement of current (the transport of ions) passing through a specified volume of water. In water, the more ions that are in solution, the more that can carry a charge from one electrode to the other. While it is obvious that conductivity must relate to ionic strength, the relation between the two is not completely straightforward. At equal ionic strengths, ions with lower atomic weight will move through the water faster and more efficiently than ions with higher atomic weight. In reality, light ions such as H^+ from HCl will move much more directly from one electrode to another than, say, heavier ionic species like Na^+ ions from NaCl added to the water at the same molar concentration (as evidenced by the conductivity of 0.01 M solutions of HCl and NaCl, 4,118 μS/cm and 1,185 μS/cm, respectively (*CRC*, 2002, pp. 5–94).

Aqueous solutions that are 'isotonic' (i.e. the same 'tonicity' or ion concentration) to painted surfaces to be cleaned generally cause the least swelling and therefore the least damaging effects on the films. Soils, as well as pigments, binders, and other paint film and preparatory layer constituents, contribute to the overall ionic strength of surfaces when wet with water. Isotonicity is usually in the range of 50–300 μS for normal oil bond artists' paint; this number can vary because of the nature of the 'by-hand' preparation of artists' paints and because of the intrinsic variability (and sometimes poor quality) of the various pigments and additives used in manufacturing artists' paints (Wolbers, 2000: 116). This number also changes with artists' paint type. Acrylic dispersion paints, for instance, introduced into artists' repertoires by the 1950s, tend to exhibit much higher isotonic points (300–6000 μS/cm), largely due to the inherent incorporation of a variety of ionic materials, e.g. surfactants, thickeners, and other ionic species fundamental into those paint film types (Croll, 2007: 17). In terms of cleaning systems, 'hypertonicity' is generally considered to be at conductivities higher than about 10–20× the isotonic condition of these surfaces, and is generally avoided because of the substantial risk of swelling, the softening effect of hypertonic solutions on artists' oil paints, and the concomitant trapping and clearance problems that result from the absorption of cleaning materials into these softened films. 'Hypotonicity' (conductivity much *less* than the surface to be cleaned) is usually to be avoided as well; solutions constructed close ('close' would be considered $\pm$ 10 to 20× the surface conductivity) to isotonic are practically achievable and considered to be reasonable in terms of risk. Na^+, K^+, and NH_4^+ ions and their salts are often exploited in constructing cleaning solutions for solubility and clearance reasons; however, as mentioned above, all ionic materials (buffers, acids, bases, salts, etc.) contribute to the overall cleaning solution conductivity. Certain other ions should generally be avoided (e.g. Cl^- or NH_4^+) in cleaning solutions used on metallic powder paints due to the corrosion potential (Wolbers, 2008).

The pH of aqueous cleaning materials is easy and desirable to control, measure, and understand. pH is a measure of the hydrogen ion concentration in water expressed in 'p' or logarithmic notation; pH 7 is neutral. This value is a consequence of the thermodynamic dissociation constant of water. Concentrations higher in hydrogen ions are acidic (acids) and have a lower pH, and solutions with lower hydrogen ion concentrations (higher hydroxide concentrations) are alkaline (bases) and have pHs above 7. Adding acids or bases to a water solution will immediately change (lower or raise) the pH, and hence the H^+, and OH^- concentrations of the solution. These changes in H^+ and OH^- concentration can directly affect the solubility of soiling and paint materials. For a given acid group that is part of an organic material, the half equivalence point, equal to the pK_a, is the pH where half of the acid groups are de-protonated. If the pH is

raised, a greater percentage becomes ionised; if the pH drops below the pK_a, more of the acid groups will remain uncharged.

As organic materials age, they typically oxidise. The formation of acids (carboxylic acid groups) on organic materials, including soiling materials, is an inevitable consequence of oxidation. In the solvent world, increases in oxidation state tend to produce structures that typically require higher polarity solvents for dissolution. However, if they are sufficiently oxidised, the materials will have accumulated carboxylic acid functional groups. These acid groups can be de-protonated by aqueous solutions with higher pH values (above the pK_a of the acid groups present). Once de-protonated, an acid group becomes much more soluble in water. This increased solubility of a specific functional group can, in turn, increase the solubility of an entire molecule; therefore pH can be an exploitable property of aqueous cleaning solutions. If the rest of the molecule is sufficiently small or has a high enough polarity, the material can be brought into solution and removed by simply adjusting (raising) the pH. If, however, the pH of the cleaning solution is lowered, the now-dissolved component would be protonated, no longer be soluble in water, and would precipitate out of solution. This property could be used to keep certain materials out of solution and un-swollen in the presence of water. As such, the pH of a cleaning solution must be controlled in order to solubilise certain materials and not others. Buffering materials can help regulate the pH of aqueous solutions; buffers are weak acids or bases in solution, at pHs close (within about a unit or so) to their pK_a. At the pK_a of a buffer (the half equivalence point) there is a strong equilibrium between ionised and un-ionised buffer molecules in solution. Added H^+ ions tend to distribute themselves between ionised and un-ionised buffer moieties, and there is little change in the H^+ ion concentration in solution surrounding the buffer (hence the pH tends to stay the same or 'resist' change).

Oil films tend to exhibit pronounced swelling when exposed to aqueous cleaning solutions at pHs close to the pK_as of the free fatty acids present in the films (palmitic or stearic acid, for example, have pK_as between 4.75 and 4.95) and at the onset of saponification of the triglyceride materials that make up the film-forming materials (8.5–9.5) (Wolbers, 2000: 18). Consequently, buffers with pK_as within the range of about 5.5–8.5 can be used to stabilise the pH of aqueous cleaning preparations within this range. Both inorganic (carbonate (pK_{a1}), phosphate (pK_{a2})) and organic (Tris; triethanolamine; borate (pK_{a1}); citrate (pK_{a3}); and acetate, etc.) buffers can be used in these preparations. Generally, the amounts of buffer are commensurate with concentrations that yield ionic strengths near the isotonic point of the paint films. In practice, this amounts to buffer levels in the range of 25–50 mM. Table 30.1 represents a range of buffers and their useful pH range about each pK_a.

30.2.2   Surfactants

Surfactants with relatively low HLBs (12–20) ('hydrophile/lipophile balance' system, discussed in Section 30.3) should be chosen for aqueous cleaning solutions; often these are non-ionic structures such as Triton X-100, Ecosurf EH-6 and EH-9, Synperonic N (in Europe), Brij 35 and S-100, Tween 20 and 30, etc., due to their ease in formulation (Wolbers, 2000: 73). As non-ionics, they are more easily compatible with other common ionic materials such as buffers and chelators. The cloud points of these non-ionic surfactants (their limiting solubility temperature) tend to be well above room temperature to avoid phase separation and adsorption on to oil paint surfaces. These non-ionics are generally used in dilute ionic strength preparations and in the presence of mono-valent ions such as Na^+, K^+, NH_4^+, and triethanolate ion to avoid any substantial cloud point depression from divalent ions (SO_3^{-2}, CO_3^{-2}) (Wolbers, 2008). Higher HLB surfactants (anionic surfactants such as sodium lauryl sulphate (SLS, sodium dodecyl sulphate, SDS) and Vulpex) have been used by some conservators in the past. However, these materials tend to be rather strong solubilisers of hydrophobic paint film constituents (including the oil-binding materials themselves) and tend to be the strongest water/oil type emulsion formers. Hence they should probably be avoided, as prolonged contact with high-HLB surfactants will emulsify a water phase into artists' oil paints. Artists' oil paints are not impervious to water; they exhibit pronounced swelling and dissolution effects when exposed

Table 30.1 Common buffers, pK_as, and ranges for buffering effects

Buffer range	pK_a	Buffer
2.2–4.0	3.13	citrate (pK_{a1})
3.9–5.7	4.76	citrate (pK_{a2})
3.9–5.7	4.756	acetate
5.5–7.3	6.352	carbonate (pK_{a1})
5.5–7.3	6.40	citrate (pK_{a3})
6.3–8.1	7.21	phosphate (pK_{a2})
6.9–8.7	7.76	triethanolamine (TEA)
7.2–9.0	8.072	Tris
8.3–10.1	9.24	borate (pK_{a1})
9.4–11.2	10.329	carbonate (pK_{a2})

Note: citrate and phosphate ions are also chelating agents. Values taken from Modular Cleaning Program with permission.

to water-miscible solvent additions to aqueous preparations with strong or high HLB surfactants and at elevated ionic strengths and pHs.

