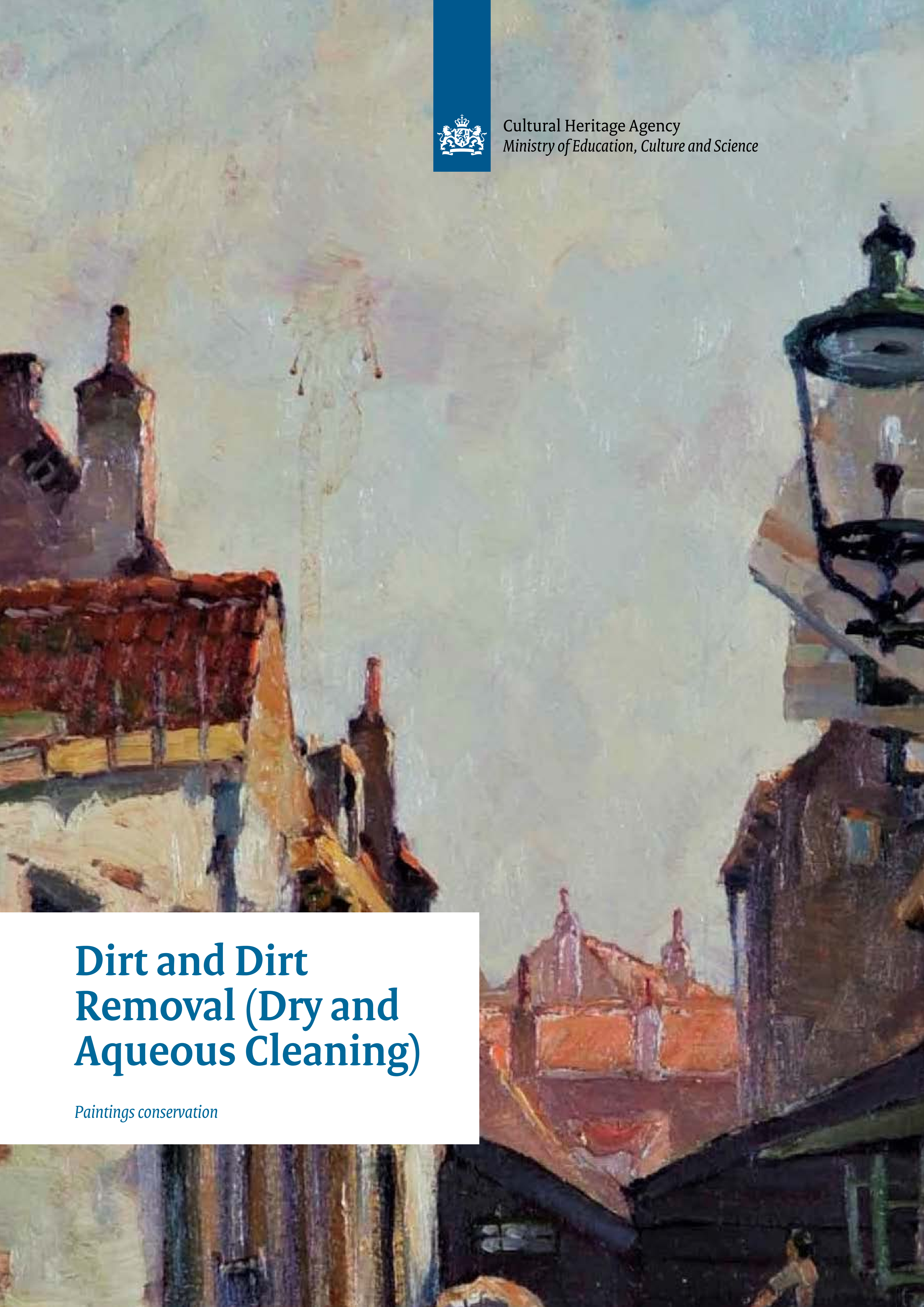


Cultural Heritage Agency
Ministry of Education, Culture and Science

Dirt and Dirt Removal (Dry and Aqueous Cleaning)

Paintings conservation

Dirt and Dirt Removal (Dry and Aqueous Cleaning)

Paintings conservation Part 1

"As if a thin grey veil has been lifted…"

SRAL
The
conservation
institute

SCI | Foundation for
Cultural Inventory

Colophon

Dirt and Dirt Removal (Dry and Aqueous Cleaning)
Paintings Conservation Part 1

Department: Cultural Heritage Agency of the Netherlands (RCE)
Ministry of Education Culture and Science
Project name: (Shared cultural heritage) International heritage cooperation
Date: 2022
Contact: Klaas Jan van den Berg, Cultural Heritage Agency of the Netherlands
Authors: Julia M. van den Burg (MA PD. Res.; Private conservator),
Kate Seymour (MA (Hons, MA; Head of Education and Senior Painting Conservator,
Stichting Restauratie Atelier Limburg)
Editing: Klaas Jan van den Berg (RCE), Lia Gorter (Foundation for Cultural Inventory, SCI)
Photos: All photos are produced by Julia M. van den Burg, unless otherwise stated
Design and print: Xerox/Osage, the Netherlands
Front cover: Detail of G. Wiegman (1875-1964), Alleyway in Schiedam, 1940, oil on canvas. Daylight conditions, before dirt removal.
Back cover: Detail of G. Wiegman (1875-1964), Alleyway in Schiedam, 1940, oil on canvas. Daylight conditions, after dirt removal.

Cultural Heritage Agency of the Netherlands
P.O. Box 1600
3800 BP Amersfoort
The Netherlands
www.cultureelerfgoed.nl

Table of Contents

Foreword

Before you lies one of six brochures created for conservators of paintings and panels wishing to keep up with and learn how to apply rapidly advancing techniques in their field. The brochures in this series are:

1. Dirt and Dirt Removal
2. Varnish Removal
3. Consolidation of Flaking Paint
4. Filling Losses in Paint
5. Structural Conservation of Canvas and Panels
6. Varnishing and Inpainting.

The brochures were compiled to serve as a reference, bringing together knowledge about new materials and methods for practical use.

Conservation practice has developed at an astounding pace. This knowledge is concentrated at a few large institutions with the capabilities to take major steps in the development and application of new methods. Smaller and medium-sized museums meanwhile do not have the resources to hire a permanent conservator for their collections, and often send paintings to be restored externally. For those not employed at large institutions, accessing such knowledge can be difficult.
These brochures are designed to bridge this gap.
They can also help conservators seeking to refresh and update their knowledge.

The need for this reference material became apparent during a series of masterclasses and conferences organized by the Foundation for Cultural Inventory (SCI) in India, the Russian Federation and elsewhere, in association with SRAL - The Conservation Institute, the Cultural Heritage Agency of the Netherlands and Dutch embassies in the partner countries.
These gatherings, centring on mutual exchange and deepening knowledge in relation to the local contexts, were held under the auspices of the Shared Cultural Heritage programme.

This programme has since been succeeded by the International Heritage Cooperation programme, which more than ever emphasizes the comparable societal challenges countries face and the value of learning from each other to address them. The brochures show how much can be accomplished through cooperation and not only exchanging but also pooling and sharing knowledge.

We are providing this reference material in the hope and anticipation that it will aid conservators of paintings and panels in their work, so that future generations can continue to enjoy this heritage for a long time to come.

We thank scientist René Peschar (University of Amsterdam) and paintings conservator Louise Wijnberg for valuable input.

Lia Gorter
Director, SCI Foundation for Cultural Inventory

Jinna Smit
Programme Director, International Heritage Cooperation
Cultural Heritage Agency of the Netherlands

Layers of surface dirt can obscure the original colour palette and hide details such as brushstrokes and use of colour. *Landscape with windmill*, thought to be by Jacob Maris (1837-1899), viewed in daylight conditions, before surface dirt removal.

Introduction

The removal of surface dirt from a painted surface (varnished or unvarnished) can have a notable effect on the appearance of the painting. Surface dirt removal is therefore frequently, and often routinely, an activity undertaken by conservators.

Dirt is the term used to refer to dust, grime, grease, soil, accretions, accumulations, stains, soot, salts, fibre, particulates, growths, debris and deposits that settle, are produced by, or are applied to a surface. Pollen, moulds, spores and fungi, although in essence biological material, can also be considered ‘dirt’. Surface dirt will accumulate over time and can slowly alter the appearance of a painting making the colours duller and disturbing gloss. It will also attract further deposits. Furthermore, surface dirt can over time bond more readily with underlying original materials, partly due to its propensity to hold atmospheric moisture, leading to further decay and deterioration.

It is thus important to remove these layers from painted (varnish or unvarnished) surfaces on a routine basis.[1] This can be done using dry methods, or if the dirt is more well-adhered, using tailored aqueous solutions. This brochure contains information on the following: what dirt consists of; how dirt bonds to the surface; the ethical reasons to remove surface dirt and the procedure for how to do so; and will provide an overview of selected methods and materials commonly used to remove surface dirt.

---

[1] This may mean gently brushing off loose surface dirt on a bi-weekly or monthly basis, as often occurs in museums with high levels of foot traffic, or regularly checking for, and removing, surface dirt when deemed to be necessary. A risk assessment should always be completed prior to such interventions, weighing up the balance between the presentability of the artwork with a thin layer of dirt and potential risks associated with dirt removal, against the potential dangers of leaving the surface dirt on the artwork till a later point in time.

Landscape with windmill, thought to be by Jacob Maris (1837-1899), viewed in ultraviolet induced-visible fluorescence. The surface has a dull appearance, as the dirt obscures the fluorescence of the aged varnish beneath it. The edges, which have been protected by the frame, have less dirt and show the fluorescence of the varnish.

Surface Dirt

Sources of surface dirt

The sources of dirt can be divided into two categories:

- Foreign matter, i.e., that which is produced extraneously and deposited on the surface of the painting (soot, grease stains, adhesives, residues, dust, fibres, particulates and so forth) and
- Degradation/alteration products, matter which is produced within the painting and transported to the surface where it is deposited at the paint or varnish interface. These can be salts, crusts, growths etc. They include those that result from a reaction between molecules within the artwork and the atmosphere, such as metal soaps that have been found on the surface of old master paintings, and epsomite crystals on young oil paint surfaces.[2]

Dirt derives from a variety of sources including human debris (hair and skin), combustion exhaust fumes, particulate pollutants (such as carbon particles (soot) and gases), cooking fat or oils, nicotine, inorganic compounds (sodium chloride, sulphur, minerals and salts etc.), plants (pollen, mould or fungi), insects (bodies or accretions), and fabric (fibres). Dirt on surfaces therefore usually comprises of a combination of organic and inorganic particulate matter, found together in the presence of oily or hydrophobic organic substances, accumulating over a period of time. The composition of dirt will depend on the conditions in which the painting is held. The presence of electronics (televisions, screens) and temperature controlling devices (air conditioning units or heating ducts and stoves) will cause dust and dirt to be attracted to these units and be deposited on surrounding areas.

Degradation or alteration products relating to the surface layer may be found lying directly on the surface of the object or at the intersection between the varnish layer and paint.

Dirt deposits on an unvarnished painting, or paintings with porous or friable surfaces may become integrated with the paint and thus do not constitute as a discrete or separate layer. These surfaces are problematic to clean

Detail image of dirt and drips down the surface of an unvarnished painting.

---

[2] Silvester G., Burnstock A., Megens L., Learner T., Chiari G., Van den Berg K.J., A cause of water-sensitivity in modern oil paint films: the formation of magnesium sulphate, 2014, in: *Studies in Conservation*, 59 (1), pp 38-51
Sawicka A., A. Burnstock A., Izzo F., Keune K., Boon J., Kirsch K., van den Berg K.J., Metal soap efflorescence in contemporary oil paintings, In K.J. van den Berg, et al. (eds). Issues in Contemporary Oil Paint. Springer International Publishing Switzerland 2014. pp. 311-332. DOI 10.1007/978-3-319-10100-2__21

Detail image of insect excretions and oily residues on the surface of an unvarnished painting.

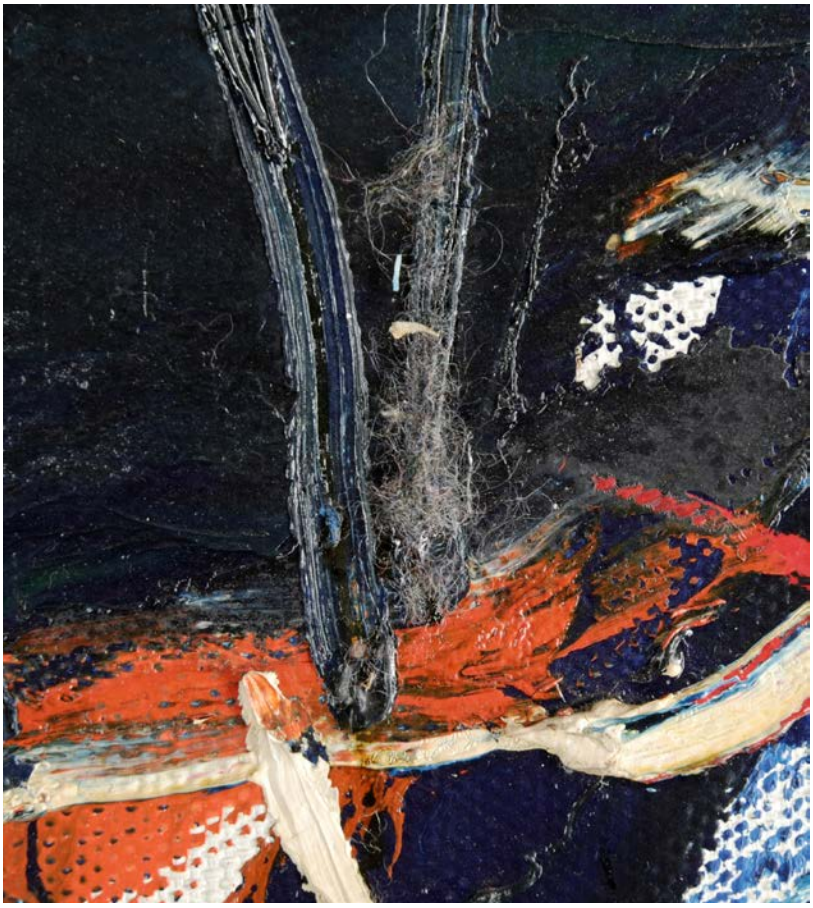
due to the penetration of the unwanted material into the original paint layer. Specialised cleaning solutions will be discussed later in this brochure.

Dirt and surface properties will affect the amount, type and location of the dirt deposited on the surface of the painting. The surface roughness or texture, magnitude of adhesive forces, particle shape, elasticity and plasticity will all influence the degree of adhesion of the dirt to the surface.[3] The wettability of the surface regulates the degree of molecular forces present between the dirt and surface. The greatest molecular interaction occurs when the dirt and surface have similar polarities. Hydrophobic surfaces reduce the adhesion of most types of dirt; this forms the basis of anti-soiling coatings used in industry. Greasy or oily surfaces may form part of the dirt itself, or result as a contaminant from handling or staining. The presence of a greasy layer increases the amount of dirt pick-up due to its inherent tackiness.

Dirt is attracted to surfaces through static electricity and diffusion dynamics. Dust/dirt particulate matter is often light enough to be held in the air. Dust motes will move from areas of high concentration to areas of low concentration. This movement is aggravated with temperature shifts with dust being attracted more to areas of cold air than warm and by moisture shifts with dust being attracted to damp conditions more than dry conditions. This means that dry, warm areas will be intrinsically less dusty than cold, damp environments. Controlling relative humidity and temperature, as well as reducing the sources of dirt particulates, can improve the rate of deposition and the frequency of cleaning. Furthermore, placing (fragile) objects out of drafts (opposite doors, or in the path of air extraction units) will lower the build-up of dirt layers on the surface. The need for cleaning will therefore be reduced.

---

[3] Surfaces with a low Tg (the Glass Transition temperature), will deform and trap more dirt. This is especially an issue with unvarnished acrylic painted surfaces and fresh oil paint surfaces which have a low Tg. Dirt particles on these surfaces can become imbedded or imbibed in the uppermost interface of these surfaces.



Detail image of fibres from an unknown source found imbibed in paint.

At this point it is important to note that literature often refers to 'Surface Cleaning'. For the sake of clarity, this term will not be used in this document, as it may also refer to varnish removal (which is discussed in the brochure 'Varnish Removal'). Cleaning may refer to 'all aspects of the visual improvement of pictures by removal either fully or in part of surface deposits accretions or applied coatings.'[4] Therefore this brochure will refer to 'dirt' and 'surface dirt removal'.

Why remove surface dirt?

The deposition of dirt on a surface will impact an artwork in a number of ways. Aesthetically, dirt deposition results in an increase of light scattering on the surface with desaturation of hues and decrease in luminosity for both light and dark colours as a result. Dirt can alter the perception of optical depth and decrease the legibility of the image. Dirt deposited on an unvarnished painting will adhere directly to the painted surface and in time may become imbibed, thus permanently disfiguring or decreasing the legibility of the image. The longer the dirt layer is left on a surface, the stronger the dirt particles will adhere to that surface via intermolecular bonds. It is thus beneficial to employ regular dusting of surfaces to ensure that dirt layers do not build up.

Surface dirt encourages the degradation and deterioration of a work of art. Dirt is hygroscopic in nature and will encourage the growth of moulds and other micro-organisms or provide a food source for insects. (Acidic) insect accretions especially are detrimental to works of art, they react with the surface resulting in etching or corroding of the paint. Components of dirt may react with materials inherent to the artwork, forming by-products that can be difficult to remove without affecting the integrity of the artwork. The hygroscopic nature of dirt may also speed up the

---

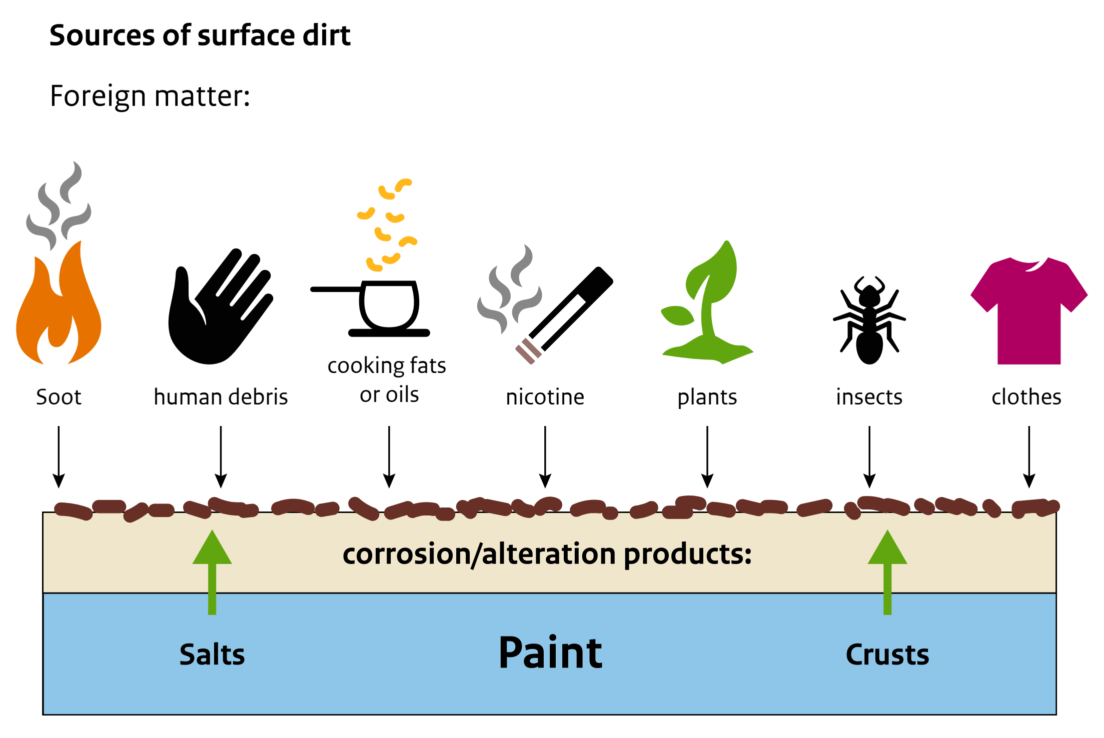
[4] Phenix, A. *The science and technology of the cleaning of pictures: Past, present and future.*, Konservatorskolen det Kongelige Danske Kunstakademi, Preprints of the Jubilee symposium 1998 pp 109-119.

formation of inorganic by-products, increasing the corrosion of original material through interaction of the salts in dirt with free fatty acids from the paint layers, creating insoluble metal soaps and crusts. Dirt that lies on the surface of an artwork may, by its hygroscopicity, cause a variety of surface whitening effects such as blanching, blooming or crazing. This often occurs in the varnish layer, but will also occur on and in unvarnished paint layers.

The presence of dirt will affect the effectiveness of subsequent treatments. For instance, glues do not adhere well to a dirty surface. The presence of dirt may prevent the consolidation of delaminated layers by inhibiting the flow of glue under the lifted or flaking paint. Additionally, if consolidation is carried out prior to dirt removal, the dirt particles may become intrinsically bonded to the original materials, making it impossible to remove them and resulting in permanent change to the artwork. It should be noted that the fragile nature of powdery, flaking or crumbling paint layers may not permit dirt removal prior to consolidation and compromises may be necessary. Surface dirt will also interfere with the solubility parameters of underlying layers, such as varnish. It is always necessary to remove surface dirt before commencing with varnish removal, as this may otherwise be almost impossible to do.

Detail image of nicotine deposits on the surface of *Drenthe II* (S. van den Berg, 1949, collection of the Cultural Heritage Agency). Note that the deposits have been removed on the right part of the image. Seen in daylight conditions.

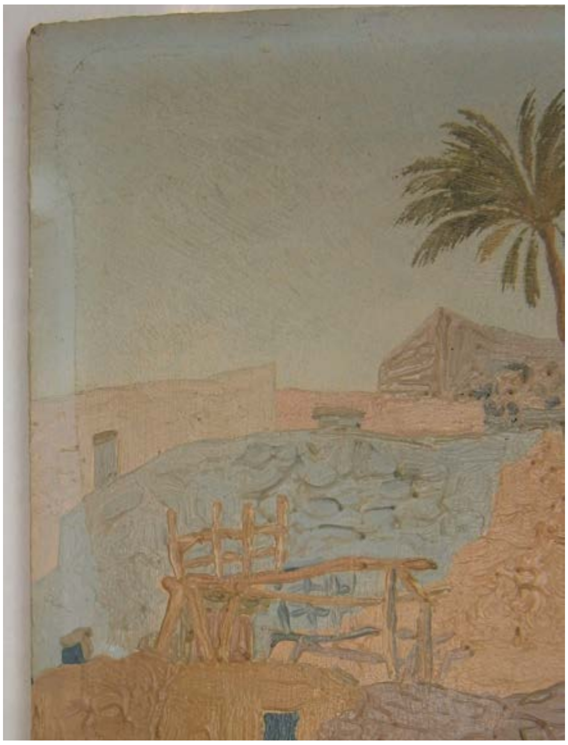
Loose surface dirt on an unvarnished painting, seen in raking light. *City View*, C. van Eijsden, ca. 1950, oil on canvas, collection of the Cultural Heritage Agency.



Sources of surface dirt: Foreign matter and corrosion/alteration products

Condition Reporting, Conservation History and Imaging

Prior to the commencement of any treatment, it is imperative to establish as much as possible about the painting as a whole: the medium and support, the technique used, the approximate date, the current condition of the artwork and any past restoration-conservation treatments. To ascertain these various aspects, observation of the artwork in good daylight conditions, raking/oblique light and ultraviolet light is required. If possible, images taken with infra-red light can be used to further identify artistic practice or the presence of overpaints. Cross-sections are also a possibility for understanding the build-up of layers; however, this is a destructive technique and should only be used when the above-mentioned non-invasive approaches do not give sufficient information. Past conservation reports may give clues to the condition of the object at a previous moment in time and any non-original materials applied. Archival research and conversing with fellow conservators and curators as well as cultural historians and the objects' owners may give a broader insight into the cultural use of the object and provide explanations of grime, deposits or stains. Discussions with the aforementioned parties is also essential to establishing the desired outcomes of treatment and may dictate to what extent the artwork is treated.



