Northumbria Research Link

Citation: Colbourne, Jane and Singer, Brian (2009) The removal of natural resin varnishes from hand-coloured oil printed media. In: Research in book and paper conservation in Europe: a state of the art. Verlag Berger Horn, Vienna. ISBN 978-3850284905

Published by: Verlag Berger Horn

URL:

This version was downloaded from Northumbria Research Link: https://nrl.northumbria.ac.uk/id/eprint/2270/

Northumbria University has developed Northumbria Research Link (NRL) to enable users to access the University's research output. Copyright © and moral rights for items on NRL are retained by the individual author(s) and/or other copyright owners. Single copies of full items can be reproduced, displayed or performed, and given to third parties in any format or medium for personal research or study, educational, or not-for-profit purposes without prior permission or charge, provided the authors, title and full bibliographic details are given, as well as a hyperlink and/or URL to the original metadata page. The content must not be changed in any way. Full items must not be sold commercially in any format or medium without formal permission of the copyright holder. The full policy is available online: http://nrl.northumbria.ac.uk/policies.html

This document may differ from the final, published version of the research and has been made available online in accordance with publisher policies. To read and/or cite from the published version of the research, please visit the publisher's website (a subscription may be required.)





The Removal of Natural Resin Varnishes from Hand-Coloured Oil Printed Media

Abstract

Removing a varnish coating from an intaglio or planographic print is a potentially hazardous procedure. Difficulties are compounded if the ink contains additives and adulterants or the print has been hand-coloured with solvent sensitive media. In the case of seriously discoloured and damaged artefacts the risks involved in removing a varnish may be justified. Traditionally the paper conservator's choice of options has been rather limited which heightens potential risks. Solvent poultices and gels may offer certain advantages over more traditional approaches and, although fears as to the long-term implications of residues have yet to be fully researched, current experiments look encouraging.

1 Introduction

An interest in the removal of organic resin varnishes from oil printed media on paper from the 19th and early 20th century began several years ago when a series of individual and unrelated paper artefacts were presented to Northumbria University for conservation.

A literature review revealed two factors, which did not seem to be commonly known: how varnish coatings may affect prints and how removal techniques involving organic solvents may influence appearance, longevity and vulnerability to subsequent cleaning treatments.

Drawing on references from the field of painting conservation and other case studies, the risks and benefits associated with varnish removal are here postulated. Treatment approaches involving solvent gels and poultices are reviewed and two preliminary studies carried out by our own group are reported.

2 Historical Context

The considerable advancements in science and technology during the 19th and early 20th centuries gave rise to many patents that served to improve the rapidly developing commercial and art printing industry.

Large edition artist prints depicting popular themes of the day provided affordable decorative pieces for the home and were often purchased hand-coloured, attached to canvas/paper backings, framed and varnished in an attempt to imitate oil paintings. Rudolf Ackerman,2 entrepreneur and publisher who set up the successful "Repository of Arts" in the Strand, London, was one of the many who offered the service of mounting and varnishing prints. His particular method was known as the "Ackerman Style", which involved cutting the engraving close to the plate mark, removing all inscriptions and attaching it to a sheet of support paper.3 The cut-off title was attached below the print and the whole varnished, eliminating the need for the print to be protected by glass. From a commercial point of view prints treated in this way, now considered to be more or less spoilt, strongly reflect the collecting and display trends of the period and are a common feature in museums, historic and private collections. Varnishing was not only confined to artist prints; maps, plans, posters and other printed ephemera were also treated in a similar manner in an attempt to make them more durable for handling and display.

The varnishes Ackerman and others would have used during this period would have been based on natural resin varnishes such as copal, mastic and dammar⁴ common to easel painting and

¹ Over 400 individual English patents relating to printing inks dating from 1821 to 1935 are listed in Mitchell (1937), pp. 370–393.

² Established in 1795

³ All prints published in England after 1735 had by law to display a publication line listing date, originator, printer and place of publication.