Effective surfactant concentrations are determined by their CMCs (critical micelle concentrations, the concentration at which they begin to form micelles or solubilise materials), which vary with solution conditions (temperature, ion concentration, pH). Only a slight excess of surfactant beyond the CMC is needed for effective cleaning or solubilisation to take place (5× the CMC). Surfactant HLBs are generally kept as low as needed (in the range of 12–20) (Wolbers, 2008).

Deoxycholic acid, a bile acid, and the natural resin acids (abietic and alueritic acids) are known as 'affinity' surfactants (Wolbers, 2000: 39), i.e. surfactants that have been adopted because they can often solubilise specific substrate materials. Deoxycholic acid tends to bind specifically free fatty acids, and the latter two resin acids have been used to solubilise other di- and tri-terpenoid materials, based on their stereospecificity for these materials. Free fatty acids or their metal salts often comprise the weathering materials on oil paint surfaces; degraded di- and tri-terpenoids are often associated with natural resin varnishes, which have been applied to oil paintings for centuries as varnishes.
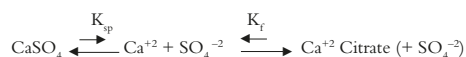
30.2.3   Chelators

Chelating materials are widely used in aqueous preparations for cleaning fine art surfaces. They function as aids in dissociating relatively low-solubility-product salts present in the form of soils or deterioration products from the paints themselves. (The 'p' notation indicates a logarithmic function; the higher the pK_{sp} number, the more insoluble a salt is in solution.) Chelators can also have an 'anti-biological' or preservative effect. However, it is the dissociative function that is most often exploited in terms of cleaning effects. Citric acid is used most often, but EDTA, HEDTA, DTPA, and NTA can also be effective. Their adoption follows from the specific formation constants required and the solubility products of the materials to be solubilised. (Note that several chelators are suspected human carcinogens and/or pose hazards to reproductive health and should be used with appropriate safeguards.)

Chelators generally work because they are water-soluble molecules that can attract and bind metal ions while remaining in solution even when associated or complexed with the metal ion. Chelators are usually molecules that carry very polar or multiple ionisable groups on their structure. Citrate, a good example of a chelator, contains three ionisable carboxylic acid groups and an additional -OH group. When at least two of the ionisable acid groups are above their pK_as (i.e. when they are fully ionised) both can attract the oppositely charged ion and hold on to it. The -OH group also helps attract and hold metals by sharing

un-bonded electrons on the oxygen in that group with the metal. The ability of a molecule such as citric acid to act as a chelator is pH dependent; citric acid as the free acid is virtually uncharged in solution (pH 2), but as the pH rises above the pK_a of each of the three acid groups present on the molecule (3.13, 4.76, 6.4), the force of attraction possible with metal ions increases dramatically. The force of attraction is usually expressed with a logarithmic 'p' number, the pK_f for the metal ion and the chelator. The pK_fs reach a maximum when all three acid groups on citrate are fully ionised (above a pH of 7.3). Every chelator is different; each has different pK_as and abilities to bind metals, but they all act in a similar fashion. Binding force is dependent on the number of available binding sites as a function of pH and the steric availability of those binding sites due to chelate structure (Wolbers, 2000: 109).

The pK_f for a given metal ion for a chelator must be larger (by an order of magnitude or so) than the pK_{sp} of the concomitant metal salt for complexation (and dissociation of the salt) to take place. $CaSO_4$ for example is only sparingly soluble in water; its pK_{sp} is 5.04: for each mole of $CaSO_4$, only 1×10^{-5} M will dissociate at standard temperature and pressure. The pK_{sp} is a logarithmic notation; as the number increases, the solubility of a salt at standard temperature and pressure decreases. Each unit increase means therefore a decrease in solubility by a factor of 10. Using a similar logarithmic notation, the affinity of a chelator for a metal ion increases as the pK_f goes up. For each unit increase in the pK_f, the strength of binding to the chelator goes up by a factor of 10. For chelation to take place, the K_f must be larger than the K_{sp}. For $CaSO_4$ to be solubilised by a chelator (in other words to move the reactions towards complex formation or to the right, below), K_f for citrate/calcium must be greater than the K_{sp} of $CaSO_4$:

$$CaSO_4 \quad \xrightleftharpoons[\quad]{K_{sp}} \quad Ca^{+2} + SO_4^{-2} \quad \xrightleftharpoons[\quad]{K_f} \quad Ca^{+2} \text{ Citrate } (+ SO_4^{-2})$$

The challenge is to select a chelator that can help dissociate a soil salt (surpass its pK_{sp}) but not be so strong as to dissociate pigments or other materials in paint films that must be retained. Table 30.2 provides typical pK_f values for fully ionised common chelators.

Table 30.3 provides pK_{sp} values for common white pigments for comparison.

Table 30.2 Common chelators and pK_f for selected metal ions

	EDTA	HEDTA	NTA	DTPA	Citrate
Ag(I)	7.32	6.71	5.2	8.61	7.1
Al(III)	16.5	14.4	11.4	18.7	
Ba(II)	7.81	6.2	4.80	8.78	
Ca(II)	10.61	8.2	8.76	10.75	4.68
Cd(II)	16.36	13.1	14.39	19.0	3.75
Co(II)	16.26	14.5	14.33	19.15	5.00
Cr(III)	23.40	14.4	>10		
Cu(II)	18.70	17.5	17.42	21.38	5.90
Fe(II)	14.27	12.2	12.8	16.4	4.4
Fe(III)	25.0	19.8	24.3	28.0	11.50
Hg(II)	21.85	20.05	14.6	26.4	10.9
Mg(II)	8.83	7.0	10.94	9.34	3.37
Mn(II)	13.81	10.8	10.94	15.51	4.15
Ni(II)	18.25	17.1	16.32	20.17	5.4
Pb(II)	17.88	15.5	11.34	18.66	4.34
Sn(II)	18.3				
Ti(III)	17.3		18.0	10.9	

Values taken from Modular Cleaning Program with permission

Table 30.3 pK$_{sp}$

Pigment	Formula	pK$_{sp}$
Titanium calcium white	TiO$_2$, CaSO$_4$	Insol., 4.58
Titanium dioxide (rutile)	TiO$_2$	Insol.
Titanium barium white	TiO$_2$•BaSO$_4$	Insol., 9.97
White lead (basic sulphate)	PbSO$_4$•PbO	7.79,
White lead (basic carbonate)	PbCO$_3$•Pb(OH)$_2$	13.13, 19.83
Lithopone	ZnS•BaSO$_4$	23.67, 9.97
Antimony oxide	Sb$_2$O$_3$	5.22
Zinc white	ZnO	7.64
Aluminum stearate	Al(C$_{18}$H$_{35}$O$_2$)$_3$	Insol.
Aluminum hydrate	Al(OH)$_3$	31.17
Gypsum	CaSO$_4$•2H$_2$O	4.58
Talc	Mg$_3$Si$_4$O$_{10}$(OH)$_2$	Insol.
Chalk	CaCO$_3$	8.32
Baryte	BaSO$_4$	9.97
Barium carbonate	BaCO$_3$	8.56
Lead stearate	Pb(C$_{18}$H$_{35}$O$_2$)$_2$	5.26

Values for common white pigments from the Modular Cleaning Program, with permission

30.2.4 Enzymes

Enzymes can be used as adjunct aqueous materials to facilitate the breakdown and solubilisation of selected biopolymers associated with coating, consolidation, and retouching materials. Enzymes can be selected to hydrolyse or break down the primary ester linkages in drying oils (lipases), the glycosidic linkages in starches (amylase), and the peptide bonds in proteinaceous materials (proteases) to facilitate removal from painting supports or surfaces.