The edge of this painting has been protected by the frame. The surface dirt is thicker toward the centre. F.G. Erfmann, *Tripolitaans huisje*, 1942.

The technical information regarding the painting (method of production, condition and conservation history) can best be documented in a condition report.[1]

Considerations Prior to Testing

Establishing the nature and extent of surface dirt layers is key prior to their removal. Note that the amount and thickness of dirt may vary across a surface: Edges of a painting may have been protected by a frame rebate, lighter colours may attract dirt particles differently to darker colours, and the build-up of dirt may be thicker on three-dimensional relief surfaces such as impasto paint, frames or carvings. Dirt layers may be present between varnish layers and may need to be removed independently. The presence of dirt trapped between varnish layers may become evident in cross-section samples.

Dirt layers that have become imbibed in unvarnished paint layers and reacted with them may be considered patina.[2] Decisions to remove these dirt layers (if at all

The reverse of a painting should not be forgotten. Here the build-up of dirt and cobwebs is clearly visible.

---

[1] The information can be written in a condition report, here is an example by the Canadian Conservation Institute: *https://www.canada.ca/en/conservation-institute/services/conservation-preservation-publications/canadian-conservation-institute-notes/condition-reporting-paintings-examination-techniques.html*

[2] Patina is usually a product of interactions between original materials and atmospheric conditions, or a coating that has interacted with the original materials and has no clear interface. Discussions concerning this term are ongoing, and there are numerous publications regarding the formation and treatment of this layer.

Testing of aqueous solutions for the removal of surface dirt from the surface of a painting.

possible) may be considered differently than where an intermediate layer such as a varnish, is present and be used sacrificially (see section below on surface dirt removal from unvarnished surfaces).

The reverse of a canvas/panel or frame should not be forgotten, dust and dirt have a tendency to collect on the backs of paintings, settling between the canvas and stretcher bars, and becoming engrained in the exposed canvas. Trapped dust may accumulate and clump together causing lumps which migrate through the support, ground and paint layers causing deformations, ultimately resulting in cracking and delamination of surface layers.

Cleaning tests should be undertaken to determine the presence, nature and quantity of dirt on the painted surface. This will establish the means needed to remove the dirt and the safety margins.[3] It is imperative to begin cleaning tests with the least intrusive method available. Generally speaking, for surface dirt removal, these are dry cleaning methods, followed by aqueous methods. In a similar manner to varnish removal tests, surface dirt removal cleaning tests should be conducted on

---

[3] Safety margins relate to the ability of the underlying (original) layers' ability to withstand the application of solvent or the aqueous system applied. When testing aqueous methods, the safety margin should be at least another 10 rolls of a swab with the testing solution over the original material before any reaction is noted.

representative areas of the painted surface: close to the edge but not where the surface has been covered by the rebate of the frame. Lighter areas will help with visual observations of tonal changes from surface dirt removal.

Further observations on the progression of surface dirt removal can be verified under ultraviolet fluorescence. Layers of dirt prohibit the fluorescence of underlying varnish and paint layers; therefore, the efficacy of each cleaning agent can be checked in this way.

Prior to testing for the removal for surface dirt from the painted surface, it is wise to remove dust, dirt and other accretions from the reverse of the artwork (after unframing). Dust and dirt can be removed by brushing with a coarse hog bristle brush and with the aid of a vacuum. On occasion, it may be necessary to remove more well-adhered dirt on the reverse of the artwork with a soft rubber or a slightly damp micro-fibre cloth. Care should be taken when removing dirt and debris from between the stretcher bar and canvas, sharp objects such as stretcher keys or small pieces of wood can damage the (reverse of the) canvas. Always ensure that the pressure used does not cause deformations in either the canvas or through to the paint, and ensure that the ferrule of the brush does not make contact with the canvas support.

Thought to be by J. Maris (1837-1899). Detail of *Landscape with a Windmill*, viewed in daylight conditions. The surface dirt has been removed from the right part of the painting.

Thought to be by J. Maris (1837-1899). Detail of *Landscape with a windmill*, viewed in ultraviolet induced visible fluorescence. The surface dirt has been removed from the right part of the painting. The aged, fluorescing varnish is now clearly visible.

Dust and dirt can be removed from the reverse of the canvas using a brush and vacuum.

Surface dirt can be removed from under the stretcher bar with a feather (photo source: Kate Seymour, SRAL).

The reverse of the stretcher bar and canvas can be cleaned with a damp microfibre cloth.

Dry Methods for the Removal of Surface Dirt

Historically, dry methods of surface dirt removal received little attention, as most paintings were varnished, and cleaning methods were concentrated on the removal of varnish. Brief discussions can occasionally be found on the use of dusting brushes and cloths, erasers and sponges. Since the use of acrylic painting mediums have become more common, more attention has been turned to dry methods for surface dirt removal, due to the sensitive nature of acrylic paint systems to aqueous methods of dirt removal. Unvarnished (modern) oil paint surfaces (especially newer formulations of water-soluble oil paint) may also show sensitivity to aqueous cleaning methods, necessitating the use of dry-cleaning methods.

Dirt can be loose or well-adhered to the surface of the artwork. Dirt particles can become more strongly bonded to the surface over time as stronger forces come into play between the dirt particle and the charged surface molecules.[4]

The use of dry materials for surface dirt removal is not without risks, they may induce friction and subsequent elevation of surface temperature, may cause abrasion or polishing of the surface, result in micro-cracks or flattening of impasto areas of paint or leave particulate or chemical residues.[5] Research into dirt removal using dry methods for unvarnished painted surfaces was done at the Cultural Heritage Agency of the Netherlands. Several articles have also been published (also available online) detailing numerous products trialled for their efficacy at removing surface dirt and possible risks, such as the ability to leave residues or potential for alterations to the surface.[6]

Dry Methods for the removal of surface dirt: Loose dirt

Soft long haired (badger hair) brushes can be used to remove loose dirt from the surface of the artwork. These brushes can be used in conjunction with a vacuum cleaner to remove dislodged dirt from the surface and avoid re-deposition on other areas. The painting can be either vertically or horizontally. Note that care must be taken not to scrape the surface with the ferrule (metal part) of the brush as this can cause scratches or deformations in the surface.

The choice of dry-cleaning material will depend on the characteristics of the surface of the artwork, whether physical (porous, flaking paint, well bound, under bound) or aesthetical (monochrome, coloured zones, flat, impasto, matte, glossy), and the type of dirt (impregnated, dry, fat, smooth, or grainy). The following materials and techniques can be tested on well-adhered dirt.

Micro-fibre or Micro-filament cloths

Micro-fibre cloths can be used for both dry surface dirt removal and aqueous cleaning (with adjusted aqueous cleaning solutions). They come in various grades and roughness. Many are used in household cleaning (these are available at local supermarkets/drugstores). The principle of micro-fibre cloths is based on a rough material that is formed from small ‘hooks’ or a fibre filament profile that is designed with hooks. These cloths are therefore **NOT** suitable to use on surfaces that have adhesion issues such as raised, loose, flaking, cupped or powdery paint, as the ‘hooks’ will catch onto the raised or loose paint and remove these. Another potential downside is the potential for polishing of the surface. Note also, that when these cloths are used dry, they can generate static electricity, which in turn attracts and holds dust and dirt.

Some micro-filament cloths have been developed for more industrial purposes, such as Evolon® CR cloth. They are made with Polyethylene terephthalate (PET); a polyester, or with Nylon 6 (polyamide). These cloths have a non-woven structure and have gained popularity for both surface dirt removal and varnish removal.[7]

---

[4] For more on bonding and intermolecular bonds see: *https://chembam.com/resources-for-students/the-chemistry-of/bonding-and-intermolecular-forces/*

[5] Daudin-Schotte M., van Keulen H. (2014) Dry Cleaning: Research and Practice. In: van den Berg K. et al. (eds) Issues in Contemporary Oil Paint. Springer, Cham. *https://doi.org/10.1007/978-3-319-10100-2_24*

[6] Daudin-Schotte M, Bisschoff M, Joosten I, van Keulen H, van den Berg KJ (2013) “Dry cleaning approaches for unvarnished paint surfaces”, post prints Valencia international conference “New Insights into the cleaning of paintings, (Cleaning 2010)”. Smithsonian Institution Scholarly Press *https://www.researchgate.net/publication/281066098_Dry_Cleaning_Approaches_for_Unvarnished_Paint_Surfaces*
Daudin-Schotte M, van Keulen H, van den Berg KJ (2014) For the Cultural Heritage Agency of the Netherlands, and Giordano, A.; Saccani, I. for the Cesmar 7, collaborative paper, “Analysis and application of dry-cleaning materials on unvarnished paint surfaces, RCE project 2006–2009”, in Quaderno/Cesmar 7

[7] Baij, L., Liu, C., Buijs, J., Álvarez-Martín, A., Westert, D., Raven, L., Geels, N., Noble, P., Sprakel, J., Keune, K. Understanding and optimizing Evolon® CR for varnish removal from oil paintings. *Heritage Science*. 2021, Vol. 9 (1) *https://www.researchgate.net/publication/356586603_Understanding_and_optimizing_EvolonR_CR_for_varnish_removal_from_oil_paintings*

Microfibre cloths

Anti-static cloths

These can be used to wipe dust and dirt from the surface of objects. They can be used dry or wet and are used in industry for cleaning photograph negatives or prints. Commercial cloths are available (such as Swiffer) but many of these may leave fibres or other residues behind. When selecting an anti-static cloth, look for those that are 'lint free'. Natural fibres such as cotton or wood pulp have minimal static build-up due to their hygroscopic nature, however in very dry environments they loose their natural discharge capability and this can lead to a build-up of static.

Evolon cloth

Lint-free antistatic cloth

Make-up sponges

Soft make-up sponges (generally white or cream in colour) may suit both general and local dirt removal with a particular suitability for precise cleaning. These are available from local drugstores/pharmacies. Most makeup sponges are produced from isoprene rubber, styrene butadiene rubber (SBR), and mixtures of both on an industrial scale. Most suited are those without added cleaning solutions, or other chemicals that can be left as residues on the surface. Prior to use, they can be soaked in demineralised water to remove any chemicals that have been added, and dried by pressing between tissues. Note that soaking the sponges may reduce the plasticity of the sponges, or increase their brittleness over time. Make-up sponges can be used dry or with an aqueous cleaning solution. They are very soft and flexible, making them suited to impasto surfaces, or soft surfaces that are sensitive to pressure. Make-up sponges have proven to be efficient and the safest to use directly on painted surfaces (such as acrylic, unvarnished painted surfaces).[8]

Make-up sponges

---

[8] Daudin-Schotte M, Bisschoff M, Joosten I, van Keulen H, van den Berg KJ (2013) pp. 216

Akapad sponge (formerly Wishab sponge)

These sponges consist of a hard (blue) plastic section (solely for holding the sponge) and a soft (yellow or white) vulcanised latex rubber. The soft section of the sponge (white or yellow) is suitable for cleaning painted surfaces. The sponges are available in soft, hard and extra hard format, with the white sponge softer than the yellow sponge and more suitable to sensitive and structured surfaces. The rubber sponge is a Styrene butadiene rubber (SBR) with vulcanised castor oil.[9] The sponge works by crumbling on gentle rubbing, absorbing dirt as it does so. The Akapad sponge is useful for dust and soot, but not for oil or grease. The crumbs can be removed using a soft brush and vacuum. It is important to do this thoroughly as the residues may exasperate degradation. The sponge is self-cleaning as a new surface is created as the rubber crumbles away. A powdered version called 'Draft Clean Powder' is also available and can be used by sprinkling on the surface and rubbing gently with a cotton pad, before being removed with a soft brush and vacuum.

Akapad sponge (formerly Wishab sponge)

Smoke sponges

These sponges can be gently rubbed over the paint surface or canvas support. The dirt particulate matter is absorbed into the sponge and leaves little residue. This technique can also be effective against adhered dirt. The sponge is made of vulcanised latex rubber and isoprene rubber. The smoke sponge is especially useful for large and greasy particles of dirt. Smoke sponges should be stored in airtight containers, as exposure will result in a harder, unusable surface after several months. As this sponge does not crumble, the risk of leaving residues that can breakdown is minimised.

Smoke sponge

Blitz-Fix sponges[10]

Blitz-fix sponges are PVA-based material (Polyvinyl Alcohol) and can be gently wiped over a paint surface. These sponges are hard when they are dry, and must be soaked in water to soften them. Before use, the water can be squeezed out to minimise the amount of water that is in contact with the surface. They can be used multiple times, but will eventually start to crumble. When new, they do not leave residues on the surface.

Blitz-fix sponge

---

[9] Note that sulphur is used in the vulcanisation process. Sulphur can react with oxygen in the presence of water to produce sulphuric acid.

[10] *https://deffner-johann.de/de/blitz-fix-saugschwamm.html*

Solid Eraser

Solid erasers are block erasers that can be rubbed over the area to be cleaned. The crumbs produced and the dirt eliminated can be removed using a soft brush and vacuum. Solid erasers may be more effective in removing strongly adhered dirt, however it should be noted that erasers can be relatively abrasive and should be used with caution. In particular, the paint surface may change as a result of friction, becoming glossier or matte. Solid erasers are available at stationary suppliers. They are made of either Polyvinyl chloride (PVC) and di-isooctyl phthalate (DIOP) or Factice (vulcanized vegetable oil) and chalk (these are generally softer and produce more crumbs). The inert filler can be abrasive to the surface. Research on dry cleaning materials found that solid erasers left chemical residues (plasticizers) on the paint surface, which is of concern as plasticizers can soften the paint surface, leaving it more sensitive to dust and vulnerable to abrasion or polishing.[11]

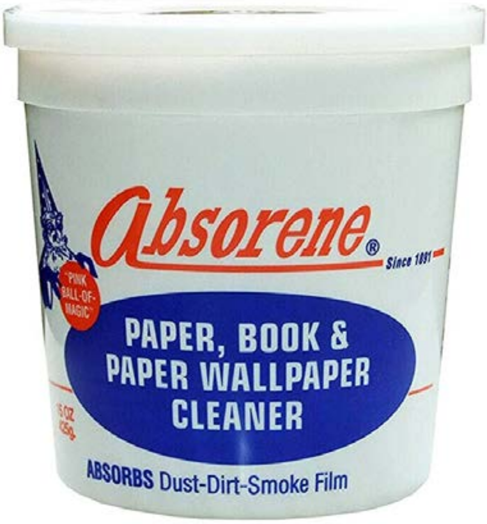
Solid eraser

Groom/StickTM Dry cleaning putty

Groom/StickTM is a malleable gum rubber which can be used to pick up dirt.[12] It is an isoprene rubber. It can be shaped as required and will leave very little residue on the surface. It is useful for dry types of dirt as well as more greasy substances. Because it is sticky, it is not suitable for paint layers or surfaces with adhesion issues, as it can dislodge poorly bound original material.

Absorene Putty Cleaner is a product that works in a similar way.[13] It is a malleable putty that can be moulded into the shape required and leaves very little residue on the surface. It is composed of starch (the filler) and white spirit (the solvent). It is commonly used in book and paper conservation. Absorene crumbs that may remain on the surface can be removed with a soft brush and vacuum.

Both Groom/StickTM and Absorene Putty Cleaner were found to leave a film deposit or particulate residue during testing of dry-cleaning methods on unpainted surfaces.[14]



Absorene book and paper cleaner

Groomstick dry cleaning putty

---

[11] Daudin-Schotte M, Bisschoff M, Joosten I, van Keulen H, van den Berg KJ (2013) pp. 215

[12] Available from: *https://www.picreator.co.uk/?page_id=176*

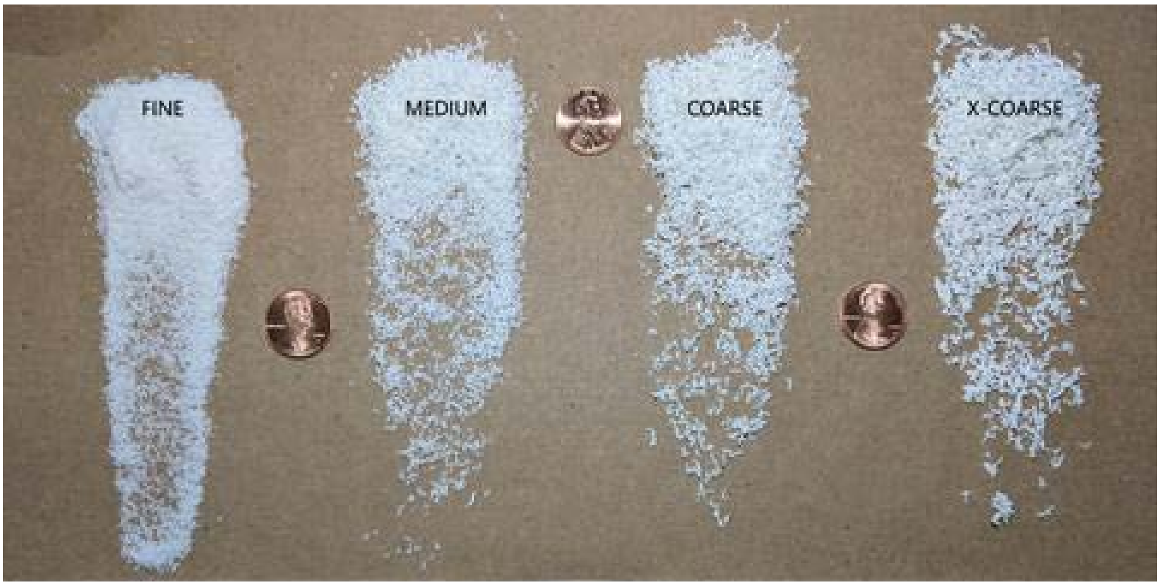
[13] *http://absorene.com/absoreneputtycleaner/*

[14] Daudin-Schotte M, Bisschoff M, Joosten I, van Keulen H, van den Berg KJ (2013) pp. 215

Groomstick

Grated or Powdered Eraser

Powdered or grated eraser can be used by depositing on the surface of the artwork and rubbed gently with either a cotton pad or small brush. The dirt and eraser particles can then be removed using a soft brush and vacuum. This technique can be useful for removing loose and particulate dirt, but it is less effective in removing well-adhered dirt and grime. The downfalls of grated or powdered eraser is the amount of fine residue that may remain on or in the paint surface, and the risk of changes to the paint surface such as increased glossiness as a result of friction.



Grated eraser crumbs

Aqueous Methods for the Removal of Surface Dirt

If, after testing one or more dry dirt removal methods, not all the layers of surface dirt are completely or satisfactorily removed, and if the surface of the artwork allows for it, aqueous methods can then be trialled.

Before commencing with trialling aqueous methods for surface dirt removal, a number of factors should be considered. Cleaning with aqueous methods should always take into account the type of surface being cleaned i.e. varnished oil paint, unvarnished oil paint, unvarnished acrylic paint, unvarnished surfaces with other binding media etc., the aims of surface dirt removal with aqueous methods, the surface characteristics of the surface, the properties of the aqueous solution, the different types of solutions in relation to the surface, the different forms of aqueous solutions ('free' solutions, oil-in-water solutions and emulsions, water-in oil solutions and emulsions, (rigid) gels etc.) and the type of dirt to be removed.

Aims when tailoring an Aqueous cleaning medium

When constructing an aqueous cleaning medium for the removal of surface dirt, the main goal is to remove surface dirt without disturbing and protecting the surface from which the dirt is being removed. The conservator should aim for limited and controlled contact between the surface to be cleaned and the aqueous cleaning medium. Variables such as the length of time the aqueous cleaning medium is on the surface, the method of application (such as with a swab dipped in free solution and gently rolled on the surface or applied with a brush through a tissue), and the structure of the solution (whether in 'free' aqueous solution, emulsion or gel, for example) should all be considered in relation to the surface requiring dirt removal. Another factor requiring consideration is whether the remaining surface dirt (after dry surface dirt removal) can be removed in one step, or if multiple steps are required to remove the dirt in phases. It is also important to ascertain prior to aqueous cleaning whether the remaining surface dirt is homogenous over the entire surface, or if it is a localised phenomenon. Another aim should be to limit the exposure of the paint to organic solvents (and vapours) if they are deemed necessary for aqueous cleaning. It is important to note that testing should start with the simplest system first, only adding variables as necessary.

The conservator should also consider the type of dirt requiring removal, as this will also guide the choice of additives to any aqueous solution (chelators, surfactants etc.). Dirt containing minerals and metal ions will require a chelating agent to aid in its removal, dirt with greasy or fatty (oily) components will require the addition of a surfactant for optimal removal. Buffers will help stabilise the pH of the aqueous solution and help avoid changing the pH of the surface, and changing the structure of the solution to an emulsion or gel will aid in controlling the area of exposure to the solution and inhibit the flow of the solution through the paint structure.

Different Types of Surfaces

Varnished Surfaces

Historically, artists have protected oil painting surfaces with varnish. This coating allows the surface to be brushed clean or even washed as needed to remove accumulated dirt without exposing the paint to risk.[15] Aqueous removal of surface dirt from varnished surfaces must still be undertaken with caution, especially if the varnish layer will remain on the painting. Aqueous solutions can cause blanching, crazing or crizzling (which is due to microcracking) to occur on or in a varnished surface, reducing its efficacy as a protective layer to the paint and reducing the visibility of the artwork underneath.[16] Older varnish layers may have also lost their protective function of the paint layers, for example by becoming brittle and developing micro-cracks, which means that aqueous cleaning media must be applied with caution, as they can flow through the cracks to the paint and support layers.[17] Note that if the varnish is to be removed at a later stage of treatment, it is essential to always remove the layers of surface dirt first!

---

[15] Hackney, Stephen. 2013. "The Art and Science of Cleaning Paintings." in *New Insights into the Cleaning of Paintings: Proceedings from the Cleaning 2010 International Conference, Universidad Politecnica de Valencia and Museum Conservation Institute*, edited by Mecklenburg, Marion F., Charola, A. Elena, and Koestler, Robert J., 11–15. Smithsonian Contributions to Museum Conservation. Washington, DC: Smithsonian Institution. Pp 11-16 *https://repository.si.edu/bitstream/handle/10088/20481/03.Hackney.SCMC3.Mecklenburg.Web.pdf?sequence=1*

[16] When the difference in pH between the varnish and the aqueous solution is two or more on the scale, an acid-base reaction can occur, resulting in blanching. To resolve this, the pH of the cleaning solution can be reduced so that the pH is closer to that of the (acidic) resin.

[17] Varnishes, and especially natural resins, are able to transport water on a molecular level. The OH- groups (on the carboxylic acid degradation groups) can absorb water and swell.