Enzymes are catalysts; they can increase the speed of chemical reactions without undergoing any permanent chemical change themselves. They are neither used up in the reaction nor do they appear as reaction products. They facilitate reactions that are already favoured thermodynamically by lowering the activation energy required for the catalysed reaction to go forwards.

All known enzymes are proteins. They are high molecular weight compounds made up principally of chains of amino acids linked together by peptide bonds. Their molecular weights range from 10,000 to 2,000,000 Daltons (Wolbers, 2000: 128).

One of the properties of enzymes that make them attractive as reagents is the specificity they exhibit relative to the reactions they catalyse. A few enzymes exhibit absolute specificity; they will catalyse only one particular reaction. Other enzymes will be specific for a particular type of chemical bond or functional group. There are four types of specificity associated with enzyme catalysed reactions: absolute specificity (the enzyme will catalyse only one reaction), group specificity (the enzyme will act only on molecules that have specific functional groups), linkage specificity (the enzyme will act on a particular type of chemical bond regardless of the rest of the molecular structure), and stereo–chemical specificity (the enzyme will act on a particular steric or optical isomer).

Enzymes can be classified by the kind of chemical reaction catalysed. Hydrolases, for instance, are the enzymes used most often for conservation cleaning purposes. They catalyse the addition or removal of water. They include: esterases (e.g. lipase), carbohydrases (e.g. amylase or pullulanase), nucleases, deaminases, amidases, and proteases (e.g. trypsin or pepsin). Other reactions could be used to modify and help solubilise other materials. Other broad classes of enzymes include: hydrases (which catalyse the transfer of electrons),

Table 30.4 Common enzymes and their properties

Enzyme	Commercial example	Optimum pH	Optimum temperature	Specificity; co-factors
Lipase Type VI-S (Porcine pancreas)	Sigma-Aldrich L0382 ≥20,000 units/mg	7.7	37°C	Ca^{++} ion needed for activity
Lipase (Fungal; *Mucor miehei*)	Sigma-Aldrich L9031 ≥4,000 units/mg	7.7	37°C	Ca^{++} ion needed for activity
Lipase Type VII (Fungal: *Candida rugosa*))	Sigma-Aldrich L1754 ≥700 units/mg	7.2	37°C	Ca^{++} ion needed for activity
Pepsin (Porcine gastric mucosa)	Sigma-Aldrich P6887 3,200–4,500 units/mg	2.0–4.0	37°C	Cleaves C-terminal to Phe, Leu & Glu
Trypsin Type I (Bovine pancreas)	Sigma-Aldrich T8003 10,000 units/mg	7.6	25°C	Cleaves C-terminal to Arg & Lys
α-Amylase (*Bacillus lichenformis*)	Sigma-Aldrich A4551 500–1,500 units/mg	6.9	20°C	Cl^- ion needed for activity
β -Amylase Type I-B (Sweet potato)	Sigma-Aldrich A7005 ≥750 units/mg	4.8	20°C	Cl^- ion needed for activity

From the Modular Cleaning Program, with permission

oxidases (which promote oxidation/reduction type reactions), dehydrogenases (transfer of protons), lyases (transfer of functional groups), desmolases (cleavage of carbon-to-carbon bonds), isomerases (structural re-arrangements within molecules), and kinases (phosphorylases) (Wolbers, 2000: 129).

Enzymes are generally used only in aqueous solutions; their activity in solution in water is often sensitive to temperature, pH, specific ion concentrations, and can easily be denatured or rendered inactive on contact with air or through inadvertent drying. Enzymes can be denatured and precipitated with certain salts, solvents, and other reagents. Extremely high or low pH values usually result in complete loss of activity for most enzymes. (See Table 30.4 for some of the general properties of the enzymes that have been used for conservation treatments.)

Many enzymes require the presence of other compounds – co-factors – before their catalytic ability is manifested. This entire active complex is referred to as the 'holoenzyme', comprising an 'apoenzyme' (protein portion) plus any co-factor (coenzyme, prosthetic group, or metal-ion activator) required for its activity (de Bolster, 1997).

Enzymes are proteins; therefore the regimens for their extraction from their native biological sources (mammalian, bacterial, fungal cells, etc.) follow from normal biochemical techniques such as precipitation, column chromatography, electrophoresis, etc. The specific activity (the ability of the enzyme to carry out a specific reaction at a measured or assayable rate) is an important aspect of its purification. Most purification schemes tend to increase the specific activity per unit weight of protein as it is purified or separated from the other native materials around it (most often proteins). The level of activity needed for practical purposes is estimated to be about 1000 units of activity/ml of aqueous solution (based on a standard 'unit' of activity or SI unit of 1 μg/min of product produced by the enzyme at its optimum pH and temperature). Standardised dye-substrate molecules have been used to determine in-situ enzyme activity.

Enzyme reaction kinetics are consistent with their catalytic role. Michaelis–Menten (fullwiki.org, 2010) has shown that if the amount of the enzyme is kept constant and the substrate concentration is then gradually increased, the reaction velocity will increase until it reaches a maximum. After this point, increases in substrate concentration will not increase the overall velocity of the enzyme-catalysed reaction.

Enzymatically catalysed reactions are difficult or slow when substrate materials are solids ('out of solution' or 'un-available', 'inaccessible' etc.), which is often the case for the materials encountered in restoration (e.g. glues, pastes, or drying oils). Enzyme activity is slowed tremendously when other solutes or materials are in solution or are inter-mixed with the substrate material (e.g. the resin component in an oleo-resinous clear coating or binding material being treated with a lipase).

30.2.5   Oxidation/reduction reagents

Mild oxidants (or reductants) are not usually used in these preparations because of fear of altering the paint film constituents and their ageing, reactivity, etc. However, carbimide peroxide (5 per cent) and the peroxy compounds ammonium and sodium persulphate have been used to increase the water solubility of hydro-carbon materials accumulated on these surfaces (Wolbers, 2008). By oxidising accrued surface materials, their aqueous solubility can be dramatically increased. However, the use of mild oxidants on easily oxidised surfaces generally will involve some considerable risk due to the possible permanent alteration of binding and pigment materials.

30.2.6   Preservatives

Normally, anti-biologicals are not necessary for these solutions because of the small quantities involved and the rapid turnover of the preparations in normal use. However, propyl- and ethyl-parabens (food grade) can be used as preservatives, as can aromatic alcohols such as phenoxyethanol and benzyl alcohol. Anti-biologicals must not be reactive to paint film materials; formaldehyde-generating materials such as the hydantoins, azides, and halogenated materials should be avoided (Wolbers, 2008).

30.2.7   Thickeners

Aqueous thickeners increase rheological control over aqueous preparations: they inhibit but do not eliminate the penetration and diffusion of water and aqueous soluble materials into paint; they limit spreading (dripping, running) over surfaces; they slow the evaporation of volatiles from gelled preparation; they can increase dwell or contact time on surfaces; they can act as adjuvants (soil suspension aids) to facilitate detergency; and the polyanionic thickeners can additionally act as weak complexing agents. Thickening agents in paintings conservation have been drawn from a range of commercially available gums or polysaccharides (xanthan gum, agarose), various cellulosic derivatives [methyl cellulose (MC), ethyl cellulose (EC), hydroxy ethyl cellulose (HEC), hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC), carboxy methyl cellulose (CMC)), and polymeric materials: (polyacrylates (PAA), polyacryl-amide (PAM), and co-polymers of PAA-PAM].

Methylcellulose is manufactured by reacting alkali cellulose with methyl chloride. Methyl substitutions can occur at the 2, 3, and 6 alcohols of cellobiose; the degree of substitution (DS) for the methylation reaction is expressed as the average number of methyl groups reacted per cellobiose unit (i.e. from 0–3). Hydroxypropylmethyl cellulose can be manufactured in essentially the same way: by adding both pro-pylene oxide and methyl chloride to alkali cellulose in various proportions. Of the cellulose ethers, HPMC is the most common gelling agent used in aqueous conservation cleaning preparations, followed closely by MC. Both have lent themselves to 'by-hand' or bench formulations because they are readily soluble in water at room temperature, are neutral (will not alter pH and ionic strength of solutions), and can tolerate wide pH and electrolyte conditions.

Commercial HPMCs are available with widely varying weight per cent methoxy (17–30 per cent) and hydroxylpropyl (4–32 per cent) substitution levels, as well as cellulose chain lengths (see Table 30.5). At the highest substitutions of these hydrophobic groups, water-miscible organic solvents and alcohols can be

Table 30.5 Commercial cellulosic ethers: solution properties

Product	Manufacturer	MC content weight percent	HP content weight percent	Viscosity 2 per cent solution at 20°C
Methocel A15	Dow	27.1–31.1	0	15 cP
Methocel E50	Dow	28–30	7–12	50 cP
Methocel E4M	Dow	28–30	7–12	4,000 cP
Methocel E10M	Dow	28–30	7–12	10,000 cP
Methocel K15M	Dow	19–24	7–12	15,000 cP
Methocel K100M	Dow	19–24	7–12	100,000 cP
Benecel Type A	Hercules/Aqualon	27.5–31.5	0	15–3,600 cP
Benecel Type F	Hercules/Aqualon	19–30	3–12	40–14,000 cP
Benecel Type K	Hercules/Aqualon	20–24	7–12	80–280,000 cP
Benecel Type E	Hercules/Aqualon	28–30	7–12	40–14,000 cP

Values taken from Modular Cleaning Program with permission

Table 30.6 Recommended thickeners with various surfactant types

Surfactant	Cellulosic ether
Alkyl ether sulfonates; Fatty acid soaps; 'Resin soaps' (affinity surfactants)	HPMC
Alkyl sulphates	HEC
Amphoterics	HPC
Non-ionics	HPMC; MC; HEC

Values taken from Modular Cleaning Program with permission

tolerated (75 per cent v/v). Higher methyl and hydroxypropyl substitutions impart a higher surface-active property to these polymers in solution (HPMC solutions for instance, can exhibit a surface tension of between 45–51 dynes/cm). Lower substitution cellulosics are generally preferred over higher ones for gelation of aqueous cleaning mixtures due to concern over clearance of the polymers from hydrophobic (e.g. oil or alkyd) paint surfaces. While the gelation (flocculation) temperature for these cellulosic derivatives is in the range of 60–90°C, for the cleaning of painted surfaces, they are most often used at ambient temperatures. HPCs generally have the lowest flocculation temperature of the listed cellulosics (40–45°C) and are generally not used because of the low flocculation temperature and high adsorption onto hydrophobic surfaces.

Cellulosic ethers tend to act as adjuvants to surfactants; they act as both suspension aids (through weak complexation effects to metal and metal oxides in solution) and as neutral materials that will not generally alter surfactant cloud points or precipitate anionic or cationic surfactants.

Generally, the cellulosic ethers used most often with specific classes of surfactant are summarised in Table 30.6.

Carboxymethyl celluloses (CMCs) are anionic polymers that combine methyl and carboxylate substitution groups on cellulose. The degree of substitution (DS) for common commercially available products is between 0.4 and 1.4 (below a DS of 0.3, CMC is soluble only in alkaline solutions). Because they can impart thixotropic properties to aqueous solutions and are ionic in nature, CMCs tend to exhibit better flow properties in cleaning mixtures and higher complex formation (higher binding constants) for metals and metal oxides in solution than the neutral cellulosic ethers. Because of their anionic character, CMCs are not generally used with amphoteric or cationic surfactants.

Table 30.7 CMC grades and viscosities

Product	Manufacturer	Weight percent Na	Viscosity 2 per cent solution at 20°C
FLX	Anqiu Eagle		25–40 cP
FMX	Anqiu Eagle		400–2,000 cP
Blanose 7m31C	Hercules/Aqualon	7.0–8.9	1,500–3,100 cP
Blanose 12m31P	Hercules/Aqualon	10.2–10.8	1,500–3,100 cP
CA-192	Spectrum		400–800 cP

Values taken from Modular Cleaning Program with permission

Table 30.8 Gel properties of xanthan gum (Vanzan)

Material	Concentration (w/v)	Viscosity retained after 3 months
Acetic acid	20%	75%
Citric acid	20%	80%
Sulfuric acid	10%	85%
NaCl	20%	105%
KCl	20%	105%
$MgSO_4$	20%	105%
$CaCl_2$	20%	110%

Values taken from Modular Cleaning Program with permission

Xanthan gums have also been adapted for aqueous rheological purposes in conservation cleaning applications. Xanthan gums are cellulosic backbone polymers that are substituted with mannose acetate/glucuronic acid/mannose tri-saccharide side groups. The end mannose unit on the tri-saccharide is often substituted (60 per cent on average) with an additional pyruvate group. The pyruvate/glucuronate combination imparts an overall anionic character to the native polymers. The polymer is usually derived from the growth medium of the bacterium *Xanthomonas campestris* as an exudate from the bacterium.

Xanthan gums are attractive as gelling agents due to their ability to form highly viscous gels at relatively low concentrations (0.5–2 per cent w/v). They also exhibit an unusually high tolerance to: mineral acids, high concentrations of chelates, and a wide range and concentration of inorganic salts. These properties make them useful on wall paintings and other complex inorganic support materials (see Table 30.8). Additionally, entangled, amorphous branches within the structure of a xanthan gum solution provide hydrophobic pockets within the gelated structure, allowing for the stabilisation of solvents that are not miscible with water. For example, a typical 2 per cent w/v xanthan gum gel at pH 6 can hold approximately 20 per cent w/w of a non-miscible solvent.

The inherent pH of the commercial Xanthan gums (Vanderbilt Chemical Co: Grades NF, NF-F, and NF-C) is nominally between 6 and 8 without adjustment with additional acids, bases, or buffers. A typical 1 per cent (w/v) solution of the Vanzan −NFC (Personal Care/Pharmaceutical grade, which yields a clear gel at 25°C) might be in the range of 1300–1700 cP.