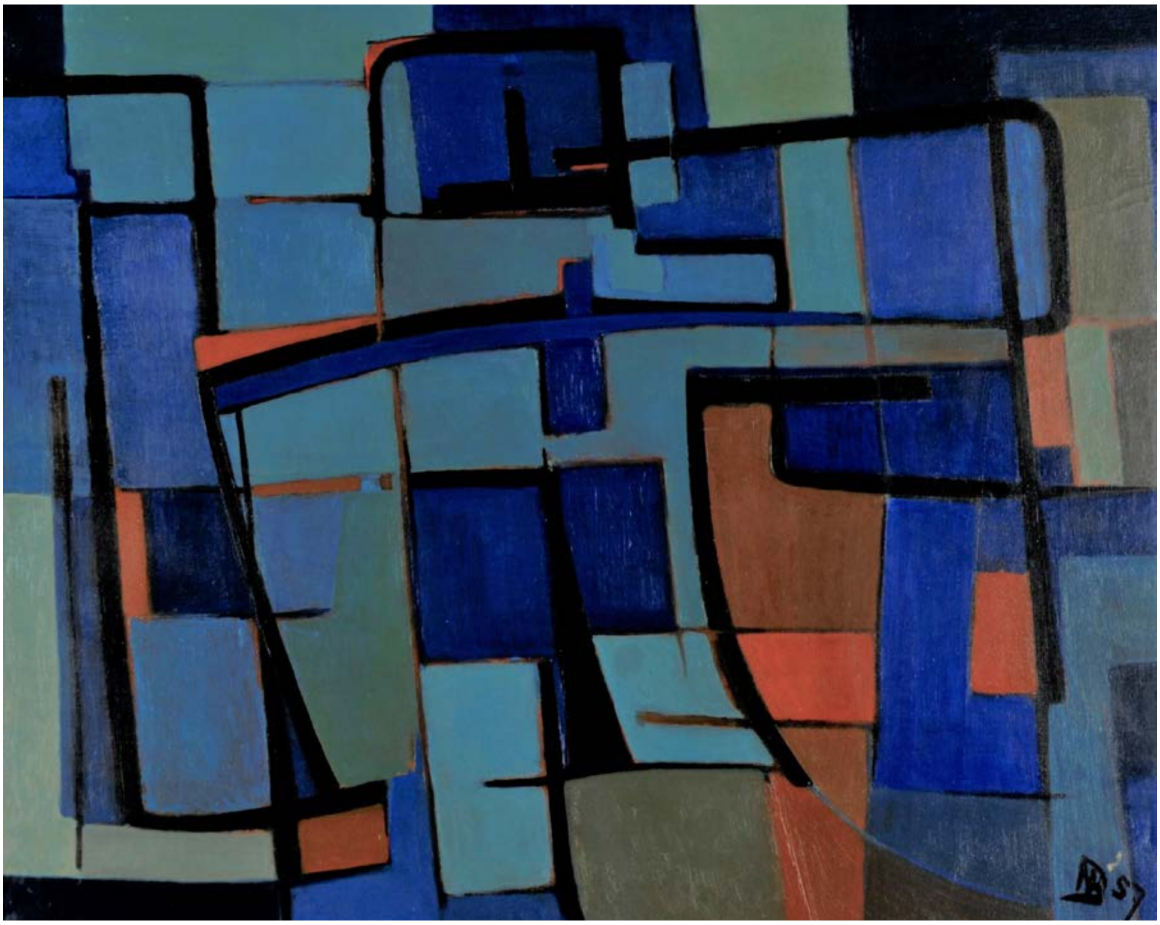
William Hogarth, 1761, *Time Smoking a Picture* (Museum Boijmans van Beuningen)

Unvarnished Oil and Acrylic Surfaces: Water Sensitivity

Unvarnished paintings pose a different type of challenge to conservators. Developments in the production of paint for artists, such as the invention of the portable paint tube in the 1840's, the development of acrylic and acrylic emulsion paints after the second world war, and more recently, the development of water-soluble oil paints have led to many artists abandoning the use of varnish. At the same time, changes in philosophies surrounding art and the notion of permanence and longevity were replaced with more modern concepts of creativity and originality and fleetingness.[18] From the Impressionists onwards then, many artists have moved away from varnishing their paintings, with a matte, flat or soft aesthetic as the goal.

The lack of a protective layer on a painted surface implies that the paint layer itself is in contact with the environmental conditions in which the artwork is held, and therefore more vulnerable to the changes in temperature, humidity, dirt and pollution. The aforementioned technological developments in paints for artists have also led to long-term negative effects for paintings with regard to sensitivity to solvents, and in particular, water.

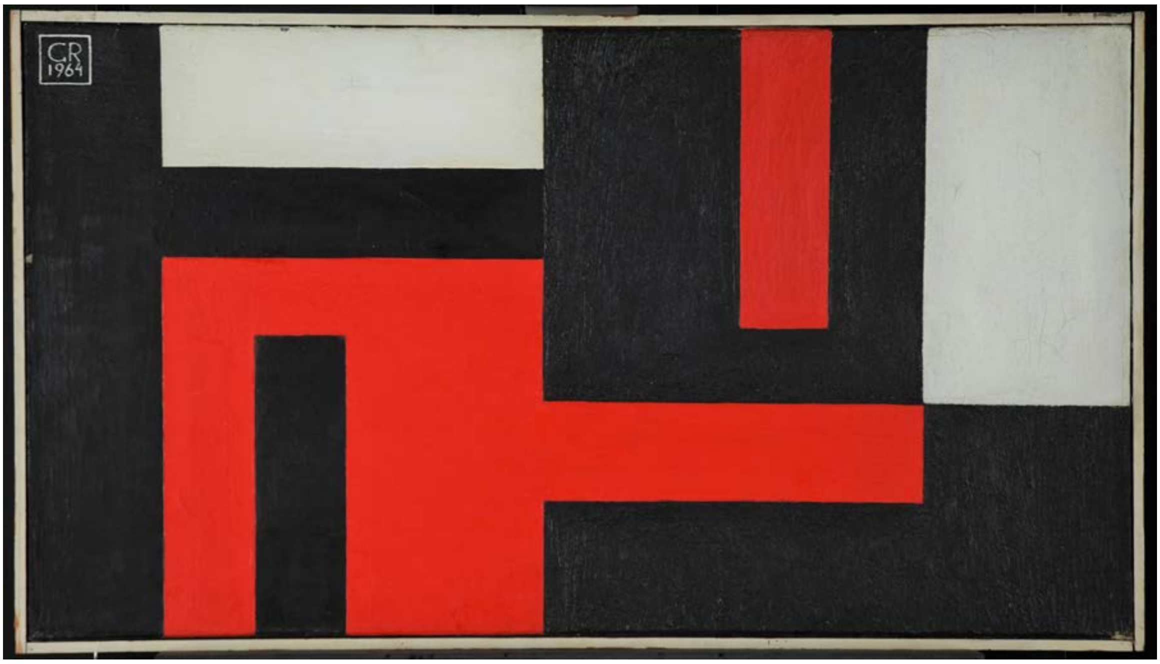
Water sensitivity is an extensive topic with regard to unvarnished modern paints and surface dirt removal. It refers to the (negative) effect that aqueous solutions have on paint. It indicates that when an aqueous solution comes into contact with (oil) paint, the paint can swell or can be damaged/removed during physical contact with, for example, a wet swab. Water sensitivity is most often



N. Boers, *Compositie*, 1957 (Cultural Heritage Agency collection). Water sensitivity in unvarnished paintings is an extensive topic. This painting is extremely sensitive to aqueous solutions, making it difficult to clean.

---

[18] Hackney, S., 2013, pp 13.



G. Ruyter, No.2 *Compositie*, 1964 (Cultural Heritage Agency collection). This modern, unvarnished painting showed sensitivity to water in the red areas.

present on paintings from the 50's through to the 90's,[19] although all periods since the 1900's have paint films which have been found to be water sensitive.[20] Surface dirt removal with aqueous solutions may remove water-soluble additives which may result in an uneven surface at micro level, visually resulting in less saturated or glossy colour. Aqueous treatments may also swell additives in the (acrylic) paint, such as surfactants, disturbing the paint layer.

Oil Paints

Modern oil paints also pose many challenges for the removal of surface dirt. Most modern oil paints are unvarnished, with the dirt at the immediate surface of the paint. Modern oil paints often have soft, water-soluble, medium-rich skins or layers on their surfaces. They are often soft and sticky, and sensitive to pigment pick up and are soluble in polar solvents. Modern oil paints may exhibit the formation of crystalline epsomite salts and crusts on their surfaces.[21] Studies have shown that manufacturer's formulations are contributing to one of the known causes of water sensitivity: the formation of magnesium sulphate heptahydrate, or Epsomite crystals ($MgSO_4.7H_2O$) on the surface of oil paint. These crystalline entities are thought to be formed due to an interaction between the paint extender magnesium carbonate, an additive in some twentieth-century oil paints, and atmospheric sulphur dioxide (SO_2) at elevated humidity.[22] The peaks in environmental sulphur dioxide levels during the industrial periods in Europe and North America of the 1950's to the 1970's correlate with the peak number of oil paintings known to exhibit water

---

[19] Cooper A., Burnstock A., van den Berg K.J., Ormsby B., *Water sensitive oil paints in the twentieth century: a study of the distribution of water-soluble degradation products in modern oil paint films*, 2014, in: *Issues in Contemporary oil paint*, pp 295-310

[20] A summary of the topic of water sensitivity in modern paints and research into water sensitivity of both oil and acrylic paints can be found at: *https://paint.tool.cultureelerfgoed.nl/water-sensitivity*

[21] Ormsby, B., Chung, J.Y., Lee, J., Burnstock, A., van den Berg, K.J., *An investigation of options for surface cleaning unvarnished water-sensitive oil paints based on recent developments for acrylic paints*, ICOM Committee for Conservation 18th Triennial Meeting Copenhagen Denmark 4-8 September 2017 *https://www.icom-cc-publications-online.org/1564/An-investigation-of-options-for-surface-cleaning-unvarnished-water-sensitive-oil-paints-based-on-recent-developments-for-acrylic-paints*

[22] Silvester G., Burnstock A., Megens L., Learner T., Chiari G., Van den Berg K.J., *A cause of water-sensitivity in modern oil paint films: the formation of magnesium sulphate*, 2014, in: *Studies in Conservation*, 59 (1), pp 38-51, Tempest H., Burnstock A., Saltmarsh P., van den Berg KJ., *Sensitivity of oil paint surfaces to aqueous and other solvents*, 2013, in: *New Insights into the cleaning of paintings. Proceedings from the cleaning 2010 international conference Universidad Politécnica de Valencia and Museum Conservation Institute. Smithsonian Institution Scholarly Press, Washington DC*, pp 107-117 *https://repository.si.edu/bitstream/handle/10088/20496/18.Tempest.SCMC3.Mecklenburg.Web.pdf?sequence=1&isAllowed=y*

Willem Raaphorst (1870-1963) Detail of *Still Life with Flowers*. Testing with various aqueous solutions showed the green oil paint to be highly sensitive to water.

sensitivity to aqueous cleaning methods of this same period.[23]

The composition of medium skins from modern oil paints have been shown to contain an abundance of diacids. This indicates that the oil medium has oxidised to a relatively high degree. The skins have a lower pigment concentration than the bulk paint beneath which indicates that the skins are more vulnerable to water and solvents, and to damage or removal through mechanical action.[24]

In general, modern and young oil paints have a lower pH (more acidic) so a more acidic aqueous solution or phase in an emulsion may be suitable for surface dirt removal. Induced swelling of the surface material (young oil paint or acrylic emulsion) will be reduced if the pH value of the cleaning solution is close.[25]

Acrylic Paints

Acrylic paints are also known for their sensitivity to aqueous solutions. Water and solvents can affect an acrylic paint film by swelling the film and extraction of paint film components.[26] These can lead to various changes in the appearance of the paint, including changes to colour, gloss and adhesion. Acrylic paint films are generally found to be more flexible and have less cracking than traditional (more rigid, brittle) oil paint. Acrylic paint films have a low Glass Transition temperature (Tg) at ambient temperatures, which is caused by surfactants acting as plasticisers to the paint film. A low Tg indicates a softness of the paint, and combined with the separation and migration of surfactants to the surface of the paint films, acrylic paints are particularly vulnerable to attract dirt, which becomes imbibed in the surface. Often finger marks and scuffs from handling are found in their surfaces, along with

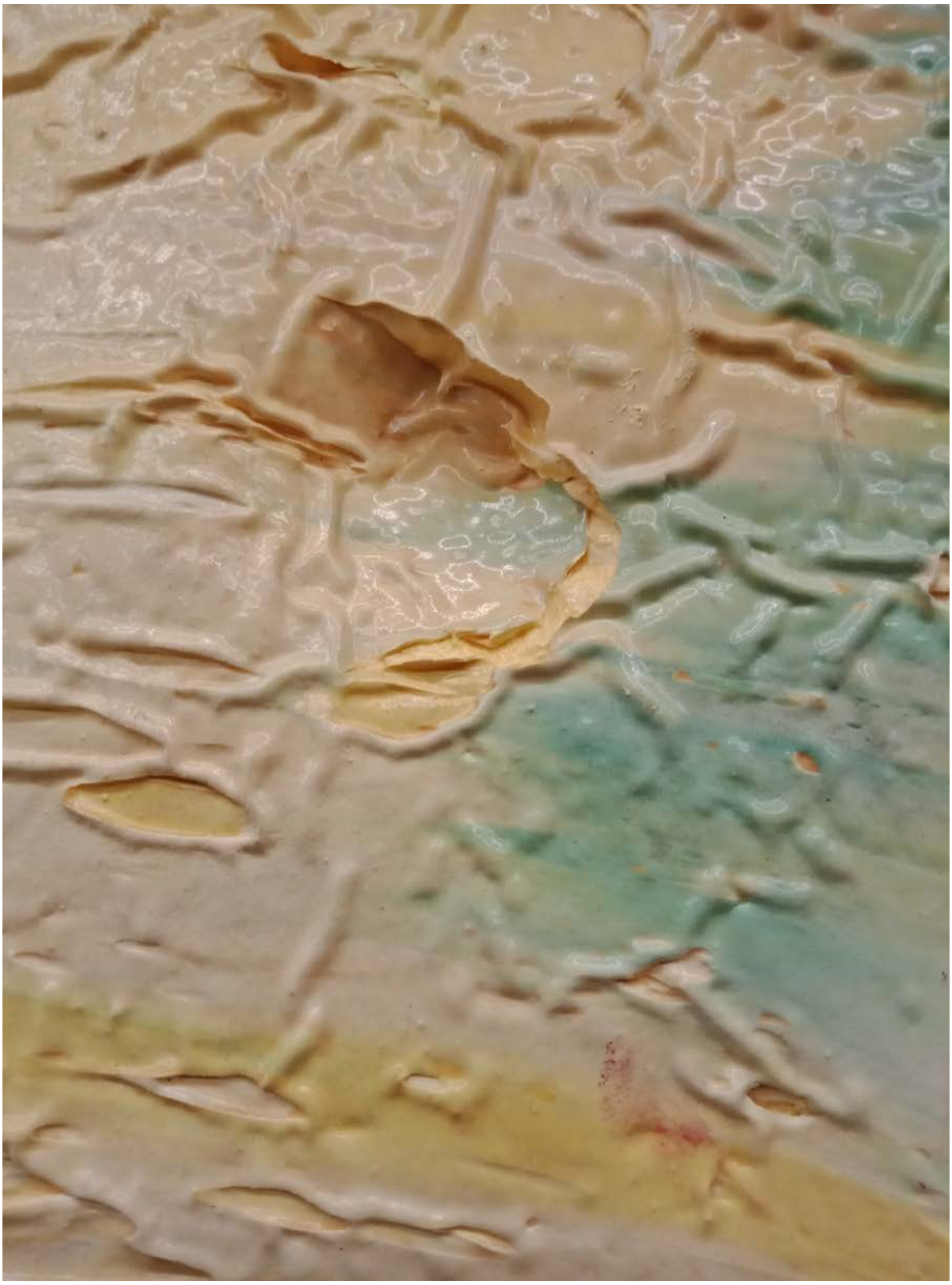
---

[23] Cooper A., Burnstock A., van den Berg K.J., Ormsby B., *Water sensitive oil paints in the twentieth century: a study of the distribution of water-soluble degradation products in modern oil paint films*, 2014, in: *Issues in Contemporary oil paint*, pp 295-310

[24] Ormsby, B., et.al. 2017. *https://www.icom-cc-publications-online.org/1564/An-investigation-of-options-for-surface-cleaning-unvarnished-water-sensitive-oil-paints-based-on-recent-developments-for-acrylic-paints*

[25] To measure the pH of the surface, see Appendix i: Measuring the pH of the surface.

[26] Water will cause swelling of the acrylic polymers resulting in a loss of definition of the paint film – impastos can be deformed. Water (without surfactants), especially at pH ranges above 6, can also extract migrated surfactants from the surface or pull out the surfactants from the bulk of the acrylic paint



Acrylic paint films have a low Glass Transition Temperature (Tg).

Dirt can often be imbibed in the surface of the paint. Here, streaks of dirt are imbibed in the orange and blue paint, almost impossible to remove.

accumulated surface and imbibed grime.[27] The problem is further exacerbated by the fact that acrylic resins are non-conductors and tend to have electrostatic charges on their surface which attracts dirt.

As dirt is often imbibed or well-adhered to modern oil and acrylic paint films, dry cleaning methods are not always effective, and can leave their own specific types of damage on these films (residues, changes to surface gloss, streakiness, for example). This means that, despite the risks, 'wet' solutions such as aqueous systems or those based on solvents are required to remove dirt. Additionally, aqueous solutions are known to have the greatest effect for the removal of surface dirt.[28] New approaches to cleaning these sensitive surfaces include the use of micro-emulsions and rigid gels which utilise the cleaning potential of water but brought to the water sensitive surface in an apolar medium.

Non-ionic and ionic surfactants are used in the production of acrylic and acrylic emulsion paints. They are added as stabilisers, anti-foamers and pigment wetting agents. They have a function in keeping the acrylic resin molecules in suspension in the aqueous environment and in ensuring a 'smooth' painting experience for the artist. Over time, they are often found to be concentrated on the surface of acrylic paint films, having migrated there from the bulk of the paint, and of course they are also found in the bulk of the paint film too. These surface surfactant molecules can be degraded by light, and can have various optical effects on the paint layer, creating matte spots or a mottled effect, or alter the appearance of a surface over a section or entire paint film by forming a haze.[29]

Other Binding Media

Aqueous cleaning methods for the removal of surface dirt from paint surfaces with other (aqueous) binding media, such as encaustic, tempera, gum or perhaps an artists' own mixture should be approached with caution. Generally speaking, aqueous solutions in 'free' form cannot be used to clean paints made with these types of binding media, as they will dissolve the paint. Surface dirt removal may be possible in rigid gel form, or through a protective barrier such as a piece of Japanese tissue, but careful testing should be conducted prior to any dirt removal attempt.[30]

---

[27] Perry, R., Problems of dirt accumulation and its removal from unvarnished paintings: a practical review. In: Hackney, S., Townsend T., Eastaugh N. (eds.) Dirt and Pictures Separated (1990) The United Kingdom Institute for Conservation of Historic and Artistic works, London, pp 3-10.
Stavroudis C., *Silicone Based solvents in Conservation- As free solvents and components of gel systems and microemulsions, 2016, in: Colore e Conservazione, 13–14 November 2015, Politecnico di Milano. Padova, pp 176-184*

[28] Ormsby B., Learner T., *Recent Developments in the cleaning of modern paints*, 2016, in: *Conservation Perspectives, Fall 2016, Conserving Modern Paints, The Getty Conservation Institute,*
http://www.getty.edu/conservation/publications_resources/newsletters/31_2/feature.html

[29] Ormsby B., Kampasakali E., Learner T. *Surfactants and Acrylic Dispersion paints: Evaluating changes induced by wet surface cleaning treatments*, 2013. New Insights into the cleaning of paintings. Proceedings from the cleaning 2010 international conference Universidad Politécnica de Valencia and Museum Conservation Institute. Smithsonian Institution Scholarly Press, Washington DC, Mecklenburg M.F., Charola, A.E., Koestler R.J. pp 159-164

[30] The author (JvdBurg) has had success in removing surface dirt from underbound matte paint and paint with Arabic gum as the binding medium using low concentrations of JunFunori through a tissue, which worked as a consolidant and aided in the removal of surface dirt, simultaneously.

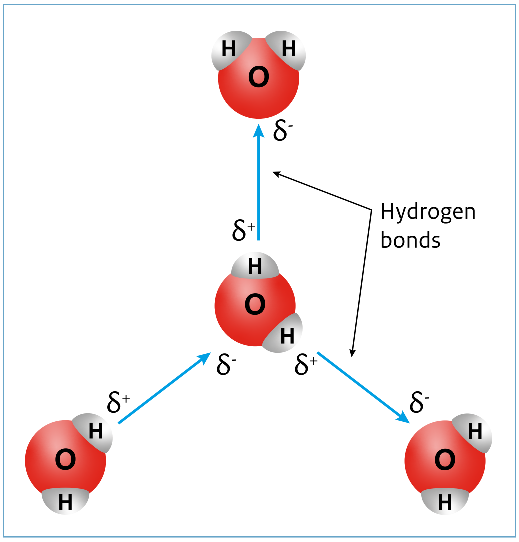
Aqueous Cleaning Methods

Types of Water

Water is a very important cleaning agent or solvent. It has an individual molecular structure with very particular characteristics, two hydrogen atoms bonded covalently to one oxygen atom. The combination of the molecular shape of water (an angular structure) and the difference in electronegativity between the oxygen and hydrogen atoms mean that water is a polar molecule. Because of this uneven distribution, water molecules interact with a high capacity for hydrogen bonds and dipole-dipole bonding. They are able to self-dissociate (split into smaller particles, ions or atoms) into Hydrogen (H+) and Hydroxide (OH-) ions. This is a reversible process. Water molecules are also able to induce dissociation of other (ionic) compounds, such as salts, and to ionise (larger) molecules.

Because of the potential to form strong intermolecular bonds, water is not particularly effective as a cleaning agent on its own; its ability to wet the surfaces of paint, varnish and dirt particles is restricted by its polarity and high surface tension, and thus low surface wetting capacity. Conversely, the ability of ions and other molecules to dissolve in water is due to polarity. The introduction of additives to water (see section on surfactants) reduces the surface tension of the water and increases its efficacy as a cleaning agent for relatively non-polar/ oily surface dirt removal.

All water sources contain impurities in the form of bacterial and foreign solid substances (soluble and insoluble non-ionised and ionised minerals and salts). The purity of water will affect its properties as a cleaning agent. Purified water is water from any source that is physically processed to remove impurities.[31] **Distilled water** is water that has virtually all bacterial impurities removed through distillation (boiling the water and condensing the steam into a clean container), but this does leave some water-soluble salts behind. Ion exchange systems can soften water, reducing the **hardness** of the water by exchanging cations that can precipitate calcium and magnesium (Ca++ and Mg++) for other soluble cations that do not precipitate such as sodium. **Deionised** or **demineralised** water has had the mineral content (water soluble salts) removed. Water softening or demineralisation is carried out using an ion exchange system where dissolved ions are replaced by other, more desirable, ions of a similar charge. Demineralisation effectively removes nearly all of the dissolved salt and mineral content from water, such as cations of sodium, calcium, iron, copper and anions of chloride or bromide. Deionisation is a physical process which uses specially manufactured ion exchange resins which bind to and filter out the mineral salts from water. Alternatively, membrane filtration technologies (reverse osmosis) or electro-deionisation processes can be utilised.[32] Distilled water will still have ions present, and thus may not be pH neutral. Deionised water should have a pH value of 5.8 (as the self-dissociated water molecules produce a charge, and from the absorbance of CO_2 molecules, to become in equilibrium with the atmosphere), however the pH should be checked before use as the ion exchange columns may out of balance.



Hydrogen water bonding and the transfer of protons between water molecules.