Polyacrylates of various types are also useful as aqueous gelling materials. The Carbopols (Noveon/Lubrizol's 934, 940, and 941) were the first in this class of materials to be introduced to conservation cleaning applications (Wolbers, 2008). These are lightly cross-linked polyacrylic acid polymers (PAA) that

Table 30.9 Gel properties of various polyacrylates

Polyacrylate	Concentration % (w/v)	pH	Viscosity at 25°C
Carbopol 934	0.2	7.5	2,500–5,450 cP
	0.5		30,500–39,400 cP
Carbopol 940	0.05	7.5	19,000–35,000 cP
	0.2		40,000–60,000 cP
	0.5		45,000–80,000 cP
Carbopol 941	0.05	7.5	700–3,000 cP
	0.2		1,950–7,000 cP
	0.5		4,000–10,000 cP
Ultrez 10	0.5	7.5	45,000–65,000 cP
Ultrez 20	1.0	6	55,000 cP
Ultrez 21	0.5	7	60,000 cP
ETD 2020	1.0	7.5	47,000–77,000 cP
ETD 2050	0.05	5.8–6.3	700–3,000 cP
	0.2		4,000–9,000 cP
	0.5		8,500–16.500 cP
Carbopol EZ-4	10.	7.7	47,000–67,000 cP
Pemulen TR-1	0.2	7.3–7.8	6,500–15,500 cP
Pemulen TR-2	0.2	7.3–7.8	1,700–4,500 cP

Values taken from Modular Cleaning Program with permission

contain varying poly alkenyl polyether bridges or cross-links (alkyl ethers of sucrose (934); or alkyl ethers of pentaerythritol (940, 941)). They can be neutralised with a variety of common bases (NaOH, KOH, triethanolamine) to produce highly viscous, crystal-clear gels. They tend to gel over a well defined but broad pH range (6–10). This same polyacrylate chemistry is also present in the 'easy-to-disperse' versions of these polyacrylates (Noveon/Lubrizol's ETD 2020 and 2050; and Carbopol EZ-4). These C10-C30 polyacrylate/PAA co-polymers/cross polymer preparations are manufactured for easier dispersal with the inclusion of proprietary surfactant materials. The 'rapid or self-swelling' versions of these C10-C30 polyacrylate co-polymers (Noveon/Lubrizol's Ultrez 10, 20, and 21) have also been used for this purpose. The addition of amines to PAA gels is a means of providing a stable bridge between the acid groups on the polymeric network and a solvent phase, producing what has traditionally been referred to as a 'solvent gel' in the field.

The advantages of these gelling materials include their ability to form clear, extremely viscous gels. But as well, these materials can act efficiently as suspension aids and weak chelating materials (in a manner similar to other polyanionics such as CMC). The pKa (≈6.0) for these polyacrylates is also an advantage when used on oil paints that tend to evolve more acidic (lower pK_a) fatty acids as they break down (stearic acid pK_a = 4.75; palmitic acid pK_a = 4.95).

Recent additions to the arsenal of polyacrylate thickeners for aqueous preparations include the Noveon/Lubrizol materials Pemulen TR-1 and TR-2. These are again C10-C30 polyacrylate/PAA co-polymers/cross polymer preparations, with the added feature that the C10-C30 acrylate groups are 'blocked' or grouped in such a way that the polymers can create hydrophobic 'pockets' and can also act as emulsifiers. TR-1, for instance, at low concentrations (1.0 per cent), can hold up to 30 per cent by weight emulsified 'oil' phase materials as stable dispersions within the gel structure. TR-2 can hold up to 80 per cent. An advantage of these highly viscous gels is that they can create stable oil-in-water-type dispersions without the addition of surfactants. They can easily be combined with Carbopols to increase viscosity if needed.

Case study 30.1: The use of aqueous surface cleaning mixtures to clean a nineteenth-century landscape by American artist Maurice Braun
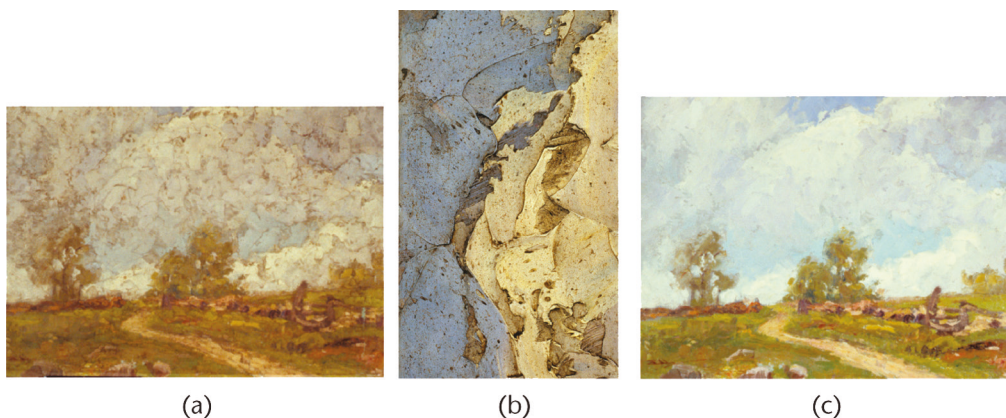

(a)   (b)   (c)

Figure 30.1   A nineteenth-century landscape by American artist Maurice Braun. (a) Before treatment. (b) Detail, UL. (c) After treatment

Source: Courtesy of Winterthur/UD Program in Art Conservation

Formula

100 ml De-ionised water
0.05 ml Triton XL-80N (HLB=12.5)
0.1 g NH_4Cl
1 g $(NH_4)_2H$ citrate
0.75 ml triethanolamine
(pH to 8.5 with 1M HCl)
1.5 g methylcellulose (Benecel Type A)

While this is an older treatment, it shows that the basic ideas worked out in the mid-1980s remain current. Water is the 'workhorse' in this mixture for removing soiling materials. The pH is slightly elevated (8.5) to solubilise as much soiling material as possible while still minimising the risk of swelling or saponification of the oil paint itself. Triethanolamine (pK_a=7.76) is used as the general buffer in this preparation to maintain the desired pH in contact with the paint surface.

    This preparation was adjusted to a reasonable conductivity (about 6000 μS), which is just slightly hypertonic to the oil paint surface to be cleaned. Ammoniate ion is the primary contributor to building and adjusting the conductivity aided by both the particular citrate salt used (di-ammonium citrate) and NH_4Cl added to the mixture. Citrate acts as a chelator at this pH and will help solubilise some of the metal salts present on the paint surface from the deteriorating ground and paint (pigment) materials.

    Generally these surface cleaning preparations do not require a surfactant; however, one is included here with an HLB of about 12 (just strong enough to help solubilise soiling materials that are not soluble at this pH and with citrate, but not so strong – higher HLB – as to begin to solubilise oil paint film constituents or to emulsify water into the paint film and cause blanching).

As a non-ionic, Triton XL-80N is compatible with the other ingredients in this preparation and should be used at about 5× its CMC. (The recipe above has been modified because the value for the CMC of Triton XL-80N was not known previously. As used and originally published, the Triton concentration was 0.5 per cent, which is 50× the CMC.)

A low concentration of methylcellulose was added to help thicken the mixture and control the penetration and the spreading of the cleaning mixture over the paint surface. The methylcellulose is neutral and is also compatible with the other ingredients, including the Triton XL-80N.

The landscape painting pictured here was surface cleaned of soils by raising and holding the pH to 8.5 with the adjutancy of a weak surfactant and weak chelator. All of the applied materials are, by definition, water soluble, and can be removed with a water rinse; however, the use of organic bases in particular (ammonia, TEA) for buffering and other materials allows for an additional clearance method with aliphatic hydrocarbon solvents if needed (Wolbers, 1992: 74).

Case study 30.2: The use of an enzyme-containing aqueous cleaning solution: *Portrait of Anne Ross Hopkins* (1801) by Jacob Eichholtz

(a)   (b)   (c)

Figure 30.2   Portrait of Anne Ross Hopkins (1801) by Jacob Eichholtz.

(a) Cleaning tests, LCR. (b) After oil removal. (c) Detail after removal of a linseed oil coating, showing preservation of fine details under a remaining original varnish

Source: Courtesy of Winterthur/UD Program in Art Conservation

Formula

100 ml de-ionised water
1g lipase type VII (Sigma 1000 U/mg)
0.1 ml Triton X-100

500 mg Tris-HCl pH 8.4

1.6 g hydroxypropyl methylcellulose (4000 cP)

Commentary

This is an example of an aqueous cleaning solution that contains an enzyme (lipase) in its formula to aid in the breakdown of oily surface materials that might otherwise be hard to solubilise directly in water. The particular enzyme was chosen for its concentration (a high enough purity and specific activity per unit weight) and for the conditions it will be expected to work under. The 'Type VII' lipase has a high specific activity (1000 U/mg) and optimally breaks down or hydrolyses triglycerides (such as linseed oil structures that might be present) at around a pH of 8.0 and at room temperature. Tris is a convenient buffer to use to help maintain a pH of 8.4 (pK_a Tris-HCl = 8.1) in this system. To improve on the original formulation, a surfactant, 2% sodium deoxycholate, a natural bile acid (which cooperatively works with the lipase in solution to sequester the fatty acid hydrolysis products generated by the enzyme as it breaks down triglycerides, without denaturing the enzyme itself) would be added to the system.