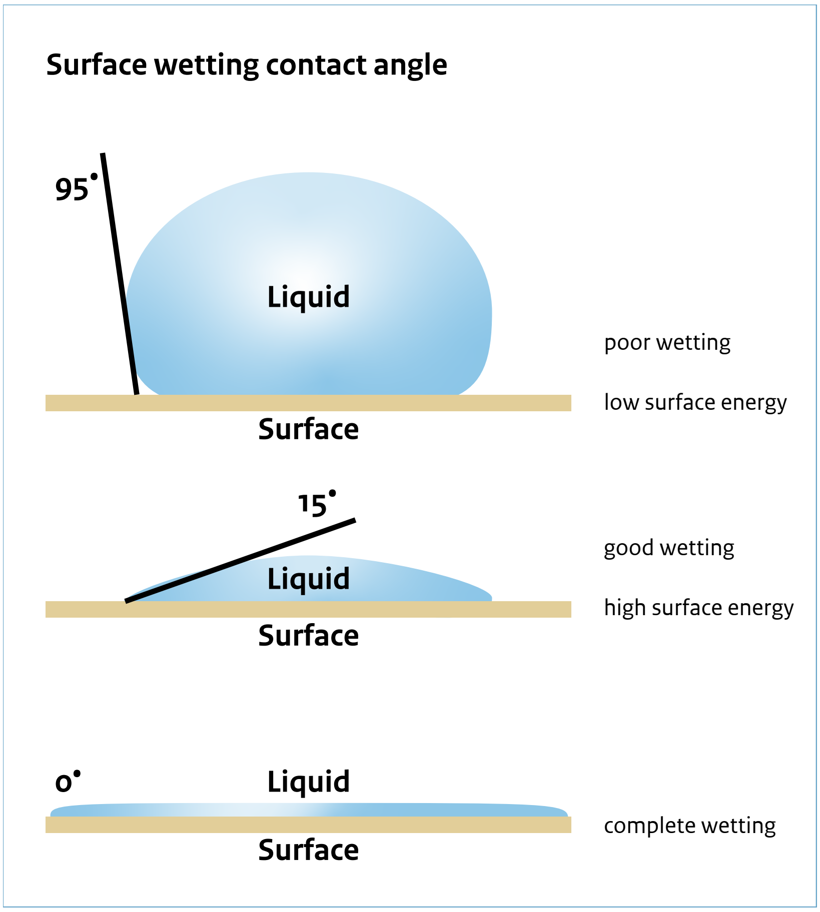
Hypertonic, hypotonic and isotonic solutions

Hypertonicity, hypotonicity and isotonicity refer to the concentration of a solution in comparison to another solution. A **hypertonic** solution contains a **higher** concentration of solutes compared to another solution. A **hypotonic** solution contains a **lower** concentration of solutes compared to another solution. An **isotonic** solution contains an **equal** concentration of solutes

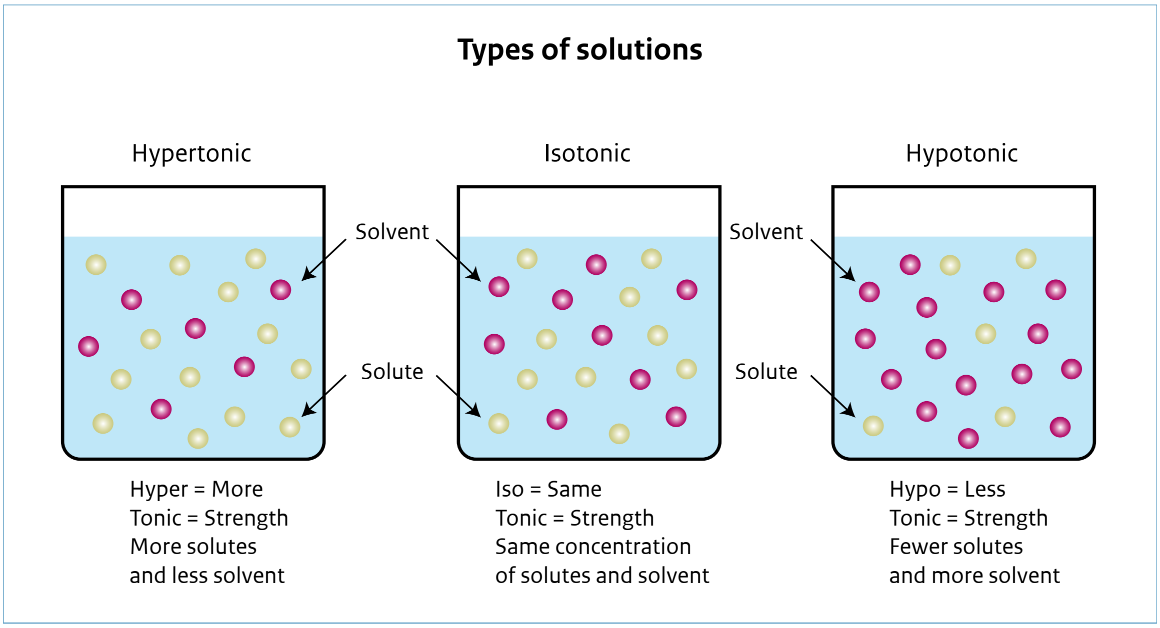
---

[31] Pure water does not really exist, as water will readily absorb CO_2 molecules from the atmosphere, thus becoming carbonated. Carbonated water has a slightly acidic pH value and can be useful for rinsing aqueous cleaning solutions with additives (buffers, chelators and surfactants).

[32] These remove the following: produce water that is nearly 100% free of minerals and salts including (but not limited to): Alkalinity (CO_3^{2-}, HCO_3^-), Calcium (Ca^{2+}), Chloride (Cl^-), Iron (Fe^{3+}), Magnesium (Mg^{2+}), Manganese (Mn^{2+}), Nitrate (NO_3^-), Potassium (K^+), ionic Silica, Sodium (Na^+) and Sulphates (SO_4^{2-}).



Surface wetting contact angles.



Hypertonic, Isotonic and Hypotonic solutions.

pH Scale

- pH scale is based on dissociation constant of water K_w
- $K_w = A_{H+} A_{OH-} = 10^{-7} . 10^{-7} = 10^{-14}$ mol/liter at 25°C (and ONLY at 25°C)

pH	Hydrogen Ion [H^+]	Hydroxyl Ion [OH^-]
0 Acidic	1.0	0.00000000000001
1	0.1	0.0000000000001
2	0.01	0.000000000001
3	0.001	0.00000000001
4	0.0001	0.0000000001
5	0.00001	0.000000001
6	0.000001	0.00000001
7 Neutral	0.0000001	0.0000001
8	0.00000001	0.000001
9	0.000000001	0.00001
10	0.0000000001	0.0001
11	0.00000000001	0.001
12	0.000000000001	0.01
13	0.0000000000001	0.1
14 Basic	0.00000000000001	1.0

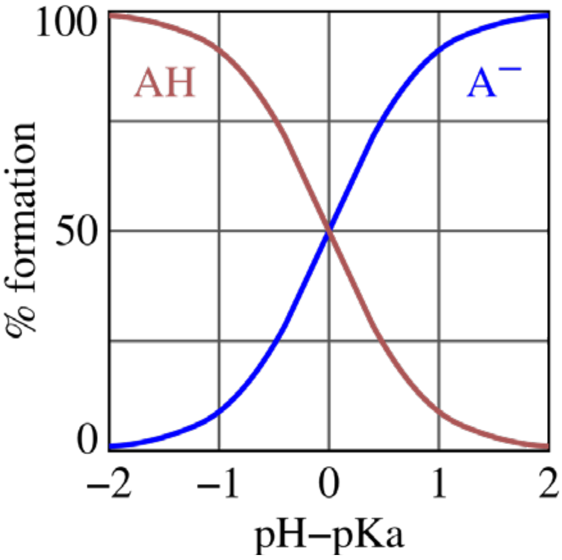
The pH scale is a logarithmic scale.

Buffered solutions can be bought off the shelf to calibrate pH meters.

The pH of a solution can be measured either with a pH indicator (paper) which varies in colour according to the pH of the solution, or with a pH meter containing pH selective electrodes.

Two buffer solutions used for testing for the removal of surface dirt from varnished and unvarnished paintings.

compared to another solution. It is important to understand these concepts, as the concentration of an aqueous solution will have an effect on the paint surface. When two solutions of different concentrations are placed in a container and separated by a semi-permeable membrane, molecules will pass in the direction that tends to equalize the solute concentrations on the two sides (so from a high concentration to a low concentration) in a process known as osmosis. When an aqueous solution has a high concentration of molecules compared to the paint surface, molecules will attempt to flow into the paint surface, and cause swelling of the paint film. When the concentration of an aqueous solution is lower than that of a paint film, it will draw out molecules from the film (leaching). Note that deionised water is a hypotonic solution, which will draw out film material, like surfactants. Hypertonic solutions, on the other hand, with high conductivity, are less likely to draw out materials but can swell paint films.



Variation of the percentage (%) formation of a monoprotic acid, AH, and its conjugate base, A−, with the difference between the pH and the pKa of the acid.

pH levels of Aqueous solutions

pH (power of hydrogen) is a measure of the hydrogen ion concentration of the water as ranked on a scale of 1.0 to 14.0. It is used to measure acidity or alkalinity (base) of a solution, where pH 7 is neutral, below pH 7 is acidic and above pH 7 is basic (in ambient temperatures). In a neutral solution at a pH of 7, the Hydrogen (H+) ions equal the Hydroxide ions (OH-), at any given temperature. A lower pH indicates that there are more Hydrogen ions present in solution, while a higher pH indicates that there are more Hydroxide ions in solution. Acids and Bases are molecules or salts that will dissociate in water (break up into ions – cations (positive) and anions (negative)). Strong acids and bases will completely dissociate in water, whereas weak acids and bases will only partially dissociate in water. An acidic material is a substance that will give up Hydrogen ions, whereas a basic (alkaline) material will yield OH- ions. An acidic solution is defined as a solution where $[H_3O+]$ is greater than 1×10^{-7} and a basic solution where $[H_3O+]$ is less than 1×10^{-7}. It is thus a reciprocal balance of ions.[33]

The quantitative measure of the strength of an acid or base (alkali) in solution is the acid equilibrium dissociation constant (K_a) and alkaline equilibrium dissociation constant (K_b) respectively. By calculating the negative logarithm of K_a, the value K_a is converted into the pK_a value, in general a small positive number. The pK_a value relates to the (potential) acidity of a solution. In other words, the smaller the pK_a value for any acid, the stronger the acid is, and the larger the pK_a, the weaker the acid. As strong acids are said to be fully dissociated, their pK_a values will be less than 1.

Similarly, via the negative logarithm the K_b can be converted into the pK_b that expresses how strongly alkaline (= basic) a solution potentially will be. The lower the pK_b value, the more alkaline.

The pH of a solution can be measured either with a pH indicator (paper) which varies in colour according to the pH of the solution, or with a pH meter containing pH selective electrodes.

The pH of the surface of the artwork can also be tested. This can either be done with a drop of water ('free' solution) or with a small gel disk. See: *Appendix I* for an explanation of these methods.

Buffers

The pH of a solution can adjusted by the addition of a soluble substance, either acidic or alkaline in nature (note that dissolved biological materials will also alter pH). The pH of a solution can change over time (also through contact with air). They are therefore not stable. To stabilise the desired pH a buffer or buffering agent is used. Buffers are usually either acidic or alkaline in nature themselves. The function of a buffer is to keep an acidic or basic solution within a certain pH range and prevent or lessen change in this pH (within two pH degrees). It therefore works as a balance. In a solution, half of a buffers' molecules will dissociate (carry a charge/become ionised) and half will remain neutral. If additional material is added to the solution and dissociates, then either some of the neutral buffer molecules will disassociate or some of the disassociated buffer molecules will neutralise (either re-form or form a neutral by-product), thus balancing the pH.

Buffering agents have variable properties in themselves and some are more soluble than others, some are weakly acidic and some are weakly basic. In practice, a buffer is made using an acidic or alkaline starting material, and adjusting the pH by adding a standard strong alkaline or strong acidic solution until the optimal buffer pH state has been reached.

It is important to buffer solutions for aqueous cleaning as aged surfaces are not often neutral in behaviour. Over time they tend to become either more acidic or basic. Typically, aged varnish material becomes more acidic over time as more carboxylic functional groups are formed. On the other hand, aged proteins become more alkaline over time. The pH of a surface can be measured prior to surface dirt removal to help choose a solution with a suitable pH (see Appendix for measuring the pH of a surface).

In order to retain the potency of the solution, it is essential that the pH of the solution when applied to the paint surface (which will have its own pH) is maintained. Thus, in order to maintain a given pH of a liquid applied to either an acidic or basic surface it is thus important to have a buffered solution to ensure that the desired pH of the solution is maintained as the dirt is dissolved into the solution.

---

[33] Note that the pH scale is logarithmic. A change of one unit on the pH scale represents a change in the concentration of hydrogen ions by a factor of 10, a change in two units represents a change in the concentration of hydrogen ions by a factor of 100. Thus, small changes in pH represent large changes in the concentrations of hydrogen ions. The pH of a solution will be affected not only by its components, but also by the level of concentration of a solution and the ambient temperature.

Simple solutions are composed of water (de-ionised or distilled) with either an acid or a base added. Low concentrations are used, as roughly 0.5-2% is sufficient to produce the desired cleaning effect.[34] Buffered solutions can either be used directly on the paint surface or gelled to inhibit penetration (see below, section on gelling).

Buffered pH aqueous recipes

The following recipes can be used to buffer water at various pH's. Cleaning of dirt particulate from aged varnish surfaces should begin with a pH of 5.5. Tests can be carried out with slight increased pH values in a step-wise manner to establish the most effective cleaning solution. This is the methodology explained within the Modular Cleaning Program.[35] Note that concentrates can be made up and diluted prior to use. All cleaning solutions can be gelled with hydroxy-propyl cellulose. All buffered cleaning solutions should be rinsed. Rinsing solutions can be made with a volatile buffer such as one with acetic acid. Rinsing solutions should be tested also, starting with one of similar pH as the cleaning solution. Note that if this is causing swelling, the pH of the rinsing solution can be dropped. Final rinses can be made with carbonated water (made in a Sodastream using distilled water).[36] Alternative rinsing systems exist depending on the buffering material. If the surface is sensitive to water, a hydrocarbon solvent may be appropriate.

The following recipes have been modified from the Modular Cleaning Program, designed by Chris Stavroudis (a private conservator in los Angeles). See note 39 for further information.

100 mL Buffered water at pH 5.5 with MES Hydrate (4-Morpholineethanesulfonic acid):

5.33 g MES hydrate
1.31 mL sodium hydroxide (NaOH) 10% (w/v) (0.25M) in solution
Ca. 100mL distilled water[37]

Measure 5.33 g of MES hydrate in 88.4 mL of distilled water. Adjust the pH slowly by adding approximately 1.31 mL of NaOH (10%) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

100 mL Buffered water at pH 6.5 with Bis-Tris (Bis(2-hydroxyethyl)amino-tris(hydroxymethyl)methane):

5.23 Bis-Tris
10.3 mL hydrochloric acid (HCl) 10% (v/v) (2.87M) in solution
Ca. 100 mL distilled water

Measure 5.23 g of Bis-Tris in 79.5 mL of distilled water. Adjust the pH slowly by adding approximately 10.3 mL of HCl solution while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

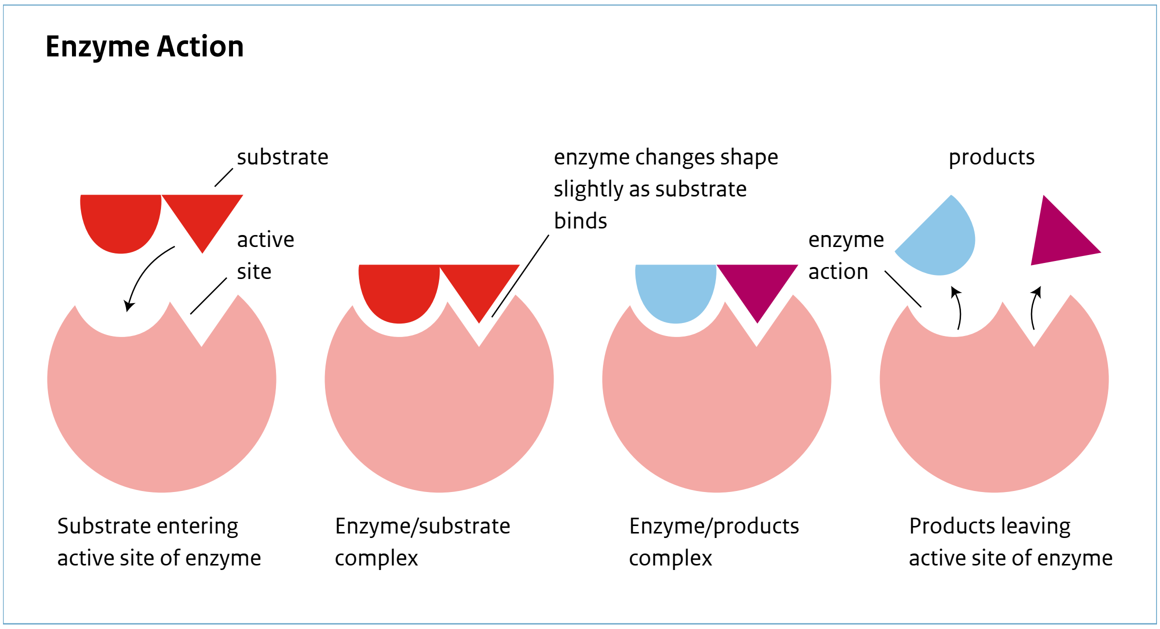
---

[34] This is related to the concentration of solutions in relation to surfaces and how highly concentrated solutions create hyper or hypotonic cleaning environments.

[35] The Modular Cleaning Program (MCP) was designed by Chris Stavroudis (a private conservator) in 2002. The Modular Cleaning Program is both an approach to cleaning and a FileMaker Pro database. He has codified the scientific basis of aqueous cleaning and solvent theories into the logic of the computer database. The program models aqueous chemistry at a given pH, reflects an ad-hoc theory of solvent gel formulation, and makes calculations in Hansen solubility space as it guides the conservator in the preparation of test cleaning solutions. The software is free and can be accessed by a key, provided by the developer. The programme can be downloaded from the following website (registration necessary): *https://cool.culturalheritage.org/byauth/stavroudis/mcp/*
See also the Facebook group: The Modular Cleaning Program *https://www.facebook.com/groups/268187987869905 run by Luke Addington Craig Deller, Chris Stavroudis, Nina Roth-Wells and Tiarna Doherty.*

[36] Sodastream systems carbonate tap water and can be bought from a variety of suppliers, such as *https://sodastream.com/*

[37] Distilled water is recommended, as the quality and cleanliness and purity of tap water varies per country/area/city.



The mechanism of an enzyme on the substrate.

100 mL Buffered water at pH 7.5 with Tris/Trizma base (Tris(hydroxymethyl)aminomethane):

3.03 g Trizma base
16.55 mL Hydrochloric acid (HCl) 10% (v/v) (2.87M) in solution
Ca. 100 mL distilled water

Measure 3.03 g of Trizma base in 74.5 mL of distilled water. Adjust the pH slowly by adding approximately 16.55 mL of HCl solution while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

100 mL Buffered water at pH 8.5 with Bicine (N,N-Bis(2-hydroxyethyl)glycine):

4.08 g Bicine
5.35 mL sodium hydroxide (NaOH) 10% (w/v) (0.25M) in solution
Ca. 100 mL distilled water

Measure approximately 4.08 g Bicine in 85.6 mL of distilled water. Adjust the pH slowly by adding approximately 5.35 mL of NaOH solution while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

Enzymes

Enzymes are naturally occurring protein molecules, which are found in living tissues. Enzymes work as a catalyst propagating a reactive breakdown procedure and need specific environmental conditions (temperature and pH) in order to work. Saliva is composed of ca. 98% water and many other substances including electrolytes, antibacterial compounds and various enzymes. The main enzyme found in saliva is α-amylase, which is also the most common enzyme used in conservation. Saliva also carries many important ions such as calcium, phosphate and fluoride, which may aid ionic exchange with particulate dirt on the surface and dirt 'pick up'. Synthetic saliva is available, but note that many enzymes have a short shelf life and must be used at certain temperatures and pH levels.[38] They can also be expensive but are an accurate cleaning technique. Other enzymes that may be useful are Protease which is useful for the breakdown of proteins, and Lipase, which is useful for the breakdown of oils.

The enzymes in saliva are non-volatile, thus it is always necessary to rinse the surface to remove residues from the surface.

---

[38] Synthetic saliva is available from Phase Restoration Products, in Italy: *https://www.phaseitalia.it/negozio/saliva-artificiale-phase/*

Chelating Agents

Chelating agents are weak acids (chemical compounds) that, if sufficiently deprotonated (ionised) when dissolved in water, react with inorganic (mineral) compounds without precipitating.[39] The ionised chelator has sufficient 'power' to disassociate specific compounds, locking onto the charged metal ion (cation) to form a stable, water-soluble complex. They are also known as chelators or sequestering agents. Their ability to deprotonate are influenced by pH and temperature.

Chelating agents have a molecular structure consisting of 'arms', called ligands. A ligand is an ion or (part of a) molecule which can bond to a metal ion by donating a pair of electrons to the central metal atom or ion to form a coordination complex. The chelator is an electron donor and the metal ion is the electron acceptor. A chelator must have at least two such ligands capable of forming bonds with the charged cation (metal ion) allowing it to be pulled apart (disassociated) from its anion. The number of ligands (bonding sites) will dictate the strength of the chelator, so a chelator with 6 ligands will be a strong chelator, whereas a ligand with 3 is considered a weak chelator. The more ligands there are, the stronger the bond to the metal ion will be. Stronger chelators will also have an affinity for metal ions carrying a higher charge. Once the charged metal ion is locked in position, the formed complex has a ring-like structure. The separated anion remains suspended in the aqueous solution, and can form a new compound with appropriate un-associated cations present.

In surface dirt removal, chelating agents will lock onto the metal ions contained within the dirt particulate.[40]

Before we decide on which chelator is appropriate to disassociate a compound, we first need to know if the chelator molecule will become ionised (charged) in an aqueous solution, at what pH values this occurs, and to what degree deprotonation occurs. This is rather complicated because not all ligands on a multi-ligand chelator molecule will become deprotonated at the same pH value. Thus, as pH raises more ligands will become charged. Understanding this and utilising it will be key in using chelators effectively.

The pK_a value is one method used to indicate the degree of deprotonation of a specific chelator. This value, provided in material data sheets, is used to indicate the strength of any acid. A lower pK_a value indicates a stronger acid (ie that the acid will fully dissociate in water).[41] This value is related to pH.[42] Essentially, **pK_a** tells you what the **pH** needs to be in order for a chemical species to donate or accept a proton. It therefore provides an indication how much ionisation will happen at an equivalent pH value. Chelating agents with multi-ligands will therefore have multiple pK_a values. For instance, a tri-ligand chelator will have three pK_a values, where at the highest pH all ligands are ionised, and a hexa(6)- ligand chelator will have 6 pK_a values. Chelators will still function, but less effectively, if only 2 ligands are ionised. This point is essential as we will see later.[43]

Chelators can be either inorganic or organic in structure, however organic chelators are more commonly used in conservation. Chelating agents commonly used in conservation are Citric Acid, Triammonium Citrate (TAC), Ethylenediaminetetraacetic acid (EDTA), Sodium Tripolyphosphate (STPP) and Diethylenetriaminepentaacetic acid (DTPA).[44]

In order to select the correct chelator for the task at hand, two values should be considered. First, the potential of the unwanted material to dissolve in water. This can be quantified using a scale pK_{sp}, denoting solubility product.[45] Here, the higher the value the less potential for disassociation to occur. This denotes the dynamic equilibrium between the two ion concentrations (cation and anion) deriving from the starting compound.[46] The larger the constant (ie the larger the pK_{sp} values), the fewer the number of ions present in solution, and therefore the less soluble the compound. The pH is important for the dissociation level of the chelating agent. Only if the chelating agent is sufficiently deprotonated, and provided it has sufficient affinity for a metal cation, the poorly soluble solid may dissociate

---

[39] **Deprotonation** is the removal (transfer) of a *proton* (or *hydron*, or hydrogen cation), (H^+) from a *Brønsted–Lowry acid* in an *acid–base reaction*.

[40] This includes particles such as sulphates or carbonates or phosphates. Chelators also have the potential to disassociate pigments that are inorganic mineral compounds. Due care should be taken when selecting a chelator in order not to effect paint layers, especially of unvarnished paintings. Understanding the chemistry of chelation is therefore essential.

[41] The **pK_a** value used to indicate the strength of an acid. pK_a is the negative log of the acid dissociation constant or Ka value. A lower pKa value indicates a stronger acid.

[42] The **pH** is a measure of the concentration of hydrogen ions in an aqueous solution. The relationship between **pH and pK_a** is described by the Henderson-Hasselbalch equation.

[43] It should also be noted that partially charged weak chelators, such as citric acid, can be used as a buffer.

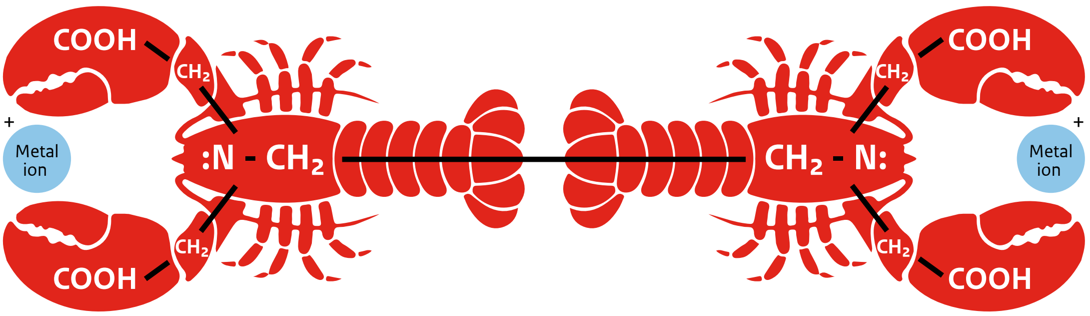
[44] EDTA has 6 ligands (bonding sites) so it is considered a strong chelator. The pK_a of EDTA is: at pH 0.0, 1.5, 1.99, 2.67, 6.16 and 10.26. Citric acid has 3 ligands (bonding sites) so it is considered a weak chelator. It's pK_a's are at pH 3.13, 4.76 and 6.40. Citric acid also works as a buffer between a pH of 2 and 7.

[45] The solubility product CANNOT be related to pH or pKa values.

[46] Calcium carbonate ($CaCO_3$) disassociates into Calcium cations (Ca^{2+}) and Carbonate anions (CO_3^{2-}). $K_{sp} = [Ca^{2+}][CO_3^{2-}]$. Manganese Hydroxide ($Mg(OH)_2$) has a $K_{sp} = [Mg][OH]^2$

Chelating agent structure (EDTA)

Chele - crab's claw (Greek)
Ligare - to bind



Chelating agent structure (EDTA). Chele means crab's claw in Greek, and ligare 'to bind'. So, the structure of the chelating agent resembles a crab's claw, which binds to the metal ion.

because the chelating agent-cation bond is stronger than the cation-anion bond in the poorly soluble solid. In effect, knowing the pK_{sp} value will help us to predict the solubility of a compound. The solubility product of common materials at given concentrations are available in reference tables.

A chelator needs to have sufficient 'power' to dissociate (break up) the ionic bond present in the compound. This 'power' will increase according to the number of ligands (and their ionisation potential). But it is also relative to the metal ion attracted and subsequently bonded to the chelating agent.

Different chelating agents have different affinities for different metal ions.[47] The attraction of the metal ion to the chelator must be higher than the attraction to the anion before sequestering will occur. This can be expressed using the logarithmic scale pK_{dis}, with K_{dis} denoting the equilibrium constant of the disassociation of the metal ion – ligand complex. The pK_{dis} value therefore denotes the ability of the chelator to attract the metal ion. This is the second value that is key to designing the optimal chelator cleaning solution. Note that if two compounds, containing metal ions, are present, the ionised chelator will sequester the metal ion it is most attracted too, leaving the other compound unaffected.

When selecting a chelator for use, it is wise to know what metal ion needs to be sequestered and to design the cleaning solution to the correct pH to optimise this occurrence. We therefore need to know the pK_a, the pH, pK_{dis} and the pK_{sp} values. It should be noted that effective cleaning may occur when not all ligands of the chelator are charged. A cleaning solution can be designed to effectively remove dirt particles, such as calcium sulphate (present in gypsum/concrete), while leaving calcium carbonate containing pigments or substrates unaffected (note that lead white often contains calcium carbonate as a bulking filler and ground layers in norther European practice will contain chalk).

But what if the characterisation of the dirt particulate is not possible? And values such as pK_{dis} and pK_{sp} are not known? This is where a different approach is required. The methodology behind the Modular Cleaning Program takes this into consideration.[48] The cleaning program utilises a pre-made set of testing solutions designed in increments of 0.5 pH ranges with a variety of chelators of increasing potential to sequester metal ions. Implementing a sequential and comparative testing regime will allow the conservator to evaluate results and select the most appropriate solution.

Note that it is also essential to use a buffer when cleaning with chelators. A buffer will hold the pH of the designed

---

[47] TAC has a strong affinity for Iron (III) and Copper (II) ions. DTPA has a strong affinity for Calcium, Magnesium and Copper (II). EDTA complexes with Iron (III), Lead and Calcium, and Citric acid with Calcium, Copper (II) and Iron (III). This means that these chelating agents are potentially hazardous when used directly on paint with metal ion containing pigments, such as Cadmiums, Lead white, Prussian Blue, Vermillion, Chalk (Calcium Carbonate), Chrome pigments, Orpiment and so forth.

[48] See note 31 regarding the MCP

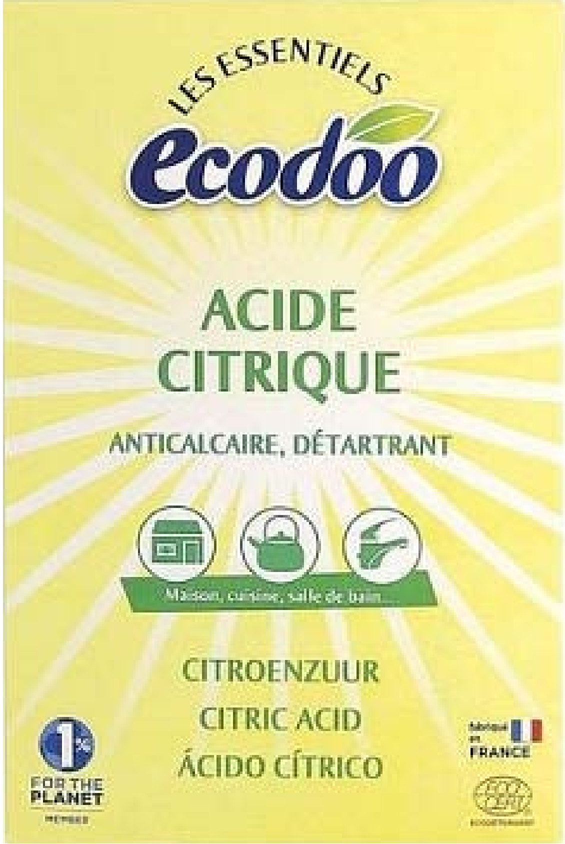
cleaning solution at the desired value. It acts as a balance, counter acting against sharp swings of increased ionic contribution as compounds are disassociated by the chelator. Citric acid (pK_a 3.13, 4.76, 6.4) needs to be sufficiently deprotonated (till at least pH 6), otherwise the chelating power of the citrate isn't strong enough. This deprotonation is typically carried out by adding a (standard) strong alkaline solution, such as NaOH 10% (w/v), until the desired pH is reached. Be aware that in the pH interval 5.4-7.4 the citrate anions form a self-buffering system, so no extra buffer needed. However, if the pH needed is larger than 7.4, an extra buffer would be needed to keep the pH constant.

Note: Chelating agents must be dissolved in deionised water, otherwise the reagent will react with the metal ions present in water, sequestering them rather than the metal ions found in the dirt particulates!

TAC and Citric acid have also been found to be effective at removing the oily organic compounds that cannot be sequestered. Other processes such as deflocculation, dispersion and peptization are responsible.[49] This may be aided by the chelating properties of the citrate molecules. The downside is that the binding medium of unvarnished oil paint could also be vulnerable to the efficiency of citrate solutions.

The other factor to consider when using chelators is the concentration. Although some conservators are comfortable using citrate (Citric acid and Triammonium citrate) solutions at high concentrations, dilute solutions pose less risk to the paint film and can be effective at concentrations as low as 0.1% w/v.[50] It is recommended to use these solutions at under 10 x the conductivity level of the surface you wish to maintain. As few conservators have access to conductivity meters, we recommend a concentration of no more than 2% w/v.

Any residues should be neutralised and removed from the surface to reduce the possibility that the chelator continues to react chemically with the paint components. Rinsing solutions can be made with volatile acids such as acetic acid or carbonic acid (carbonated water).[51] The rinsing solution needs to be of similar pH value or lower to be effective. Note that if the surface you wish to maintain appears sensitive (i.e. colour is observed on your swab) to a rinsing solution of the same pH, it is best to use a lower pH solution. The surface should always be air dried after cleaning with the chelator before rinsing.



Citric acid is a chelating agent that is available from most pharmacies and health food stores.

Studies show that using low concentrations of citrate solutions (ca. 0.5-1.5%), followed by rinsing with demineralised/deionised water, after the surface has dried, is effective at removing any residual citrate from the surface.[52]

At a pH of 7, TAC is fully ionised with all three ligands charged. At this pH, the molecules of TAC have the greatest affinity for the positively charged cations contained in the dirt layer. Therefore, it is useful to use TAC in a solution with a pH ranging from 6.5-7.4.

Note: Extremes of pH must be avoided to prevent the breakdown of paint or varnish components. Strongly

---

[49] Alan Phenix & Aviva Burnstock (1992) THE REMOVAL OF SURFACE DIRT ON PAINTINGS WITH CHELATING AGENTS, The Conservator, 16:1, 28-38, DOI: *10.1080/01400096.1992.9635624*

[50] See the section on hypertonic, hypotonic and isotonic solutions for further explanation.

[51] See section above for recipes.

[52] Morrison, R., Bagley-Young, A., Burnstock, A., Van den Berg, K., & Van Keulen, H. (2007). An Investigation of Parameters for the Use of Citrate Solutions for Surface Cleaning Unvarnished Paintings. *Studies in Conservation*, 52(4), 255-270. *https://www.researchgate.net/publication/259829822_An_Investigation_of_Parameters_for_the_Use_of_Citrate_Solutions_for_Surface_Cleaning_Unvarnished_Paintings*

Solutions from the MCP testing kit, ready for testing on an unvarnished painting.

alkaline solutions will saponify an oil medium and the saponified product may act as an emulsifier and thus must be avoided.

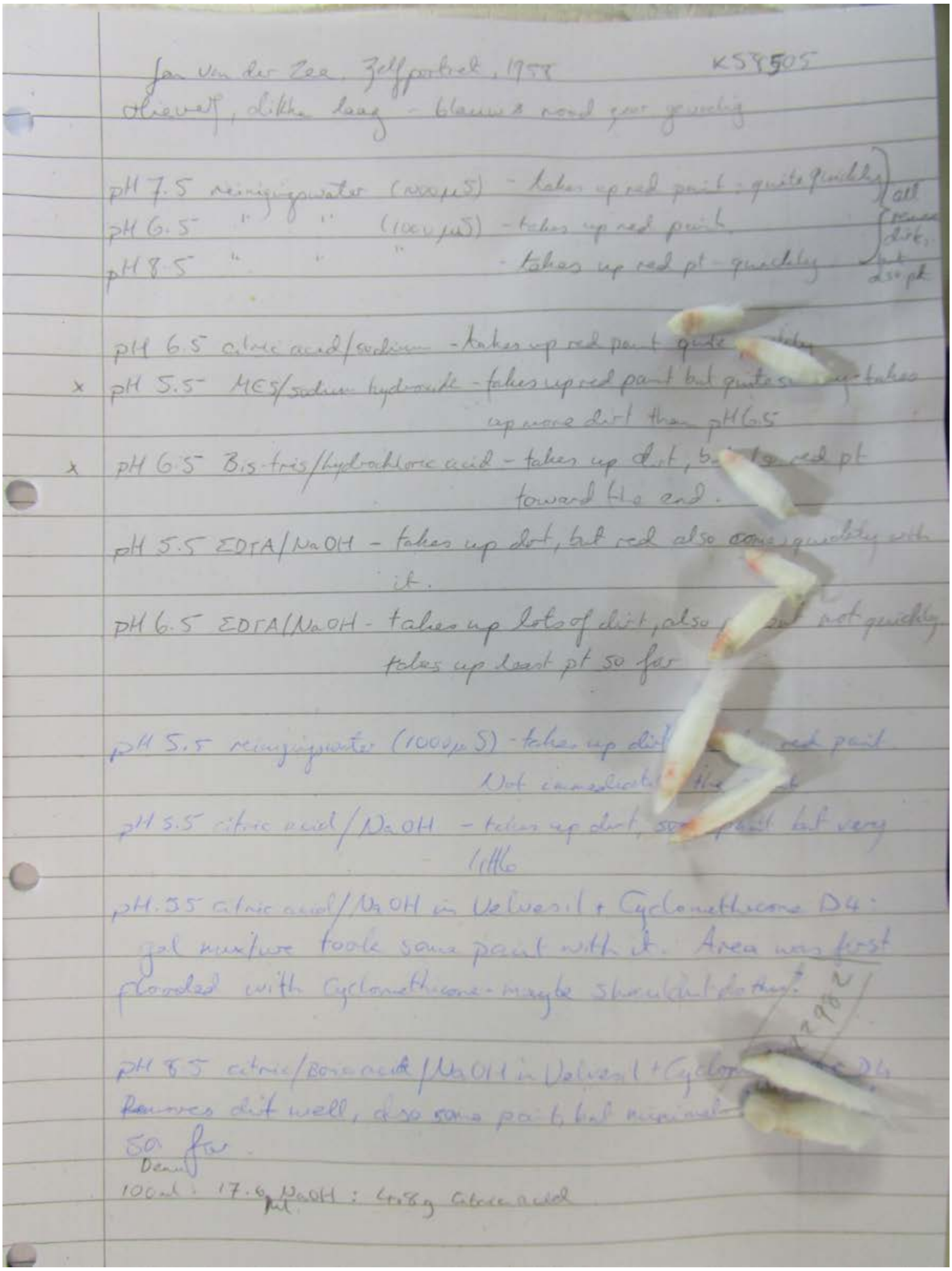
Chelating safety margins: Note that different paints will have different sensitivities to pH, and will therefore require different safety margins. Aqueous solutions with a pH between 6.0 and 8.5 are generally considered safe for oil paint (above 8.5 it will swell). Aqueous solutions for acrylic paint should have an acidic pH, ideally as low as pH 4.5.[53] More basic solutions will cause swelling of acrylic paint. Above a pH of 9, OH- ions may form products with metal ions (e.g. Fe^{3+}) which are very insoluble. These 'new' compounds can precipitate out of solution and deposit as insoluble salts/compounds on the surface.

Ammonium hydroxide solutions should not be used at a higher pH than 8.5. It should be used in a buffered solution to stabilise the pH. Ammonium hydroxide in water will lower the surface tension of water, facilitating capillary action. When used as an alkali (base) it can break down and saponify the fatty content in dirt, and in turn the saponified product can act as a surfactant. In the same way, Ammonium Hydroxide can also saponify the oil content in the binding medium (especially in unaged oil paint). Pigments such as Prussian Blue which is sensitive to alkaline solutions may also change colour. Varnishes may also blanch if exposed to ammonium hydroxide solutions. Therefore, care should always be taken when using Ammonium Hydroxide as a cleaning agent.

Note: Ammonium Hydroxide is an oxidising agent, and must not be kept next to organic solvents as it may cause an explosion!

---

[53] At this low pH, the chelating capacity of citrate will be quite limited. Another chelating agent should be chosen when this pH is required.



Jan van der Zee, Zelfportret, 1958 KS8505
olieverf, dikke laag – blauw & rood zeer gevoelig

pH 7.5 reinigingswater (2000µS) – takes up red paint quite quickly
pH 6.5 " " (1000µS) – takes up red paint
pH 8.5 " " " – takes up red pt – quickly
all remove dirt, but also pt

pH 6.5 citric acid/sodium – takes up red paint quite quickly
x pH 5.5 MES/sodium hydroxide – takes up red paint but quite s[illegible] – takes up more dirt than pH 6.5
x pH 6.5 Bis-tris/hydrochloric acid – takes up dirt, b[illegible] red pt toward the end.
pH 5.5 EDTA/NaOH – takes up dirt, but red also comes quickly with it.
pH 6.5 EDTA/NaOH – takes up lots of dirt, also [illegible] not quickly, takes up least pt so far

pH 5.5 reinigingswater (1000µS) – takes up dirt [illegible] red paint. Not immediately [illegible]
pH 5.5 citric acid/NaOH – takes up dirt, some paint but very little
pH 5.5 citric acid/NaOH in Velvesil + Cyclomethicone D4: gel mixture took some paint with it. Area was first flooded with Cyclomethicone – maybe shouldn't do that.

pH 8.5 citric/Boric acid/NaOH in Velvesil + Cyclom[illegible] D4 Removes dirt well, also some paint, but minimal so far
Demi 100ml : 17.6 ml NaOH : 4.8g Citric acid

Swabs saved from testing the various aqueous solutions from the MCP kit, with notes describing the results.

Water Recipes with Chelating Agents[54]

100 mL water at pH 5.5 with citric acid:

4.8 g of citric acid
17.6 mL sodium hydroxide (NaOH) 10% (w/v) (0.25M) in solution
Ca. 100 mL distilled water

Measure 4.8 g of Citric acid in 74.5 mL of distilled water. Adjust the pH to 5.5 by slowly adding approximately 1.76 mL of NaOH 10% (w/v) (0.25M) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

100 mL water at pH 6.5 with citric acid:

4.8 g of citric acid
23.0 mL sodium hydroxide (NaOH) 10% (w/v) (0.25M) in solution
Ca. 100 mL distilled water

Measure 4.8 g of Citric acid in 69.0 mL of distilled water. Adjust the pH to 6.5 by slowly adding approximately 23.0 mL of NaOH 10% (w/v) (0.25M) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

100 mL water at pH 7.5 with citric acid:

4.8 g of citric acid
26.4 mL sodium hydroxide (NaOH) 10% (w/v) (0.25M) in solution
Ca. 100 mL distilled water

Measure 4.8 g of Citric acid in 66.0 mL of distilled water. Adjust the pH to 7.5 by slowly adding approximately 26.4 mL of NaOH 10% (w/v) (0.25M) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

100 mL water at pH 8.5 with citric acid:

4.8 g of citric acid
27.0 mL sodium hydroxide (NaOH) 10% (w/v) (0.25M) in solution
Ca. 100 mL distilled water

Measure 4.8 g of Citric acid in 65.0 mL of distilled water. Adjust the pH to 8.5 by slowly adding approximately 27.0 mL of NaOH 10% (w/v) (0.25M) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

100 mL water at pH 5.5 with EDTA (Ethylenediaminetetraacetic acid)

7.3 g EDTA
19.6 mL Sodium Hydroxide (NaOH) 10% (w/v) (0.25M) in solution
100 mL distilled or deionised water

Add the EDTA to 74.5 mL of the water. Adjust the pH to 5.5 by slowly adding approximately 19.6 mL of Sodium Hydroxide 10% (w/v) (0.25M) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

100 mL water at pH 6.5 with EDTA (Ethylenediaminetetraacetic acid)

7.3 g EDTA
24.2 mL Sodium Hydroxide (NaOH) 10% (w/v) (0.25M) in solution
100 mL distilled or deionised water

Add the EDTA to 63.5 mL of the water. Adjust the pH to 6.5 by slowly adding approximately 24.2 mL of Sodium Hydroxide 10% (w/v) (0.25M) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

---

[54] These recipes have been modified from the Modular Cleaning Program (See note 39).

100 mL water at pH 7.5 with EDTA (Ethylenediaminetetraacetic acid)

7.3 g EDTA
26.6 mL Sodium Hydroxide (NaOH) 10% (w/v) (0.25M) in solution
100 mL distilled or deionised water

Add the EDTA to 61.0 mL of the water. Adjust the pH to 7.5 by slowly adding approximately 26.6 mL of Sodium Hydroxide (10%) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

100 mL water at pH 8.5 with EDTA (Ethylenediaminetetraacetic acid)

7.3 g EDTA
27.1 mL Sodium Hydroxide (NaOH) 10% (w/v) (0.25M) in solution
100 mL distilled or deionised water

Add the EDTA to 60.6 mL of the water. Adjust the pH to 8.5 by slowly adding approximately 27.1 mL of Sodium Hydroxide 10% (w/v) (0.25M) while stirring and monitoring the pH. Bring the final volume to 100 mL. Note that this recipe must be diluted 1 part to 5 parts distilled water before use!

Rinsing solution at pH 5.5 with Glacial Acetic Acid:

0.1 mL Glacial Acetic Acid
160 mL distilled water
Approximately 1.0 mL Ammonium Hydroxide (NH_4OH) 10% (w/v)

Mix the glacial acetic acid with 100 mL (1 L) of distilled water. Set the pH to 5.5 with ammonium Hydroxide 10% (w/v), added dropwise while stirring. Monitor the pH regularly. Bring the final volume to 160 mL.

Rinsing Solution at pH 6.0 with Glacial Acetic Acid:

0.1 mL Glacial Acetic Acid
180 mL distilled water
Approximately 1.1 mL Ammonium Hydroxide (NH_4OH) 10% (w/v)

Mix the glacial acetic acid with 100 mL (1 L) of distilled water. Set the pH to 6.0 with ammonium Hydroxide 10% (w/v), added dropwise while stirring. Monitor the pH regularly. Bring the final volume to 180 mL.

Rinsing solution at pH 6.5 with Glacial Acetic Acid:

0.1mL Glacial Acetic Acid
200 mL distilled water
Approximately 1.2 mL Ammonium hydroxide 10%

Mix the Glacial acetic acid with 100 mL distilled water. Set the pH to 6.5 with the Ammonium Hydroxide (10%), added dropwise while stirring. Monitor the pH regularly. Bring the final volume to 200 mL.

Rinsing solution at pH 7.5 with Glacial Acetic Acid:

0.1 mL Glacial Acetic Acid
190 mL distilled water
Approximately 1.4 mL Ammonium Hydroxide (NaOH) 10%

Mix the glacial acetic acid with 100 mL (1 L) of distilled water. Set the pH to 7.5 with ammonium Hydroxide (10%), added dropwise while stirring. Monitor the pH regularly. Bring the final volume to 190 mL.

Rinsing solution at pH 8.5 with Glacial Acetic Acid:

0.1 mL Glacial Acetic Acid
300 mL distilled water
Approximately 1.6 mL Ammonium Hydroxide (NaOH) 10%

Mix the glacial acetic acid with 100 mL (1 L) of distilled water. Set the pH to 8.5 with ammonium Hydroxide (10%), added dropwise while stirring. Monitor the pH regularly. Bring the final volume to 300 mL.

Note:

The pKa of acetic acid is 4.756 and the pKa of ammonium hydroxide is 9.25 so the pH 5.0 and 5.5 solutions will be buffered by the acetic acid/acetate ion equilibrium and the 8.5 solution will be buffered by the ammonium hydroxide/ammonium ion equilibrium. The other solutions will be pH adjusted but will have no buffering capacity.

Emulsions

Sometimes aqueous cleaning methods require mixing two immiscible substances. An emulsion is a mixture of two immiscible substances (usually liquids). To enable an emulsion to form, bonds must be made between a hydrophilic substance (that only form hydrogen or dipole bonds) and a lipophilic substance. In conservation, a surfactant is used to fulfil this task. Emulsions must be induced by shaking or stirring. Surfactants also act as stabilisers for emulsions, enabling the mixed phase to remain. In this role, surfactant additions are known as emulsifiers.

Emulsions can be classified into two groups: oil-in-water (O/W), in which a non-polar phase is dispersed in a continuous aqueous phase, or water-in-oil (W/O). Most emulsions have a cloudy appearance and are unstable without the inclusion of a surfactant, which will result in separation of the phases over time.

Emulsions can be very effective at removing hydrophilic soil from water sensitive surfaces. Water-in-oil emulsions are more commonly used in this case. Emulsions may also be effective at removing two different types of materials from a surface simultaneously, for example, a dirt layer and an unaged resin. Thus, a combination of an aqueous system and a relatively non-polar solvent might solubilise both at the same time.