A common neutral gelling agent, methylcellulose, is used to both thicken the aqueous mixture and to help suspend the enzymatic products without denaturing or interfering with the enzyme doing its work. It may seem counter-intuitive, but while this kind of preparation works well to break down oily triglyceride coating materials (e.g. oil varnishes), it is particularly weak in doing so with oil-bound paints. Pigmented oil films are poor substrates for enzymatic reagents to break down, largely due to the decreased availability of the oil binding material in densely pigmented film and the general denaturing effects of the pigments them- selves on proteins in solution.

In the case of the portrait cleaning, the enzyme preparation was used to remove an essentially pure lin- seed oil coating applied liberally over a thinly varnished early nineteenth-century American portrait. This could be carried out without disrupting the original varnish beneath and without affecting the oil paints of the portrait itself (Wolbers, 2000: 139).

30.3   Varnish removal and cleaning sensitive surfaces using aqueous systems

30.3.1   Introduction

The removal of discoloured varnish layers is often imprecisely referred to by the generic term 'cleaning' (in the UK and USA for instance), while in other countries, the terms 'varnish removal', 'reduction', or 'de-varnishing' have been the norm (in France and Italy, etc.) to describe this activity. The stereotypical cleaning of a painting involves the removal of a discoloured varnish from the surface of an oil-and-pigment film using organic solvents. Historically, varnishes were based on natural resins dissolved in a carrier solvent system and applied to the surface of the painting some months after the painting had been finished (see also Chapter 11 on varnish history and Chapter 31 on solvent cleaning). Initially, varnish is readily soluble in mild (aliphatic, aromatic) solvents so that it can be safely applied by brush to the partially dried (but often not completely cured) paint surface.

As discussed in other chapters, over time, the varnish resins oxidise and yellow due in large part to photo-oxidation-induced reactions. As natural resin varnishes age, the solubility parameters required of

solvent compositions to remove them rise concomitantly, a consequence of their change in oxidation state with ageing. However, there can be big differences in the 'bulk' film solubility properties and specific materials that accrue in these films as they age. Water increasingly has a swelling and solubilising effect on degraded varnishes as they age and become more oxidised. A natural consequence of the oxidation process is the increasing proportion of resin acid constituents within these films. If the resin acid content is high enough, water alone, raised in pH above the pK_a of the resin acids (nominally in the range of 4.3–4.7), can act as an additional solvent for the removal of these films. A common scenario preceding varnish removal is that an aged, yellowed varnish reaches a visual 'endpoint' where it aesthetically compromises the presentation of a painting long before it is completely oxidised. At this point, fractions of resinous materials from the un-oxidised to highly oxidised are probably present in these films. If the former still predominates, low-polarity solvent methods are likely to be the most useful. If the latter is true, aqueous systems are also a possibility, and it is now recognised that these alternative cleaning systems can assist or replace solvent methods to remove highly oxidised resin varnishes.

Case study 30.3 gives an example of an aqueous preparation used to remove a degraded oxidised natural resin varnish from an oil painting. It exploits a slightly alkaline pH to solubilise resin acids directly and also uses selected surfactants to solubilise the less oxidised fraction of material that is also present in a 'typical' degraded natural resin varnish.

Case study 30.3: The use of a resin soap formulation to remove varnish from a nineteenth-century Venetian canal scene (artist unknown)

(a)   (b)

Figure 30.3   A nineteenth-century Venetian canal scene (artist unknown).

(a) Before treatment. (b) After varnish removal

Source: Courtesy of Winterthur/UD Program in Art Conservation

Formula

100 ml de-ionised water
2 g abietic acid (HLB = 8.2)
5 ml triethanolamine (mix; filter immediately adjust pH to 8.5 with 1 M HCl)
1 g Brij 35 (HLB = 16.9)
2 g hydroxypropylmethyl cellulose

Commentary

This treatment is historic in that it demonstrated the power of a specific affinity surfactant (or 'resin soap') and a tailored aqueous environment to remove an oxidised varnish layer. it represents the proof of the thought experiment behind the 'resin soap': if grease can be removed from human hands by making soap from grease, varnish can be removed from a painting by making a soap from varnish. While making a soap from dammar or mastic is not practical, similarly structured analogues to these complex natural products can be used. Abietic acid is the acid fraction from pine rosin and when deprotonated, the abietate ion has a spatial configuration that is similar to molecules found in natural resins. The attraction between the abeitate end of the surfactant and the resin components is primarily through dispersion forces which increase with the surface area of contact between the surfactant and substrate, hence the term affinity surfactant.

The pH of this aqueous preparation is high enough (8.5) to swell and solubilise resin acid materials in water, but not high enough to swell the oil paint film beneath the coating. Water at this pH will solubilise a substantial amount of very oxidised resin material in this varnish but not everything. The less oxidised materials can be solubilised with the aid of a surfactant, especially one that has an increased affinity for resin materials such as abietic acid.

One of the unusual aspects of this preparation, however, is that two surfactants are combined with different HLB numbers (8.2 and 16.9). Based on their weight percents in this preparation the net HLB would be effectively 10.9. This is less than that nominally required for solubilisation to effectively be accomplished (around 12 is the usually minimum HLB for built detergent systems). However, the rationale here is that the target material to be solubilised is substantially degraded (oxidised) resin materials. The overall risk to oil paint increases with increasing HLB. Any effective way of lowering the HLB will help protect oil paints. The lowered HLB created by combining two surfactants in this system is offset by the increased affinity for the degraded resin materials of the abietic acid soap. Both are miscible with each other (anionic, non-ionic) in all proportions.

As with aqueous cleaning solutions for soil removal, the pH is kept within the range of 5.5–8.5 with triethanolamine as the buffer (pK_a = 7.76). Triethanolamine also functions as the general base to neutralise the abietic acid. in total, the overall conductivity of this preparation is kept low and slightly hypertonic to the surface to be cleaned (at most, 10–20× the wetted paint surface conductivity).

Hydroxypropylcellulose was chosen in this case to gel the preparation both for its ability to raise the viscosity (to around 4000 cps) and provide some measure of control in application of the cleaning solution. It also acts as a suspension aid for solubilised resin materials. HPMC cellulose is compatible with anionic and non-ionic surfactants.

It was possible to substantially remove one natural resin layer from an older one, in the case of the Venetian canal scene painting, with this aqueous preparation because the uppermost resin coating was more oxidised than the older one adjacent to the paint surface. This older, discontinuous, less oxidised varnish was removed by adding a cosolvent to the abietate soap system. In this case, 2 per cent of 1-methyl pyrrolidinone was sufficient to lower the overall polarity of the cleaning system sufficiently to allow the less oxidised varnish to be dispersed into the cleaning solution. This 'un-packing' of one varnish layer from another was possible because of the difference in degree of oxidation. Solvent methods might have had the opposite effect – that is solubilising the older, less oxidised, varnish first and then 'under-cutting' the second coating along with it (Wolbers, 2000: 44).

30.3.2   Emulsions

Emulsion preparations can be useful conservation cleaning systems. The traditional definition of an emulsion is the dispersion of one liquid into another non-miscible liquid; water usually comprises one of the two non-miscible phases. The combination of both aqueous and non-aqueous solvents is a challenging cleaning system to construct, but it can uniquely meet the needs of common cleaning problems.