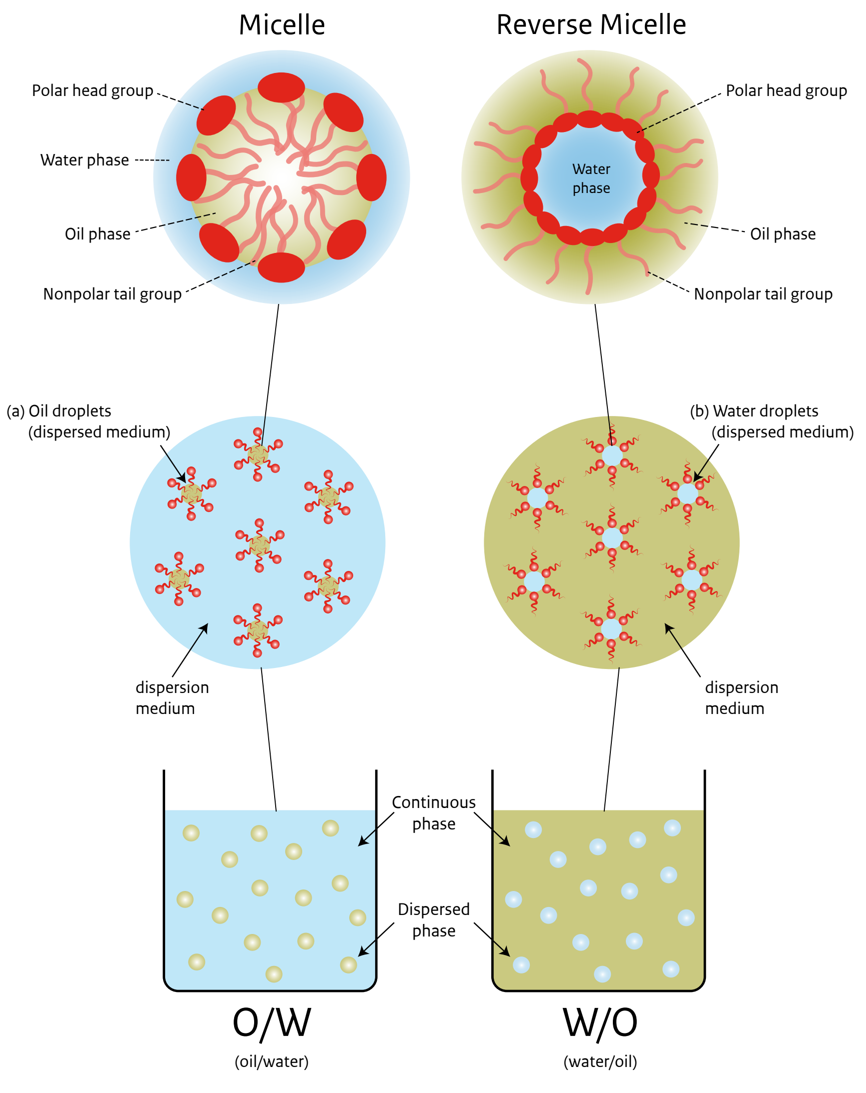


Diagram illustrating the working of an emulsion system: an oil in water emulsion and a water in oil emulsion.

Surfactants (Surface Active Agents)

Surfactants are compounds that lower the surface tension between two substances. All surfactants are amphiphilic, that is the molecule has a hydrophilic head (attracted to water, and thus will contain atoms such as nitrogen (N), sulphur (S), oxygen (O), sodium (Na) or potassium (K)) and a lipophilic tail (attracted to hydrocarbon materials, and thus is typically formed of a chain of hydrogen (H) and carbon (C) which can be either linear, branched, or cyclic). Most surfactants do show a greater affinity for either hydrophilic or lipophilic material. Surfactants are either non-ionic molecules with a non-charged hydrophilic head and a lipophilic tail (these are neutral molecules which do not become ionised in water, and tend to have a more balanced structure), or ionic compounds such as detergents (salts derived from a mineral acid) or soaps (salts of fatty acids (organic) which are products of a reaction between an acid and a base). Ionic surfactants have a polar 'head' which is can be cationic, anionic or amphoteric when in water. [55] Soaps are produced by the chemical process of saponification. This is when a fat or oil is mixed with a base, resulting with the production of glycerol and salt (soap).

Around 15 billion tons of surfactants are produced worldwide every year, and are used in a wide variety of products, detergents, fabric softeners, paints, cosmetics, shampoos, adhesives, herbicides and insecticides. Typically, surfactants used in conservation are fluids but some commonly used surfactants come in solid form. Surfactants are frequently used in aqueous solutions, especially to hold lipophilic material in suspension, but can also be included in non-aqueous solutions to hold hydrophilic material, especially adjusted water, in suspension. The former produce 'oil-in-water' emulsions, while the latter assist in forming 'water-in-oil' suspensions. The choice of a surfactant will be highly dependent on its role with in the solution and the function of that solution.

Surfactants are used in conservation to reduce the surface and interfacial tensions, and to aid in solubilising hydrophobic components or hydrophilic components, depending on the type of surfactant. Surfactants act as stabilisers allowing two immiscible substances to be mixed (an emulsion). Commonly, they are used as an assist in removing surface dirt with aqueous solutions as they will be able to pick up greasy dirt from surfaces (explained further below) or to assist in forming cleaning solutions that contain polar and non-polar solvents or cleaning agents.

Note that adding an ionic surfactant to water will shift the pH of the resulting solution. If a non-ionic surfactant only contains alcohol and/or ether groups, the pH does not change.

Non-ionic surfactants are most commonly used by conservators due to their ease of clearance because they will not be attracted to or bond to original oil paint surfaces easily. They achieve water solubility with long ethoxylate or propoxylate chains which are able to hydrogen bond using oxygen atoms in the chain typically present in an ether functional group.

The Hydrophilic-Lipophilic Balance (HLB) of a surfactant is a measure of the degree to which it can bond with water (hydrophilic) or its affinity to apolar substances (lipophilic). Originally the scale was from 0-20 and for non-ionic surfactants only, but the scale has now been extended (0-40) to include ionic surfactants. The scale allows for comparison of surfactants' abilities to stabilise emulsion systems. As mentioned, in conservation non-ionic surfactants are preferred. For stable oil-in-water emulsions, a high HLB number is needed. In general, an HLB number for these types between 13-15 is suitable for removing surface dirt from oil paint. If the surfactant contains nitrogen (N) there is the potential to saponify the underlying paint above this range. Below this range it is difficult to effectively pick up the dirt.[56] Note that the HLB of a non-ionic surfactant has to be greater than about 12-13 to act as an effective solubilising agent for soiling materials.

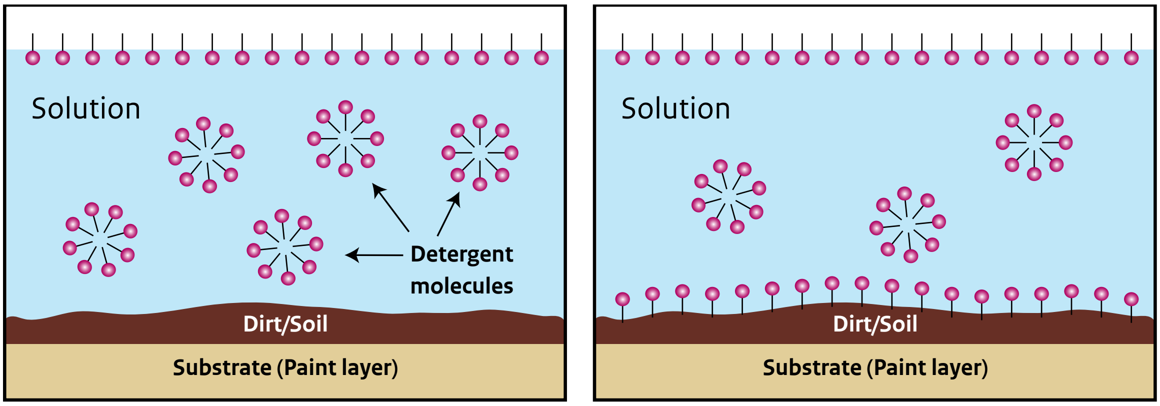
In general, the non-ionic surfactants are less hydrophilic and can be used combined with buffers to achieve different pH levels. Surfactants with a lower HLB number (under 13) cannot emulsify oil, so these dissolved in water can be used to safely clean the surface of younger oil paints.

The Critical Micelle Concentration (CMC) refers to the number of surfactant molecules required to form a micelle – this directly relates to the concentration of a surfactant in solution. A micelle is a sphere of surfactant molecules in which all the 'heads' are orientated in the same direction – this can be inwards or outwards depending on the chemical nature of the surfactant

---

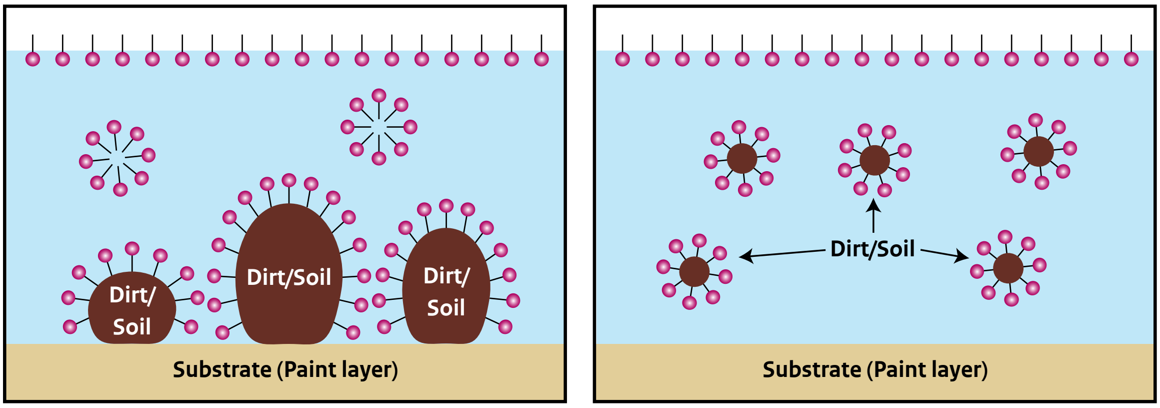
[55] *https://cool.culturalheritage.org/waac/wn/wn27/wn27-2/wn27-205.pdf*
For a non-ionic surfactant to be useful in an emulsion, there should be either a dominance of the polar head (O/W emulsions) or a dominance of the apolar tail (W/O emulsions).

[56] A higher HLB number towards the top end of the scale indicates that the surfactant will emulsify or solubilise oil components in water.



Soiled surface

Surfactants surounding soil



Soil putting from Substrate (paint)

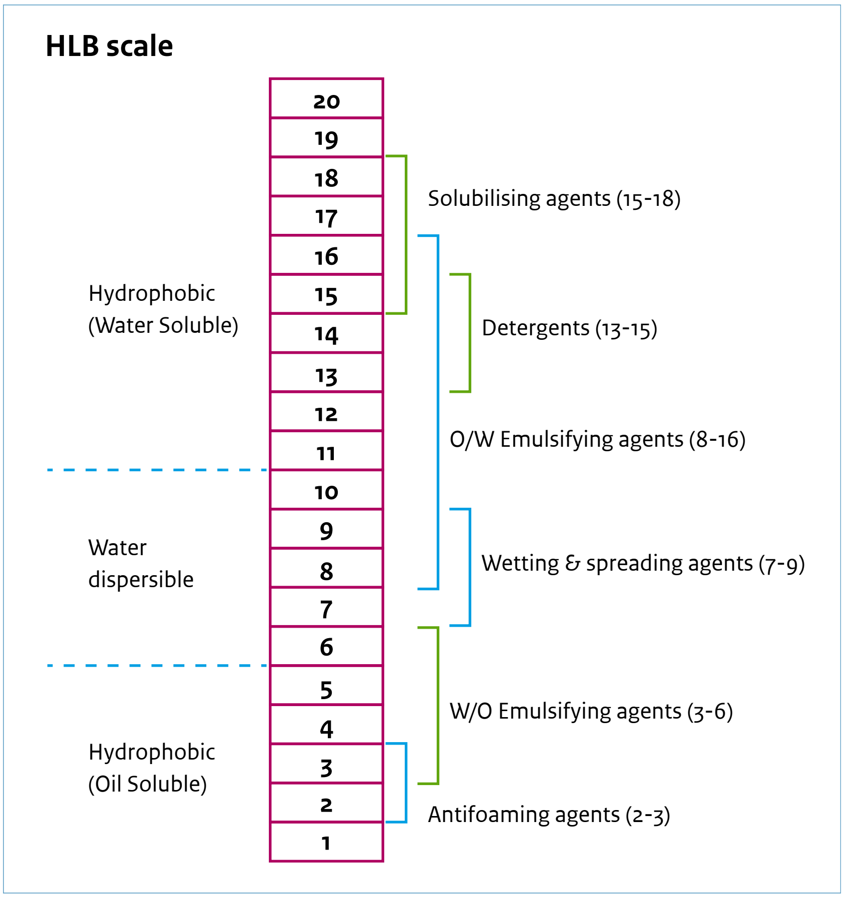
Clean surface

The mechanisms of surfactants to remove surface dirt from the substrate (paint layer).

molecule (hydrophilic or lipophilic) and the dispersing fluid (water or oi). The CMC of a surfactant in the dispersing fluid indicates the amount of surfactant needed to be added to the solution to enable the formation of micelles in that solution. Micelles are required, in addition to mechanical action, in order for surfactancy/detergency to occur.

A micelle, or bundle of surfactant molecules, is formed because this is the most stable energy coefficient scenario – as mentioned, the surfactant molecules orientate in the same direction ensuring a 'bubble' of similar polarity in the centre. Micelles are dynamic as molecules will join or leave the 'sphere' constantly, but a certain amount of molecules are necessary in order for the sphere to form. In water, the polar heads of the surfactant molecules will point outward, creating a 'bubble' which is lipophilic in nature in the middle – this is able to hold lipidic material. If these micelles encounter a surface which is lipophilic, and there is sufficient energy for the 'sphere' to break apart, the apolar section of the surfactant molecule will be attracted to the lipid containing molecule (greasy dirt), and temporarily leave the micelle. The break-up of the micelles is aided by mechanical action, delivered for instance, by gently rubbing the cleaning solution over the surface. If in sufficient concentration, the surfactant molecules attracted to the unwanted lipids will try to reform back into micelles, which as mentioned is a more energy efficient scenario. As these surfactant molecules are bundled back into the micelle, they take molecules of the attracted greasy dirt with them, wrapping the removed material into the centre of the reformed micelle. The resulting micelle is able to hold the greasy dirt in suspension due to this energy efficient scenario.

However, if used below a certain minimal concentration, the dispersed surfactant behaves as if it were a solute dissolved in a solution (lowering the freezing point, raising the Boiling Point (BP), lowering the vapour pressure, etc of the dispersing fluid) as micelles are not formed (as there is insufficient energy to bundle the molecules together in a sphere). At the CMC, the properties of the solution begin to change dramatically,



The HLB scale.

for example the conductivity, viscosity, refractive index and surface tension will increase. Above the CMC the inherent properties again change very little and there is little improvement in the performance of the solution. In fact, cleaning action may be reduced as the surfactant molecules will be more 'reluctant' to leave the micelle formation. However, there is more risk to leaving residues on the surface if higher concentrations are used as there are more surfactant molecules in the solution which can further complicate rinsing and clearance.

Non-ionic surfactants have a low CMC (<2mM).[57] In general, 1-2% (w/v) of a surfactant is sufficient. Ionic surfactants have a medium-high CMC (>2mM) and can be calculated using the following formula:

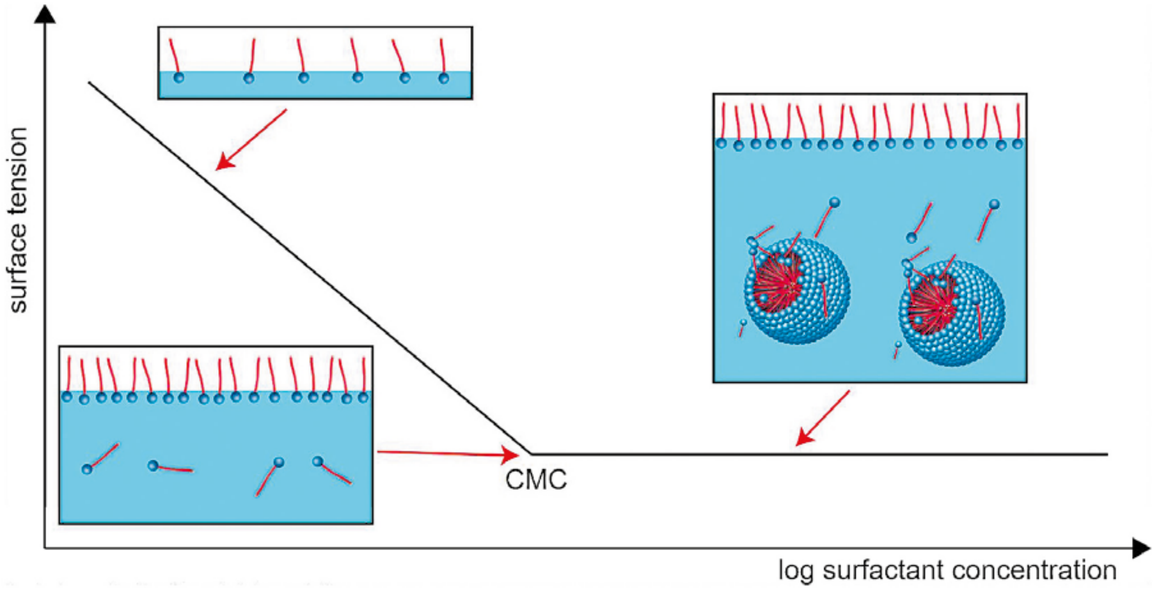
(CMC (mM) x molecular weight x 3.5) / 1000 = g surfactant in 1 L of solution

Rinsing surfactants from surfaces can be complex. The most efficient way to do this will depend on a number of factors: the chemical nature of the surfactant and the substrate being cleaned, and the sensitivity of that substrate to rinsing solutions (water or solvents). Lipophilic, ionic surfactants can be attracted by drying oil molecules (especially free fatty acids) present on the surface of oil-paint films. In an aqueous solution, the lipophilic surfactant molecules of ionic surfactants can become ionised, as will the oil molecule, resulting in inter-molecular bonds (dipole-dipole or hydrogen bonds), or even intra-molecular covalent bonds, being formed. These, especially the latter, are difficult to break. Thus, it is not advised to use ionic surfactants when cleaning oil paintings. [58]

---

[57] mM (miliMolar, milimoles/1 litre) = 1/1000 M (Molar, mols/1 litre)

[58] The exception to this is using the polyacrylic resin, Carbopol, pre-bonded to a surfactant, Ethomeen (C25 or C12) emulsions. Here the cationic surfactant molecules are ionised and pre-bonded to the Carbopol resin molecules prior to application. It is vital that water is not used to rinse these cleaning systems as this will dissociate the intra-molecular bond between the Carbopol and Ethomeen and potentially allow the free, ionised Ethomeen to bond to charged (ionised) oil molecules. These systems must be used with caution. See the Brochure on Varnish Removal.



The Critical Micelle Concentration (CMC)

Typically, aqueous solutions that contain lipophilic surfactants with a low CMC will be difficult to remove from the (oil paint) surface as the surfactant will be adsorbed on hydrocarbon surfaces (oil paint) and rinsing with water will not remove surfactant molecules bonded to the surface. To remove these surfactant residues, hydrocarbon solvents are needed. First the surface should be allowed to dry and then rinsing can be carried out with an aliphatic solvent (such as Shellsol D40 or Stoddards Solvent) applied in a cotton swab. Leaving surfactant molecules on a surface will change the characteristics of that surface, effecting the physical nature (softening, or making the surface more plastic) and chemical nature.

Surfactants and Acrylic Paintings

Using surfactants to remove surface dirt on acrylic paint surfaces can be hazardous and should be carried out with caution. Surfactants on the surface of acrylic paintings are extremely sensitive in general to aqueous solutions, as they readily dissolve in water. Using aqueous solutions will remove surfactants from the surface of the paint film, which can be contentious, from an ethical point of view. Some conservators argue that in certain circumstances, if the surfactant layer (generally only a few microns thick) has degraded and is inhibiting the reading of the artwork (along with any surface dirt imbibed in this layer), an argument can be made for its removal, as often the bulk paint layer, found directly beneath the surfactant layer is stable and not sensitive to aqueous solutions.[59] Questions remain regarding further migration of surfactants to the surface of the artwork over time, whether this is encouraged by the use of aqueous solutions during surface dirt removal, and whether this is a continuous process.[60]

Surfactants for dirt removal from oil paints

Non-Ionic Surfactants:

Surfonic JL-80X is a non-ionic surfactant. It has an HLB of 13.1 (scale 0-20) and is often included in cleaning systems for surface dirt removal.[61] It is an alkoxylated linear alcohol, which is water-soluble and biodegradable. This surfactant replaces Triton X-100 and Triton XL-80N which are often mentioned in literature. The production of Triton XL-80N has been discontinued, and Triton X-100 (HLB 13.4) breaks down into octylphenol, which has been demonstrated to mimic the hormone Oestrogen in a

---

[59] Learner, T., and B. Ormsby. 2009. Cleaning Acrylic Emulsion Paints: Putting Research into Context. In Art Today, Cultural Properties of Tomorrow. The Conservation and Restoration of Contemporary Artwork. Proceedings of the SF-IIC Conference, ed. M. Stefanaggi and R. Hocquette, pp. 193–199. Paris: Institut National du Patrimoine.
Ormsby, B., Kampasakali, E., Learner T., *Surfactants and Acrylic Dispersion Paints: Evaluating Changes Induced by Wet Surface Cleaning Treatments. Smithsonian contributions to museum conservation, 2013, Nr 3 pp 159-164.* *https://repository.si.edu/bitstream/handle/10088/20503/25.Ormsby.SCMC3.Mecklenburg.Web.pdf?sequence=1*

[60] Shawn Digney-Peer, Aviva Burnstock, Tom Learner, Herant Khanjian, Frank Hoogland & Jaap Boon (2004) THE MIGRATION OF SURFACTANTS IN ACRYLIC EMULSION PAINT FILMS, Studies in Conservation, 49:sup2, 202-207, DOI: *10.1179/sic.2004.49.s2.044*

[61] Surfonic JL-80X is produced by Huntsman and available through most conservation websites. It replaces Triton XL-80N, which is no longer produced. Triton X-100 is produced by Dow chemicals.

Brij S100 is a surfactant sometimes used to aid the removal of surface dirt from unvarnished oil paint surfaces.

Ecosurf EH9

number of animal species at extremely low levels of exposure. Although there is no direct evidence of any health hazard associated with the use of Triton X-100, caution is recommended when using it, and some countries have prohibited it's use.

Oxgall is a 'natural' surfactant that can be used to remove surface dirt.

Brij S100 (previously Brij 700) is a Polyoxyethylene (100) stearyl ether which functions as an aqueous dispersant and oil in water emulsifier. It is a very large molecule with an HLB of 18.8. It is a solid and warmth can be used to assist its going into solution in water. It is very good at solubilising straight chain fats and oils. It is not suitable for young oil paints as it will solubilise them.

Ecosurf EH-3 Ecosurf EH-6 and Ecosurf EH-9 are non-ionic surfactants based on ethoxylated/propoxylated branched alcohols. They dissolve well in both water and low polarity solvents, which gives a lot of flexibility for use in both oil-in-water and water-in-oil solutions. They are fast wetting, low foaming, low odour and readily biodegradable and stable in the presence of dilute acids, bases and salts. These are produced by Dow Chemicals and available through conservation suppliers. Ecosurf EH-3 has an HLB of 7.9, EH-6 has an HLB of 10.8 and EH-9 has a HLB of 12.5. This range of surfactants have been particularly successful when used in water-in-oil solutions for cleaning modern (young) oil paints and acrylic emulsion paintings.

Anionic Surfactants: 'Resin and Bile Soaps'

Anionic surfactants are also used in conservation, these are often known as 'resin soaps'.[62] With anionic surfactants, the water soluble end is the conjugated base of an acid group that either gains or loses electrons at a

---

[62] See: Stavroudis, C., Sorting Out Surfactants WAAC Newsletter, Vol 31 Nr.1 Jan 2009 for a detailed explanation of surfactants. *https://cool.culturalheritage.org/waac/wn/wn31/wn31-1/wn31-105.pdf*

certain pH and is characterised by a pKa (see above). Above the buffer range of the acid group, the surfactant will be fully ionised and will become soluble and will be more readily attracted to molecules that, in water solutions, carry an opposing ionised charge. Anionic surfactants are generally not used for the removal of surface dirt, but for removing (now deteriorated) layers that have been purposely applied in the past. These may consist of resinous and proteinaceous material.

Ox-gall or ox-bile is a is a lyophilised material derived from bile and has traditionally been used as a ‘natural’ surfactant. It is typically used as a wetting agent but can also be used to remove surface dirt. It contains various acids, such as Cholic Acid, Deoxycholic Acid, Taurocholic and Glycocholic Acids. It is readily available from drugstores and natural food shops and can be obtained as a powder (greenish light brown) and added to water. This solution can be effective for cleaning gilt (but not water gilded) surfaces.

Deoxycholic acid is a component of bile acid which when combined with a basic compound forms a soap. It is a weak acid with a pK_a of 6.58.[63] Its structure is similar to dammar’s major component, making it useful in varnish removal under the principle of ‘Like dissolves like’. Abietic acid (pka 7.62) is derived from pine rosin (colophony) which will also saponify when combined with a basic compound. This comes from the family of terpenoids and has had particular success in removing oleoresinous as well as di and tripterpenoid structures. Different soaps of both variants can be made using Sodium Hydroxide, Ammonium hydroxide or Triethanolamine.[64]

Sodium Lauryl Sulphate (SLS), also known as Sodium dodecyl sulphate (SDS) an anionic surfactant found in many cleaning and personal care products. It is similar to Sodium Laureth Sulphate (SLES) which is milder and less irritating than SLS. Both are synthetic organic compounds produced from palm kernel oil or coconut oil. The HLB of SLS is 40 (the highest possible for an ionic surfactant), that of SLES is 20.2 (at a pH of 8).[65] 13.6.

The use of carbonated distilled water is recommended for the removal of surface dirt from acrylic paint films.

For acrylic paint, it is advised against the use of deionised water, or adjusted water above a pH of 6, as it draws out film materials, like surfactants, as it is a hypotonic solution. Hypertonic solutions with high conductivity are less likely to draw out materials or swell the films.[66] Solutions with a high pH (of around 4-5) are also recommended for dirt removal, leaving the paint film intact. The ionic strength of a film has also been shown to be of importance, with around a 29 mM concentration recommended.[67] The use of carbonated distilled water is recommended, which naturally has a pH of around 6.3, with the addition of 1% of ethanol as this lowers the effective detergency of the cleaning solution.

Recent studies have found that an aqueous solution with a surfactant and chelating agent is suitable for the removal of surface dirt from acrylic emulsion paintings. Simple aqueous systems with an adjusted pH (to pH 4 or 5) were also found to be successful, without causing any visible change or damage during or after treatment.

---

[63] *https://www.iiconservation.org/congress/sites/iiconservation.org.congress/files/c2014polkownik.pdf*

[64] The latter two resin soaps were proposed by Richard Wolbers in the late 1980s as ‘affinity’ soaps and presented at the IIC Congress held in Brussels in 1990. Recipes combined these soaps with additional surfactants, and chelating agents, which were thickened with cellulose ether. The recipes were complex, difficult to make and required thorough rinsing as all components are non-volatile (with the exception of water). While some practitioners had success, others reported on problems of clearance. These soaps have largely fallen out of use in the last decades but may still be of use when traditional cleaning systems fail.

[65] Hashimoto N., Kawaguchi K., Yoshioka K., Dispersion granulation method leveraging pH responsiveness of Monoalkyl Sulfosuccinate, *Journal of Oleo Science*, 2015, vol. 62(2) pp 191-196

[66] Dillon C., Lagalante F., Wolbers R. *Acrylic emulsion paint films: the effect of solution pH, conductivity, and ionic strength on film swelling and surfactant removal.* 2014, Studies in Conservation, vol. 59 Issue 1, 2014, pp 187-198 *https://repository.si.edu/bitstream/handle/10088/20502/24.Wolbers.SCMC3.Mecklenburg.Web.pdf?sequence=1*

[67] Stavroudis C., Doherty T. *The Modular Cleaning Program in practice: Application to Acrylic paintings,* 2013 New Insights into the cleaning of paintings. Proceedings from the cleaning 2010 international conference Universidad Politécnica de Valencia and Museum Conservation Institute. Smithsonian Institution Scholarly Press, Washington DC, Mecklenburg M.F., Charola, A.E., Koestler R.J., pp 139-145

Surfactant that had migrated to the surface of the painting was removed to some extent.[68]

Surfactant Recipes[69]

As mentioned above, Non-ionic surfactants can be added to a solution at a concentration of 1-2%. (v/v)

Ecosurf EH-6:

1.0 g Ecosurf EH-6
100 mL distilled water

Measure the Ecosurf EH-6 and mix into 90 mL of distilled water. Bring the final volume to 100 mL.

Surfonic JL-80X (concentrate):

0.43g Surfonic Jl-80X
100 mL distilled water

Measure 0.43 g of Surfonic JL-80X and mix into 95 mL of distilled water. Bring the final volume to 100 mL. Note: this recipe must be distilled 1 part to 5 parts water before use!

Brij 700 (concentrate):

0.47 g Brij 700
100 mL distilled water

Measure the Brij 700 into 95 mL of distilled water and mix well. Bring the final volume to 100 mL. Note: this recipe must be distilled 1 part to 5 parts water before use!

Ionic surfactants have a medium-high CMC (>2mM) and can be calculated using the following formula:

(CMC (mM) x molecular weight x 3.5) / 1000 = g surfactant in 1 L of solution

NOTE: Acrylic paint:

1% Triammonium Citrate and 1% Ecosurf EH-9: best cleaning for surface dirt on acrylic paint

0.1% weight Ecosurf EH9 surfactant with dilute HCl to bring solution to a pH of 4- also good cleaning results on acrylic paint

All of the above recipes can be thickened by adding a cellulose ether; typically, hydroxy propyl methyl cellulose is used at a concentration of 2-5% (volume/weight). The decision to thicken the cleaning solution can be made after testing for effectivity of cleaning.

Anionic Surfactant Recipes

Sodium Deoxycholate (concentrate):

9.825g Deoxycholic acid
8.9 mL Sodium Hydroxide (10%)
100 mL distilled water

Measure the deoxycholate acid and add to 76.3 mL of distilled water. Mix well and adjust the pH to 8.5 by slowly adding approximately 8.9 mL of Sodium Hydroxide (10%) while stirring and monitoring the pH. Bring the final volume to 100 mL with the distilled water. This process will take time, and the surfactant will go from white to clear when completely mixed. Note: This recipe must be distilled 1 part to 5 parts water before use!

Sodium Lauryl Sulphate (concentrate):

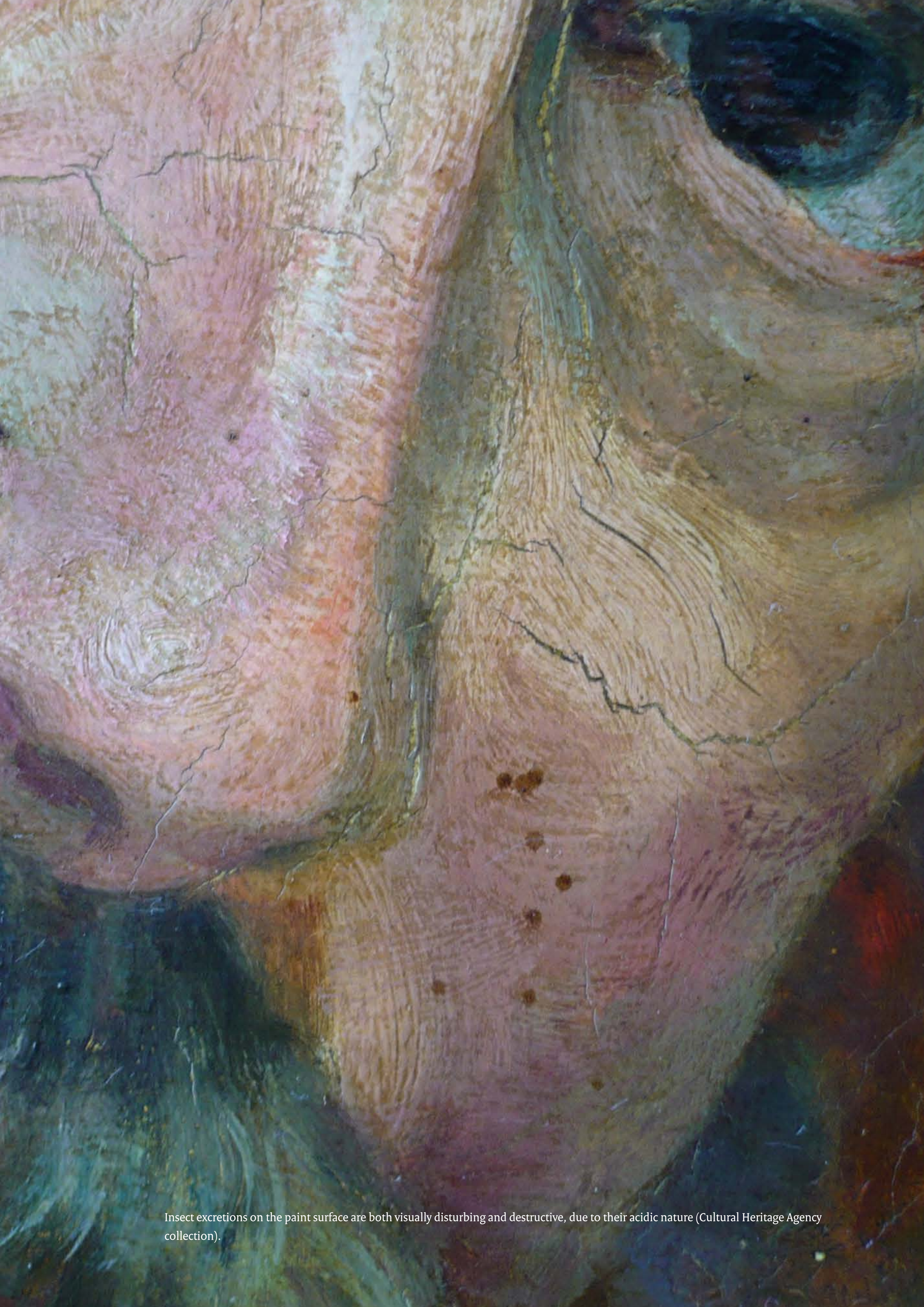
5.1 g Sodium Lauryl Sulphate
100 mL distilled water

Measure the Sodium Lauryl Sulphate into 90 mL of distilled water. Mix well and bring the final volume to 100 mL. Note: this recipe must be distilled 1 part to 5 parts water before use!

---

[68] Keefe, M., Ormsby, B., Soldano, A., Phenix, A., Learner, T., Tucker, C., Behr, A., Meyers, G Rheinhard Boomgaard, T., Peitsch, C. (2011). *Art and Industry: Novel Approaches to the Evaluation and Development of Cleaning Systems for Artists' Acrylic Latex Paints*. Journal of Coatings Technology. 8. 30. *https://www.researchgate.net/publication/279959992_Art_and_Industry_Novel_Approaches_to_the_Evaluation_and_Development_of_Cleaning_Systems_for_Artists'_Acrylic_Latex_Paints*

[69] These recipes have been modified from the Modular Cleaning Program (See note 39).



Insect excretions on the paint surface are both visually disturbing and destructive, due to their acidic nature (Cultural Heritage Agency collection).

Microemulsions

Microemulsions are similar to emulsions in that they are mixtures of immiscible liquids with a surfactant to stabilise them, but they are thermodynamically stable.[70] Microemulsions often form spontaneously (requiring little to no mixing to form) and have smaller droplets of the dispersed phase in the continuous phase than standard emulsions (the particle diameter range is 10-100nm). They are usually obtained by only mixing the non-miscible liquids together with sufficient surfactant. In general, microemulsions are transparent (compared to opaque emulsions) because of the small size of the droplets, which don't scatter light. The smallness of the micelles also allows for the microemulsion to have low viscosity.[71] This gives the added benefit of visibility of the surface during surface dirt removal. Because they are stable, they will not break up into two phases during use. Microemulsions can support a fairly high ionic content without adversely affecting the emulsion. This allows for adjustments to be made to the aqueous phase: varying pH, raising or lowering the conductivity, choosing specific ionic materials, the addition of chelating agents and so forth.

Microemulsions form when the properties of the solvent, water and surfactant are adjusted so that the solvent-surfactant and water-surfactant mixtures have the same or nearly the same surface energy. The aqueous phase of microemulsions can vary between 10 and 70%.

Microemulsions may be able to address the issues with water-based and aliphatic hydrocarbon solvent systems. Water-based systems for surface dirt removal generally have a high efficacy but may also remove original material from the surface, aliphatic hydrocarbons generally have been found to remove less surfactant from the surface and bulk of the paint film, cause considerably less swelling and have minimal effect on bulk film physical properties.[72] Microemulsions are potentially a group of materials that may combine the benefits of water-based and hydrocarbon solvent systems.[73] To produce a microemulsion, the correct combination of surfactant type, co-solvent type and solvent must be found and tailored to specific applications.

One of the largest drawbacks of microemulsions, whether based on silicone solvents, water or hydrocarbon solvents, is the need for removal with a rinsing solution. Sometimes multiple applications of the rinsing solution are necessary to remove all the microemulsion, which, if not properly tailored and investigated prior to use, may result in more damage to the surface (by either the rinsing solution or the mechanical action required to apply and remove the solution) than using a 'free' solution with volatile components in the rinsing phase.

Microemulsion Recipes

Microemulsion with SLS:

85 mL demineralised water (aqueous phase)
5 mL Petroleum ether (dispersed phase)
4 mL SLS
6 mL 1-Pentanol

Mix the ingredients from the microemulsion well either by shaking the container or using a magnetic stirrer.

Novel Materials and Approaches

Silicone based solvents for microemulsions
Unvarnished acrylic and oil paints have high levels of surfactants and other chemicals at the surface which can contribute to the securing of dirt to their surfaces and make them sensitive to aqueous and other solvent cleaning methods. This can lead to difficulties constructing aqueous solutions or (micro)emulsions that are able to remove dirt without removing or damaging

---

[70] Faust E., Cleaning assessment of a vinyl dispersion paint: comparing Velvasil Plus gel, microemulsions and aqueous solutions., in: Angelova L.V., Ormsby B., Townsend J.H., Wolbers R., *Gels in the Conservation of Art*, 2017, Archetype Publications Ltd. pp 219, 388

[71] Stavroudis, C., *More from CAPS3: Surfactants, silicone-based solvents and microemulsions.*, WAAC Newsetter, Vol. 34 (nr.3) Sept 2012 *https://cool.culturalheritage.org/waac/wn/wn34/wn34-3/wn34-306.pdf*

[72] Ormsby, B., Smithin, P., Hoogland, F., Learner, T., and Miliani, C., 2008, *A scientific investigation into the surface cleaning of acrylic emulsion paintings*, In: Preprints ICOM Committee for Conservation triennial meeting, New Delhi, Sept 2008, Vol. II 857-865 *https://www.icom-cc-publications-online.org/1951/A-scientific-evaluation-of-surface-cleaning-acrylic-emulsion-paintings*

[73] Keefe, M., Ormsby, B., Soldano, A., Phenix, A., Learner, T., Tucker, C., Behr, A., Meyers, G Rheinhard Boomgaard, T., Peitsch, C. (2011). Art and Industry: Novel Approaches to the Evaluation and Development of Cleaning Systems for Artists' Acrylic Latex Paints. Journal of Coatings Technology. 8. 30. *https://www.researchgate.net/publication/279959992_Art_and_Industry_Novel_Approaches_to_the_Evaluation_and_Development_of_Cleaning_Systems_for_Artists'_Acrylic_Latex_Paints*

the original paint surface.[74] Microemulsions based on silicone-based solvents (volatile methoxysilanes) such as Cyclomethicone D4 and Cyclomethocone D5, used for the solvent phase of a microemulsion may be a potential solution.[75]

Silicone polymers are potentially useful cleaning materials, but at present they are still at the experimental stage of use, because the influence of silicone polymers (and their residues) on paint surfaces has not yet been investigated in depth.

Shin Etsu KSG 210 or KSG 350-z are silicone polymers with ethoxylate/propoxylate chains or polyether chains to bridge between the silicone chains. These systems make water in oil (w/o) emulsions in non-polar silicone solvents without the need for surfactants. This means that there are no issues with potential surfactant residue however the silicone polymer will still need clearing from the surface. As yet, insufficient research has been carried out to establish the long-term interactions between silicone polymers and oil paint in terms of promoting chemical changes, discolouration, physical changes and embrittlement.

As the polymeric emulsion stabilizers are macromolecules, they are less able to penetrate into a surface and are therefore easily rinsed with non-polar solvents (for example cyclomethicone, a solvent with extremely low polarity, which may however be toxic).

These cleaning systems are useful for removing soil and dirt from paintings that are highly sensitive to water, aqueous cleaning systems and polar solvents. They have been successfully used for the removal of dirt and unwanted material from acrylic paintings. A 2014 film ‘Restoring Rothko’ produced by the Tate is an excellent example of engineering a cleaning solution.[76]

Recipe containing Cyclomethicone D4 and Ecosurf (surfactant):

20 mL Cyclomethicone D4|60 mL Ecosurf EH-3

20 mL Demineralised water

Measure the water and mix into the surfactant. Add in the cyclomethicone D4 and mix till dispersed through the surfactant and aqueous phase. [77]

Recipe containing Cyclomethicone D4, Ecosurf (surfactant) and EDTA (chelating agent):

40 mL Cyclomethicone D4
50 mL Ecosurf EH3

10 mL EDTA solution, adjusted to a pH of 5.5 (buffered with 1 mol/L NaOH, 10%w/v)

Measure the various components and add together. Mix until they are dispersed and the microemulsion is clear.[78]

---

[74] Lagalante, A., Wolbers, R., Particle-based silicone cleaning emulsions: studies in model paint systems for the cleaning of water-sensitive artworks, in: Angelova L.V., Ormsby B., Townsend J.H., Wolbers R., *Gels in the Conservation of Art*, 2017, Archetype Publications Ltd. pp 193-199

[75] Stavroudis, C., 2012 *https://cool.culturalheritage.org/waac/wn/wn34/wn34-3/wn34-306.pdf*

[76] *https://www.youtube.com/watch?v=AGqAggmwyMU*

[77] Taken from: Stavroudis C., 2012 *https://cool.culturalheritage.org/waac/wn/wn34/wn34-3/wn34-306.pdf*

[78] Taken from: Lagalante, A., Wolbers, R., Particle-based silicone cleaning emulsions: studies in model paint systems for the cleaning of water-sensitive artworks, in: Angelova L.V., Ormsby B., Townsend J.H., Wolbers R., *Gels in the Conservation of Art*, 2017, Archetype Publications Ltd. pp 193-199

Thickening Agents

Cellulose ether
Many of the aqueous cleaning solutions mentioned above can be thickened by adding a cellulose ether. However, for low or high pH value cleaning solutions other thickening agents may be more appropriate. The most common cellulose ether used is hydroxy propyl methyl cellulose – the high molecular weight allows this cellulose derivative to remain stable in lower pH value cleaning solutions. Other cellulose ethers include methyl cellulose, hydroxy propyl cellulose and ethyl cellulose for recipes that include some aliphatic content. The amount used of the cellulose ether will affect the viscosity and can be varied according to need and components included. Cellulose ethers will remain soluble in water and can be rinsed easily with such though other factors (see above) may dictate other rinsing solutions.

Xanthan gum
Xanthan gum can be used to thicken some aqueous cleaning solutions. It forms a water-based polymer emulsion gel that is non-toxic, biodegradable and stable at any pH. It can be used to make oil-in-water emulsions for non-water-miscible solvents. Xanthan gum is a polysaccharide polymer that is made up of tangled helix chains, which will aggregate at higher concentrations to make little cages that hold water molecules. Oxidising agents, such as bleach, and most cationic materials, such as ammonia, cannot be used as they cause the gel to collapse. Xanthan gum gels can hold non-polar solvents in intermolecular pockets (oil in water emulsion), a property which has the potential to greatly reduce the conservator's exposure to solvent. In gel form it is able to hold up to 20% solvent. As it is a water-based gel, it is not recommended for acrylics or other water sensitive surfaces. Xanthan gum can be considered non-ionic in the pH range that can safely be used on paintings.

A major downfall of Xanthan gum (and other aqueous emulsifiers) is that an extra clearance step is always required after the application of the emulsion. Xanthan gum requires an aqueous solution for clearance.

Recipe with Xanthan gum with 5% TEA at pH 8.5:

2 g Xanthan gum
100 mL demineralised water
5 mL triethanolamine (TEA)

Add approximately 5 mL TEA to 90 mL demineralised water. Check the pH and adjust with extra TEA if necessary. Add the Xanthan gum powder and mix in well. Let stand for approximately 30 minutes to form a viscous solution.

Recipe with 3% Xanthan gum with 0.5% EDTA, 0.5% Boric acid at pH 8 with 10% benzyl alcohol

Aqueous solution:
100 mL demineralised water
0.5 g EDTA (Ethylenediaminetetraacetic acid)
0.5 g Boric acid
Ca. 4 mL Sodium hydroxide ($NaOH$) 10% in solution

Emulsion Gel:
2 g Xanthan gum
50 mL Demineralised water
10 mL Benzyl alcohol

To make the aqueous solution: Add the EDTA and Boric acid to ca. 90 mL of demineralised water. Add the Sodium Hydroxide to the solution until a pH of 8 is reached. Bring the final volume to 100 mL. Set aside. Add the Xanthan gum to 50 mL of demineralised water. Mix well and set aside.

Take 25 mL of the aqueous solution and add to the Xanthan gum. Add 10 mL Benzyl alcohol to the emulsion and mix all the components well. Let stand for ca. 30 minutes until the gel has become viscous.

Xanthan gum gel concentrate:

7.47 g Xanthan gum
100 mL distilled water

Add the Xanthan gum to 20mL distilled water. Work into a smooth slurry and add 80mL distilled water to bring the final volume to 100mL.[79]

Note that Xanthan gum can take a while to thicken, it becomes much more viscous upon standing and should be left for ca.30 minutes before use.

---

[79] *https://www.getty.edu/conservation/our_projects/education/caps/modular_cleaning_recipes.pdf*

Rigid Gels for Surface Dirt Removal

The use of carbonated distilled water is recommended for the removal of surface dirt from acrylic paint films.

Removal of surface dirt, especially from water-sensitive surfaces, will sometimes require the use of alternative application methods for aqueous solutions that give greater control over the exposure of vulnerable paint surfaces to aqueous solutions, while retaining the cleaning efficacy of water. Rigid polysaccharide gels are the most widely available rigid gels and are a useful tool for surface dirt removal from water-sensitive surfaces. Currently, the two most commonly used physical gels in art conservation are Agar Agar/Agarose and Gellan gum (both form rigid gels). Agar Agar is obtained from the cell walls of some species of red algae, primarily from ogonori (*Gracilaria*) and tengusa (*Gelidiaceae*). Gellan gum is produced by the bacterium *Sphingomonas elodea*. Both are naturally occurring polysaccharides. Agar Agar is a heterogeneous mixture of two classes of polysaccharide (Agarose- around 70%- and agaropectin- around 30%-) whereas Agarose is a purer form of Agar Agar and is predominantly the polysaccharide. While agarose is electronically neutral, Gellan gum is anionic with negatively charged carboxyl groups, which are available to complex with cations present in dirt particulate.