The shorthand designations of 'w/o' and 'o/w' are adopted from general cleaning technology as conventions to refer to water-in-oil or oil-in-water arrangements. The dispersed material is listed first and the continuous phase material second. Usually, the volume of the continuous phase material exceeds the dispersed phase material. The dispersed phase material usually takes on the form of minute spherical droplets in the continuous phase. 'Oil' can stand for any hydrophobe, including non-water miscible solvents (e.g. aliphatic, aromatic, hydrocarbons, halogenated materials). A third important emulsion form, which has found considerable use in conservation cleaning applications, is what can be called an 'inversion' type of emulsion. Inversion-type emulsions tend to combine both 'oil' and 'water' phases, but in more or less equal amounts (these tend to be lamellar in arrangement, rather than dispersed-droplet arrangements, with oil and water phase combinations at nearly equal molecular volumes, i.e. at their phase inversion point). These preparations are often viscous, clear preparations.

All three emulsion forms (w/o, o/w, and inversion) can embrace both the chemistry of water (pH, ionic strength, buffers, etc.) and of solvents (low solubility parameters), and bring both to bear in a concerted way on complex mixtures of materials, helping to solvate them more efficiently. The w/o and o/w arrangements tend to have an additional advantage: their continuous phases can be used to help restrict or retard the contact of the dispersed phase material from an otherwise water- or solvent-sensitive material.

Preparing emulsions is usually a 'by-hand' endeavour within the conservation field; most emulsions used in conservation cleaning are prepared at the bench, with little or no specialised equipment and a minimum of constituents. The goal is to produce stable and predictable emulsions that are useful in day-to-day practice, with well-defined ingredients, and with associative properties that are consistent with cleaning fine art surfaces (non-reactive, non-toxic, easily cleared, etc.)

Emulsification is essentially the net effect of two competing processes: the dispersion of droplets of one immiscible phase or liquid into another and the coalescence of the separated materials back into their separate bulk phases again. Coalescence generally tends to predominate over dispersion in the end (largely because of free energy differences between dispersed and coalesced materials). To create the most stable emulsions, the forces that tend to coalesce or collapse the emulsions must be countered.

The type, intensity, and duration of the physical process, which creates the dispersion play a significant role in emulsion stability. The type and concentration of surfactants used are also key factors. The way surfactants and the other separate phase materials are brought together or mixed can affect emulsion stability, and the density of the two phases – as well as temperature – can significantly contribute to emulsion stability. (Temperature affects viscosity, interfacial tension, and surfactant adsorption.)

Selection of surfactants is a largely empirical, challenging process. In 1991, there were a daunting 30,000 trade-named surfactants available for commercial use. One widely used selection system, suggested by Griffin (1954) and still used today, is the 'HLB system'. The 'HLB' or 'hydrophile/lipophile balance' system assigns a relative number – on a scale of 1–40 – that describes the ability of a surfactant to create stable emulsions and accomplish other solution effects (e.g. wetting; solubilising solid phase materials).

Surfactants must have specific molecular characteristics

- They must combine and balance both polar and non-polar moieties in their structure. (The stronger the tendencies to be water-soluble and non-water soluble simultaneously in the same molecule, the more emulsification can occur.)
- They must orient themselves effectively and be strongly and rapidly absorbed on to the dispersed phase to form the most stable emulsion possible.
- They must lower the surface tension to just a few dynes/cm between the two separate phases. They should not be readily displaced if two dispersed droplets collide (the ionic character to some surfactants tends to do this inherently through the zeta potential or ionisation 'shell' created in the water phase).
- They must work at fairly low concentrations, be safe, non-toxic, safe to handle, inexpensive, etc.
- They must not easily be absorbed or difficult to clear from painting surfaces.

To create a stable oil–in–water emulsion or inversion point emulsion, the HLB number must be 8–18 (or greater); for water–in–oil types, a number of 4–6 or greater is necessary. Emulsions containing surfactant structures with very high HLB numbers are possible [e.g. stearates (38); Vulpex (38); lauryl sulphate (40)]. Generally, however, it is more useful to draw from non–ionic, lower HLB structures for painted surfaces (e.g. Brij 35, Tween 20, Triton X-100, Ecosurf EH-9), with HLBs in the range of 12–20. The latter choices are preferable due to their ease of mixing with other ingredients (neutrality), method of mixing (solvent miscible, next emulsified in water), and ready clearance from oil paint films (considerable aromatic/aliphatic solubility).

It is necessary to select a surfactant with a high enough HLB for a particular emulsion type; however, such a surfactant may not produce the most long-lived stable arrangement. Phase densities, droplet size, and continuous phase viscosity are also critical features.

Emulsion stability can be summarised by the Stokes equation (Vesilind *et al.*, 1994) or relationship (see below); this equation is a statement of the inter-relationship of the physical properties associated with both dispersed (d) and continuous (c) phase materials as a function of the rate (V) of sedimentation (coalescence) of the two separate phases with respect to time.

$$V = \frac{d^2 g \left(\rho_d - \rho_c \right)}{18\mu}$$

Table 30.10 HLB scale (Griffin, 1954)

	HLB range
water-in-oil emulsifiers	4–6
wetting agents	7–9
oil-in-water emulsifiers	8–18
detergents	13–15
solubilising	15–18

Table 30.11 Selective solvent densities

Solvent	Density (20°C)
H_2O	1.00 g/mL
Hexanes	0.65 g/mL
Toluene	0.87 g/mL
Xylenes	0.86 g/mL
Benzyl alcohol	1.05 g/mL
Methylene chloride	1.33 g/mL

Values taken from Modular Cleaning Program with permission

Here ρ_d and ρ_{dc} are equal to the densities of dispersed and continuous phase materials respectively; μ is the viscosity of the continuous phase; g is the gravitational constant, and d is the dispersed phase droplet diameter.

The Stokes equation serves as a guide for the design of stable emulsion preparations beyond surfactant choice. When the densities of the dispersed and continuous phase materials are close in value, phase coalescence is at a minimum. The size of the dispersed phase material also plays a role in emulsion stability; the finer the dispersion (diameter of dispersed phase droplets), the lower the rate of coalescence. Viscosity of the continuous phase is also important in emulsion stability: the higher the viscosity (μ), the lower the rate of sedimentation, coalescence. When the sedimentation rate is low, equivalent to about 1 mm/24 hours, Brownian motion will generally overcome settling and stable emulsions will result.

The gravitation constant is invariable, but the droplet diameter of the dispersed phase material is a function of the method of preparation. Droplet size decreases generally with increased agitation. Lamellar flow (pipe flow, colloid mills, and ball and roller mills), cavitation, ultrasonic, and various other turbulence phenomena can produce quite small (micron diameter 2–5 μm on average, as low as 1 μm in some cases). High-pressure membrane or diffusion-type emulsifiers can easily achieve droplet diameters of less than 1 micron. When droplet size is very small (less than about 550 μm), emulsions will appear transparent and tend to be generally stable. However, with 'by-hand' preparation (e.g. shaking or agitation in a closed vessel), droplet sizes of about 10–30 microns may be the smallest achievable.

Depending on the density difference, the critical droplet size needed to make a perfectly stable emulsion under normal room temperature conditions can be calculated.

Benzyl alcohol, for instance, as a useful emulsifiable solvent, will form emulsions with water above about 4 per cent w/v; its density is closest to water among the solvents listed in Table 30.11. With a density difference = 0.044 g/ml in water, at 1 cP (the viscosity of unthickened water), the critical droplet diameter would be on the order of 650 nm to prevent settling.

The best strategy is to increase the viscosity of the continuous phase materials in 'by-hand' preparations, given the limitation in producing droplet dispersions of a very fine nature and the limited range of emulsion-forming solvents (and densities) available. Polyacrylates, gums (e.g. xanthan gum), and various cellulosic ethers (CMC, MC, HPMC, HEC, and PC) have all been suggested or used for this purpose. In practice, however, it is difficult to produce by-hand preparations of stable o/w-type emulsions with an even consistency.