Agarose/Agar Agar and Gellan gum are available in powder form and are prepared by dispersing dry polymer in pure water—or modified aqueous solution—and heating until clear and almost boiling. As the polymer dispersions cool, both Agarose/Agar Agar and Gellan gum form helical structures.[80]

These gels, often called RIGID gels, are excellent for removing surface dirt from delicate surfaces.[81]

Agar gels can be classified as reversible sol-gels or reversible hydrocolloid gels. A sol-gel starts from a colloidal solution (the sol) that acts as the precursor for an integrated network of polymers (the gel). Once cooled, it is easily reheated to its sol state, a process that can be repeated multiple times without change to the working properties of the gel (though a loss of water through evaporation should be compensated for with each reheating). Agar gels can also be poured onto the surface when in the sol-phase to conform to the topography, or brushed onto the surface as a sol just before it cools to the gel phase, which occurs within a few seconds. When solidified, it can then be peeled off. This is especially a useful technique for impasto or textured surfaces.

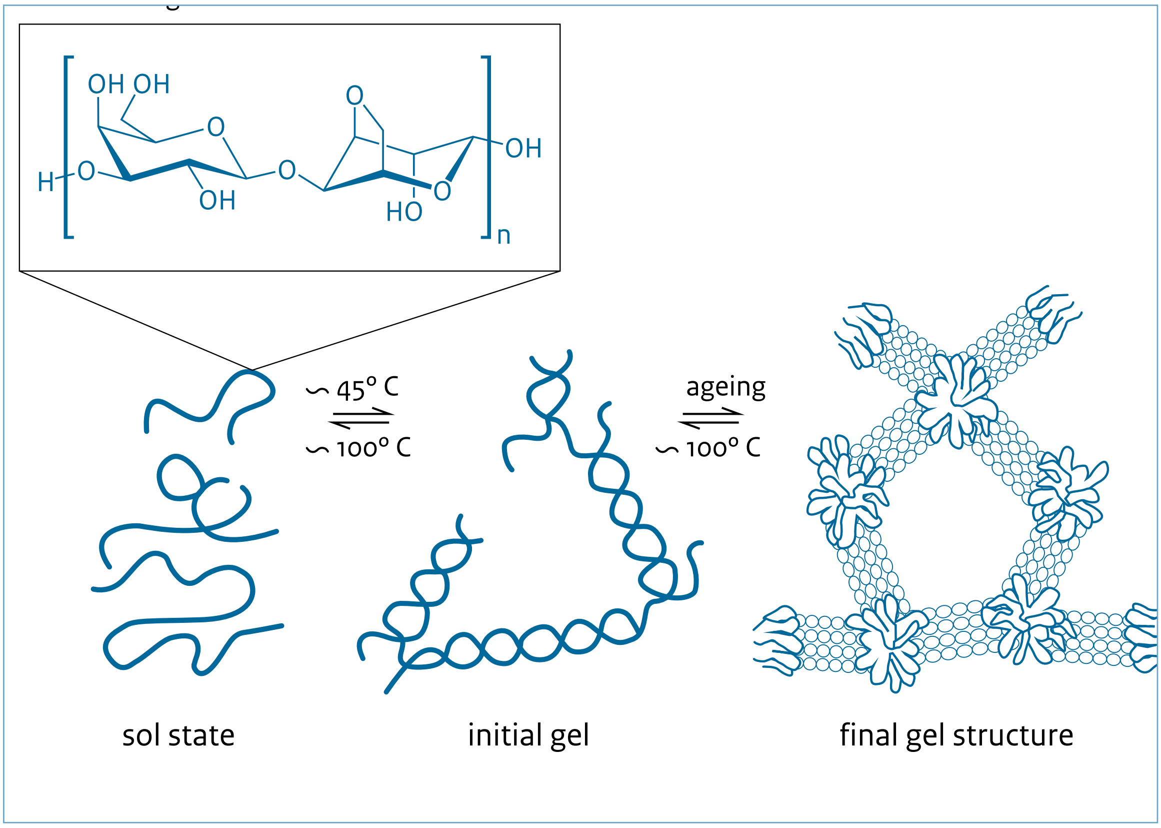
Agar gels exhibit high gel strength even at concentrations less than 5%. Rigid gels are formed starting with a concentration of 1.5% Agar Agar in water (w/v). Generally, concentrations of around 3-4% are used (lower concentrations have poorer water retention, higher concentrations are highly viscous and may be difficult to handle). The concentration will affect the pore size – the gaps left between molecules as the helix polysaccharide molecules form the gel. They are stable up to 65°C and are not enzymatically degraded by most bacterial species. They are stable in both highly alkaline and acidic conditions, and, prior to the addition of other cleaning agents, they are completely non-toxic and natural. In conservation, Agar Agar is used at a maximum concentration of 8%. Additions of some polar solvents, typically alcohols, can be added to the cooling gel and will increase effectivity removing some dirt layers.

Gellan gum is available in two forms: low-acyl and high-acyl. When prepared, low-acyl Gellan gum is typically more rigid and brittle, whereas high-acyl Gellan gum is softer and has greater conformability. Gellan gum is traditionally used in paper and textile conservation, but is gaining visibility in painting conservation. It is a transparent gel, which has the advantage that any pigment pick-up is visible, and more visibility of the surface is possible during application. It is also typically used at slightly lower concentrations than Agar Agar

---

[80] Fife G, Och JV, Stabik B, Miedema N, Seymour K. A package deal: the development of tissue gel composite cleaning at SRAL. In: ICOM-CC 16th triennial conference Lisbon 19–23 September 2011: preprints. 2011. *https://www.icom-cc-publications-online.org/PublicationDetail.aspx?cid=9cbc532d-a034-4215-8a65-36852925ca95*

[81] Kanth, A., Singh, M., Pandeys.C., Optimizing the rigidity of gellan and agar gels for cleaning sensitive acrylic emulsion painted surfaces. Volume 9, Issue 3, July-September 2018: 451-462
Kanth, A., Singh, M., Pandey, S.C., An explorative study of cleaning acrylic painted surfaces with concentrated polyelectrolytic xanthan hydrogels. *International Journal of Engineering & Science Research Dec 2017, Issue 12 pp 176-185*



Agar formation helix structure

Agar Agar powder is available at most health food stores.

Agar Agar set and ready to cut to size.

(1-2% vs 3-4%) as it has higher water retention properties. Gellan gels are very strong and more flexible than those made with Agar agar.

Agar Agar food grade can be obtained from health food stores. The more purified Agarose is acquired from chemical suppliers and is more costly than the food grade Agar Agar.

NOTE: Agar Agar and Gellan gum gels should never be used on matte, underbound paint surfaces where low cohesion and poor adhesion of the paint layer onto the substrate are evident. This will result in the removal of pigment or even entire paint flakes.

When a pure rigid gel has been used, no further clearance is required after the gel has been removed from the surface. There are no concerns regarding residues of pure

Testing a small amount of Agar Agar gel on an impasto surface.

Result of a small test of Agar Agar gel on an impasto surface

agar gels on surfaces. When a rigid gel has been modified (the pH adjusted, the addition of chelating agents or surfactants or other non-volatile materials), residues from these modifications require clearance. This is possible with the application of a pure water gel.[82]

Prepared Agar Agar (and Agarose) gels can be kept in the fridge for several days, though if contaminated mould will grow readily.

After heating, it is also possible to add a small amount of solvent (up to 10%), chelating agent, oxidizer or another cleaning agent to the agar sol. Amounts are calculated according to percentage (volume) of the original volume of the gel. Solvents must be added during cooling of the

---

[82] Volk, A., van den Berg, K.J., (2014). Agar – A New Tool for the Surface Cleaning of Water Sensitive Oil Paint? In: *Issues in Contemporary Oil Paint* pp 389-406. https://link.springer.com/chapter/10.1007%2F978-3-319-10100-2_26

Using a larger sheet of Agar Agar on an unvarnished paint surface for the removal of surface dirt. Above: The Agar Agar sheet on the surface of the paint, below: after removal of the Agar Agar sheet. Detail of *TH8*, Elbertus Majoor, 1959, gouache on hardboard (image credit: Nadia Wilting, Cultural Heritage Agency of the Netherlands).

solution just before it reaches the gel phase, due to the low boiling points of many solvents.

Note that rigid gels can be weighted to increase surface contact. Rigid gels cast to the surface will conform to the exact topography.

The following recipes are examples of different types of Agar Agar and Gellan gum recipes. Note that the concentration of each additive can be adjusted, as can the pH, and different additives can be trialled. Each paint surface will have different requirements and sensitivities so it is important to always test prior to commencing.

Recipe for 3% Agar Agar dissolved in demineralised water:

Bring 100 mL water to around 90°C. Stir in 3 g of Agar powder until completely dissolved. Remove from the heat, pour into a flat container to gel as a film of around 5mm-1cm and let cool. The solution will start to gel at around 40°C. Agar Agar can easily be prepared in the microwave. However, do not let the water boil!

Once it has gelled, the film can be cut into various sizes and shapes, according to requirements. Alternatively, the cooling solution can be poured or brushed directly onto the desired surface while in the sol-phase. It sets without penetrating into the substrate, conforming to the surface topography. This is useful for more three-dimensional surfaces, for example, impasto paint. Once set, the Agar Agar can be peeled off, leaving little to no residues.

Recipe for 3% Agar Agar gel in demineralised water with 1% Citric acid, pH 5.5:

100 mL demineralised water
3 g Agar Agar powder
1 g Citric acid
Ca. 2 mL Sodium hydroxide (NaOH) 10% (added dropwise)

Add the citric acid powder to 45 mL of the demineralised water. Adjust the pH to 5.5 by adding the ammonium hydroxide solution dropwise until a pH of 5.5 is obtained. Bring the final volume to 50mL. Heat 50 mL of the demineralised water to ca. 90-95°C and add in the Agar Agar powder. Mix well, until the powder is completely dissolved. Take the mixture from the heat source and mix in the pH adjusted water as the Agar Agar mixture is cooling. Pour into a flat container to form a film of around 5mm-1cm. The solution will gel under 40°C.

The Agar can be allowed to cool and applied as a gel cut to the desired shape and size, or applied with a brush or spatula while warm as a sol.

Recipe for 3% Agar Agar gel with 0.5% Ecosurf EH-9:

100 mL Demineralised water
3 g Agar Agar powder
0.5 g Ecosurf EH-9

Add the Ecosurf EH-9 to 100 mL of demineralised water. Mix in well. Warm the solution to ca 90-95°C and add in the Agar Agar powder. Mix well until the powder is completely dissolved. Take the mixture from the heat source and pour into a flat container to form a film around 5 mm-1 cm. The solution will gel when the temperature is under 40°C. The benefit of mixing a surfactant into a gel is that the surfactant will not foam as often occurs when used in a free solution.

Recipe for 3% Agar Agar gel with 10% SLS (Sodium Lauryl Sulphate) microemulsion

Microemulsion:
85 mL demineralised water (aqueous phase)
5 mL Petroleum ether (dispersed phase)
4 mL SLS
6 mL 1-Pentanol

Gel:
100 mL demineralised water
3 g Agar Agar powder

Mix the ingredients from the microemulsion well and set aside. Warm the demineralised water to ca. 90-95°C and add in the Agar Agar powder. Mix in well until all the powder is completely dissolved. Take the mixture from the heat source, and when the gel has cooled to around 45-50°C, take 10 mL of the emulsion mixture and add to the gel. Mix well and pour the gel into a flat container to form a film of around 5mm-1cm and allow to set.

Recipe for 2% Gellan gum with 1% Triammonium citrate pH 6:

2 g Gellan gum powder
0.04 g Calcium acetate monohydrate powder
100 mL demineralised water
1 g Triammonium citrate powder (Note that Citric Acid can be used instead)

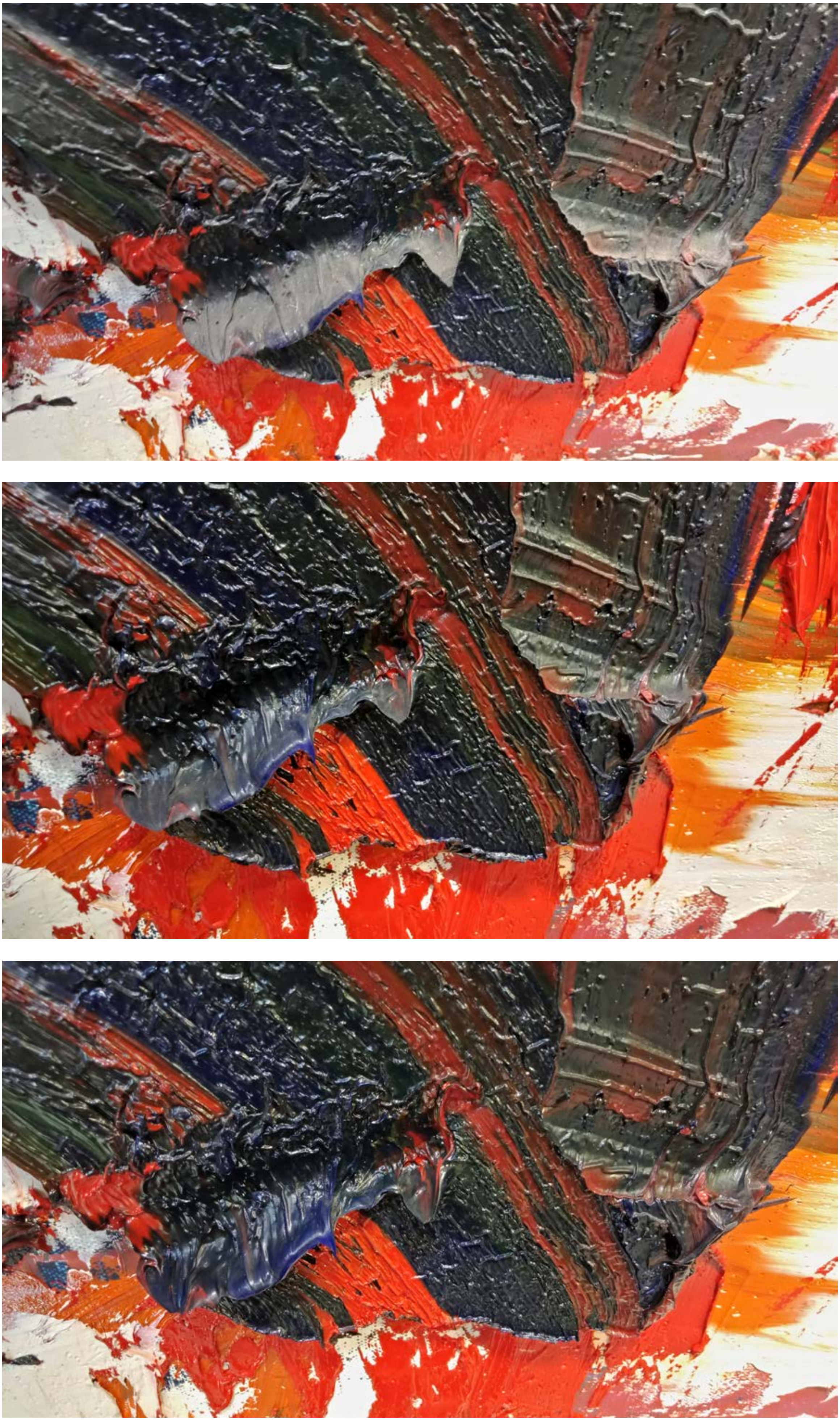
Mix the Calcium acetate monohydrate into the water. Heat the water to ca 100°C. Add the Gellan gum powder and mix well, until all the powder is completed dissolved. Remove from the heat source and allow the mixture to cool slightly. Add the Triammonium citrate powder. Mix well, until all the powder is dissolved. Allow to cool further until the gel has set.

Note: Gellan gum requires 0.4 g Calcium acetate per 1 L of water as a sequestrant.

Recipe for 2% Gellan gum with 1% Citric acid and TEA (triethanolamine) pH 8:

100 mL demineralised water
0.04g Calcium acetate monohydrate powder
2 g Gellan gum powder
1 g Citric acid powder
A few mL of TEA (triethanolamine)

Mix the citric acid into 45 mL of water. Add the TEA dropwise until a pH of 8 is reached. Bring the final volume to 50 mL. Set aside. Mix the Calcium acetate monohydrate powder into 50 mL of the water. Add the Gellan gum powder and mix well. Heat the solution to ca 95-100°C until all the Gellan gum powder is completely dissolved. Mix the citrate solution into the Gellan gum and remove from the heat. Pour the gel into a flat container to form a film of around 5mm-1cm and allow to set.



Above: Before surface dirt removal, Centre: after dry methods for surface dirt removal, Below: after aqueous methods of surface dirt removal from an impasto oil paint surface.

Aqueous Methods Testing procedure:

Dipping the swab in the aqueous solution.

Swabs of cotton wool can be used to administer the aqueous cleaning agent to the selected area. Testing areas should not be larger than 1-2cm^2 and the area should be large enough to accommodate all the materials to be tested.

To test each solution:

- Take a swab and dip it lightly in the aqueous solution. Roll it over the surface a designated number of times (for example 10 times).
- Keep the swab and make any notes regarding alterations to the colour of the surface, degree of change in gloss and colour of the swab. Discolouration of the swab may result from the removal of dirt, varnish or pigment matter. While dirt (and perhaps varnish) removal is the desired outcome, removal of pigment matter is not. If this occurs, testing of this solution must cease immediately to prevent further damage to the artwork.
- Take another swab, dip it lightly in the next aqueous solution and roll again on a NEW area for an increased designated number of times. Again, save the swab and note any material removed.
- Repeat until no more dirt is removed from the surface. Clean swabs should be employed until discolouration no longer occurs (thus the cleaning agent is no longer effective- it may mean that dirt remains but is no longer effectively removed with the chosen solution).
- Repeat with other aqueous solutions, until a satisfactory result is obtained.

Testing the first solution on the surface of the painting, by rolling the swab a set number of times.

Testing subsequent solutions on the surface of the painting, by taking a clean swab, dipping it in the aqueous solution and rolling the swab on the surface a set number of times.

Comparison of the results of the tested solutions under daylight conditions.

Comparison of the results under ultraviolet induced-visible fluorescence conditions.

Comparison of the saved swabs.

Testing the most successful aqueous solution on a larger area of the painting.

- Results of cleaning tests should also be viewed under UV fluorescence. Layers of dirt inhibit the fluorescence of underlying paint layers and varnishes, making them appear dull. Once comparative test solutions have been evaluated the most effective cleaning solution can be utilised.

Appendix

Appendix I: Testing for pH on the Surface of a painting (varnished or unvarnished)

To test the pH of the surface, a large drop of water with a neutral pH (pH 7) should be placed on the surface with a pipette and left for approximately 60 seconds. The drop of water should then be taken again from the surface with a pipette and placed in a pH meter where the pH can be determined. If no pH meter is available, it is possible to drop the water onto a pH paper indicator. The pH of the surface should be measured in several places, as it is unlikely that a single constant pH will be found. In general, the average pH measured across the surface is the pH of the solution that should be used for surface dirt removal. In general, for surface dirt removal from unvarnished oil paint, the pH should remain in the pH 6.0 - 8.5 range. Other materials will have different ranges (varnish may be between pH 5- 8.5, acrylic paint require a high pH e.g., 4-5 to leave the paint film intact). [83]

The technique described in the appendix uses a 'free' droplet of water (distilled or demineralized). An alternative is to incorporate this water droplet in a gel. A special pH meter is required to measure the pH of the gel.[84]

Appendix II: Mol/Molar Concentration

The molar concentration of a solution is the measure of the concentration of a solute in a solution at a given volume and a given temperature. The molarity is defined as the amount of solute (in mol) per unit volume of solution (mol/dm^3) so mol/L (also denoted M).

A mol is the amount of particles (6.0×10^{23}) present in the amount (in gram) of that particle which has a certain molar weight. The molar weight is the sum of the atomic weights of all atoms in that particle. For example, the atomic weights of H and O are 1.0079 g/mol and 16.00 g/mol, respectively. Thus, the molar weight of H_2O equals 2x1.0079 + 16.00 = 18.0158 g/mol. As a result, 1 mol water molecules weights 18.0158 g. The concentration of an acidic or basic solution is expressed as the amount (in mol) per litre of solution of hydrogen or hydronium ions (in water H^+ is always hydrated as H_3O^+), e.g. $[H_3O^+] = 0.010$ M.

---

[83] *https://www.youtube.com/watch?v=bOqZEE7Kb8Y*
https://www.horiba.com/gbr/water-quality/applications/arts/ph-and-conductivity-for-testing-acrylic-paint-films-and-paper-supports-and-formulating-aqueous-cleaning-solutions/

[84] Cremonesi, P., pp. 67

About the authors

Julia van den Burg

Julia van den Burg is a freelance paintings conservator who works in the Netherlands. She graduated from the University of Amsterdam in 2013 with a post-doctoral training in Conservation and Restoration, specialising in paintings. She has gained practical experience working in both the Netherlands and Australia, working on a wide variety of paintings and painted surfaces from all eras, including the ceilings of the Trippenhuis in Amsterdam and the murals of the Fremantle Prison, a UNESCO World Heritage Site. She has worked on various projects together with the Cultural Heritage Agency of the Netherlands, having also compiled the information for the Modern Paint Damage Atlas (*https://paint.tool.cultureelerfgoed.nl/info/background*).

Kate Seymour

Kate Seymour is art historian, conservator and educator. She received her MA Hons in History of Art (Aberdeen University) in 1993 and her MA in Conservation of Easel Paintings (University of Northumbria at Newcastle) in 1999, after completing a three year diploma conservation programme in Florence, Italy. She has worked at the Stichting Restauratie Atelier Limburg (SRAL), Maastricht (the Netherlands) since 1999 as a painting conservator and is currently the Head of Education at this institution. Her position entails working as part of the guest faculty at the University of Amsterdam and University of Maastricht. At the former, she supervises the practical and research work carried out by post-graduate students (paintings) following the Master of Arts Conservation and Restoration of Cultural Heritage, as well as teaching and lecturing on a variety of subjects, both academic and practical, throughout the two year Master of Science in Conservation Studies. For the latter, she also co-organises and teaches modules (FASOS and MSP) aimed at introducing conservation science, including imaging of artworks and pigment sample analysis to Liberal Arts and Science Bachelor students. Additionally, she gives workshops on conservation practice and theory to mid-career conservators internationally. Furthermore, Kate Seymour is currently chair of the ICOM-CC Directory Board (2020-2023).

Klaas Jan van den Berg

Klaas Jan van den Berg is senior scientist at the Cultural Heritage Agency of the Netherlands (RCE) and professor of Conservation Science (Painted Art) at the University of Amsterdam, Faculty of Humanities, Group of Conservation and Restoration of Cultural Heritage. He teaches organic chemistry, technical art history and other chemical aspects of painted art. His main focus is the study of formulations, techniques, material changes and surface cleaning in 20th Century oil paintings.
Klaas Jan has written or co-authored over 140 scientific publications has been supervisor of a number of students of both science and conservation background. He organised the Issues in Contemporary Oil Paint symposium in 2013, and the Conference on Modern Oil Paints in 2018, and is editor of their Proceedings (Springer Nature, 2014 and 2019). He was project leader of the HERA-JPI EU project 'Cleaning of Modern Oil Paints'. Klaas Jan is currently leading the 20th Century Cultural Heritage research programme (2021-2023) at RCE.

Lia Gorter

Lia Gorter studied at the Textil Ingenieur Schule, Künstlerische Abteilung, Krefeld, and the University of Amsterdam. She is the director of the Foundation for Cultural Inventory (SCI), Amsterdam, since 1997. SCI digitizes and documents Dutch and Flemish cultural heritage in seldom known museum collections in non-western countries. SCI organizes exhibitions; publishes books and organizes international Masterclasses on preservation and conservation of paintings. The Masterclasses SCI organizes in co-operation with SRAL, the Conservation Institute and the Cultural Heritage Agency of the Netherlands. The SCI works in Russia in the Tretyakov Gallery, Moscow; Siberia with ten Siberian Museums in the Vrubel Museum in Omsk and in Mumbai, India in the Chhatrapati Shivaji Maharaj Vastu Sangrahalaya, CSMVS, the former Prince of Wales Museum.

This is one of a series of six brochures describing various aspects of conservation practice of works of painted art:
The brochures are intended for practicing conservators as well as other professionals involved in the field of painted cultural heritage.

The Cultural Heritage Agency of the Netherlands provides knowledge and advice to give the future a past.