Self-emulsifying polymers have been introduced to conservation cleaning applications (Ravenel, 2010). Lubrizol's Pemulen TR-2, for instance, is a rheological polymer (it can increase dramatically the viscosity of water as a high molecular weight polyacrylate) and can also create physical dispersions of non-water miscible solvents. This is because it is 'blocked' (i.e. is a block polymer of polyacrylic acid and C10–30 acrylate esters) and can form stable hydrophobic dispersions or materials in water.

Case study 30.4: Emulsion formulation for the treatment of *Winter* Scene (1940), by Christine Martin
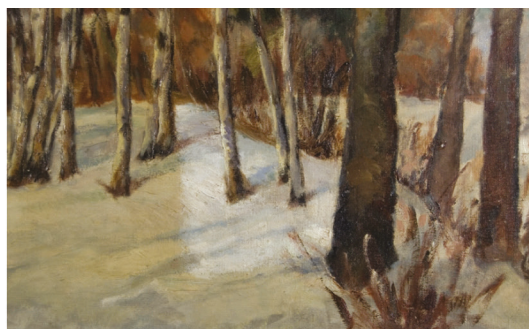
(a)   (b)

Figure 30.4   Emulsion formulation for the treatment of *Winter Scene* (1940), by Christine Martin.

(a) Partial removal of varnish and soil. (b) Detail, lower right
Source: Courtesy of Winterthur/UD Program in Art Conservation

Formula

100 ml de-ionised water
1 g Pemulen TR-2
1 g EDTA
a.n. triethanolamine
Stirred to make a rigid, clear gel
The final pH is adjusted to about 8.5
10 ml benzyl alcohol
10 ml xylene

The solvents are mixed together and 'shaken' into the gel to form a stable emulsion

Commentary

Soils intermixed with varnish coatings pose an especially difficult cleaning problem suited to emulsion systems. However, traditional emulsions using solvent/water and surfactant often require large amounts of surfactant to build stable emulsions. New polymeric emulsifiers, such as Noveon's Pemulen TR series of self-emulsifying polymers, can be used to build stable emulsion arrangements of the oil-in-water type without the use of surfactants and the concomitant clearance issues inherent in using large amounts of surfactants. At a low concentration (1 per cent w/v), TR-2 can form gels in the pH range of 6–10. These aqueous gels can hold up to 70 per cent by volume of a solvent phase in them without collapsing.

For the landscape painting here, the surface was generally de-waxed with an aliphatic solvent, and the varnish and soiling materials were solubilised in a Pemulen gel pH 8.5, which included a chelator (EDTA) and a dispersed solvent phase of equal parts of xylene and benzyl alcohol. The solubility tests

initially suggested that a much stronger (more polar) mixture of solvents would be required to solubilise the coating. But the combination of water phase (for soils and the most oxidised portions of the varnish) and a solvent phase (which combined two aromatic solvents) was sufficient to solubilise the relatively un-oxidised portions of the varnish. Here, a water/aromatic solvent mixture as an emulsion replaced a more polar single solvent system to address the solubilisation requirements for a degraded natural resin coating (McGinn, 2010).

30.3.3 Microemulsions

As mentioned above, one strategy for the formulation of a stable emulsion is to reduce the average droplet size of the dispersed phase. One can achieve such small droplet sizes by imparting significant energy into shearing and mixing; however, by combining carefully calculated proportions of an aqueous phase, a hydrophobic phase, and surfactant (sometimes with the addition of a cosurfactant/cosolvent), it is possible to reduce the interfacial tension between the immiscible liquid phases to values low enough that a thermodynamically stable microemulsion will form spontaneously. As with macroemulsions, the proportions of components determine whether the microemulsion can be classified as o/w, w/o, or inversion (bicontinous). (See Klier *et al.*, 2000 for a general discussion of microemulsion properties.) These preparations allow the conservator to formulate the aqueous phase according to the considerations described in this chapter while deciding whether that chemistry is delivered in a largely polar or nonpolar environment.

One potential drawback of microemulsion preparations is the relatively high proportion of surfactant constituents that could pose a greater risk for residue deposition; however, this risk can be mitigated through careful surfactant selection and by following appropriate clearance protocols determined by surfactant characteristics and the continuous phase of the microemulsion preparation. Much of the identification of appropriate surfactants and the mapping of microemulsion formulations was the result of the *Cleaning of Acrylic Painted Surfaces* (CAPS) initiative headed by the Getty Conservation Institute with collaborative efforts between GCI, Dow Chemical Company, and Tate. Although concerted study of microemulsion systems for the cleaning of paintings was born out of a need for new approaches specific to cleaning acrylic paint surfaces, case studies have been presented that illustrate the potential use of microemulsions for cleaning water-sensitive surfaces and for the removal of stubborn soiling (Stavroudis 2012, Ormsby *et al.*, 2016) from oil paint surfaces.

30.3.4 Pickering emulsions

Another strategy for delivery of aqueous solution chemistry without the use of traditional surfactants is through the use of Pickering emulsions, which exploit functionalised colloidal particles at the interface between immiscible liquids to form a stable arrangement. In recent years, silicone-based emulsifying particles have been used to stabilise aqueous solutions within aliphatic mineral spirits, low molecular weight dimethicone solvents, of cyclomethicone D5. Shin–Etsu (Japan) produces a range of emulsifiers (KSG-210, KSG-350z, e.g.) based on dimethicone crosslinked with PEG chains and modified with PEG and aliphatic sidechains. The KSG emulsifiers are dispersed in D5 and are capable of stabilising in excess of 60 per cent w/w of an aqueous phase (Stavroudis, 2017; Lagalante and Wolbers, 2017). Clearance of the silicone polymers is a concern with these preparations, and there are growing concerns over the safety of cyclomethicones for reproductive health. Appropriate clearance protocols and use of effective PPE is necessary.

30.3.5   Rigid gels

Of the so-called rigid gels used in conservation, agar and agarose gels are most commonly used in paintings conservation. Agar is composed of two polymeric materials: agarose (a nonionic polymer of galactose) and agaropectin (an ionisable, acidic fraction that is structurally complex). Of the two, agarose is the gelling agent, whereas agaropectin does not contribute much to the gel structure. Pure agarose is preferred for gel formulations, but the high cost of very pure agarose can be prohibitive. To form a gel, the agarose is heated in solution above its gelation temperature, and then the solution is allowed to cool, after which it forms a rigid gel. The porous structure of the gel is determined mainly by the concentration of agarose in solution; the pore size determines the rate in which water is released from the gel. In practice, the solution parameters can be modified as in any aqueous treatment, and the gel can be delivered as a rigid sheet, fractured into a crumb-like consistency and used similarly as one would use eraser crumbs, or even poured in a viscous state to allow the gel to conform to geometrically challenging surfaces. As long as the gel is not allowed to dry in place, adhesion to the surface is generally not a concern. Finally, a rigid gel can be placed in a solvent bath to 'load' the gel with some amount of solvent, if delivery of a solvent would assist in soiling removal. A good summary of the theory and use of agar gels can be found in Cremonisi and Casoli (2017).

30.4   Conclusion

Although the materials presented in this chapter are numerous, there are a few key takeaways that carry across all of their applications in the cleaning of easel paintings and painted surfaces. First, aqueous chemistry is a powerful tool for conservators; we can tailor several parameters to affect the intended cleaning. Second, we can control the delivery of that aqueous phase through the use of thickeners, gelling agents, and emulsifiers, and we can exploit properties of these additives to address water sensitivity or the complex chemical nature of a soiling material. Lastly, we can carefully control our formulations to create stable arrangements of aqueous solutions and organic solvents, exploiting our ability to control aqueous solution parameters and exploiting our understanding of organic solvents and solvent theory as described in Chapter 31 to execute cleaning treatments of very high specificity.