⁴ Spirit varnishes are largely made from soft resins such as mastic, dammar or sandarac dissolved in turpentine or alcohol. As they age they become more brittle and have poor durability. Their triterpenoid based structures however resist cross-linking the result of which makes them more readily soluble in polar organic solvents than hard resins. Oil resin varnishes are usually made from hard resins such as kauri and copal, which was particularly popular during the 19th century. They are dissolved in heated linseed

shellac⁵ common to the decorative arts. These would have been dissolved in either spirits or oil and resin with an isolating layer applied between the paper and the coating to prevent penetration and rendering the support transparent.⁶

The practice of varnishing paper was not only confined to commercial retail enterprises as the inclusion in many artists' manuals and treatises of the period testify.⁷ For example Desaint,⁸ in 1913, recommends using two parts Canada balsam to four parts turpentine over a coating of fish glue and earlier, in 1843, Riffaultin recommended dissolving sandarac and mastic in a mixture of Venice turpentine and alcohol.⁹

3 The Ageing Process of Natural Resin Varnishes and its Potential Effects on Paper and Oil Printed Media

It is well known that natural resin varnishes are vulnerable to photooxidation resulting in considerable yellow/brown discolouration, yet only recently has research explored issues relating to its increase in polarity and acidity. A shift in polarity affects resin solubility and as a

- or tung oil and thinned with turpentine or alcohol. Lead and manganese compounds were often added to aid drying. They are reported to darken considerably with age and cross-link becoming increasingly insoluble. In all the above varnishes, the autofluorescence increases with age resulting in a bright pale yellow colour under UV.
- 5 Shellac is derived from a resin secreted by the Kerria lacca Kerr insect. Also known as stick lac. Commonly used in the decorative arts particularly in Asia where it was applied in solution or by warming. Stick lac typically contains 70 to 80 % resin the rest being composed of waxes and dyes which are responsible for its characteristic bright orange fluorescence in UV. Complex in its structure it is essentially composed of low molecular weight polymers (oligomers) of which aleuritic and butolic acids are typical. Shellac is highly prone to oxidation resulting in a dramatic decrease in solubility. It is sensitive to alkalis yielding a bright red colour from the presence of erythrolaccin.
- 6 Carlyle reports that isinglass and other purified animal glues or aqueous based materials e.g. egg white, casein and gum Arabic were used as isolating layers before varnish was applied. Isinglass, also known as icthyocolla or fish glue, was readily available during 19th century as it was also used in food, liquor and textile industry. Carlyle (2002), pp. 190, 191 and 236.
- 7 The Young Artists' (1877) and Tingry (1804)
- 8 Desaint (1913)
- 9 Riffault (1843)

The

consequence more polar solvents, which potentially hold greater risk for media, are required for their removal.¹⁰

Significant for paper artefacts is the propensity that varnishes have to become more acidic as they age. Most diterpenoid resins contain carboxylic acids such as abietic acid in pine resin or sandarocopimeric acid in sandarac and copal. While these resins are not water-soluble their acidity may potentially enhance the acid catalysed hydrolysis of cellulose in paper. Furthermore, oxidised resins in varnishes also contain carbonyl compounds that may undergo Norrish type 1 reactions leading to the formation of free radicals, potentially enhancing the photo-oxidation of paper.

There is a strong case to suggest that the presence of organic resins may significantly contribute to hydrolysis, depolymerisation, and subsequent loss in tensile strength of the support.¹³ Deterioration of this type may also heighten the paper's sensitivity to solvents and reagents rendering further cleaning potentially hazardous.

Notwithstanding the chemical changes varnishes undergo during ageing, the changes in mechanical and physical properties can also dramatically alter the visual qualities of a print. Loss in plasticity and elasticity as a consequence of contraction and evaporation of the resins' essential oils may result in the formation of age cracks and fissures. ¹⁴ This not only compromises the appearance of the object but may further exacerbate acid hydrolysis by selectively allowing the ingress of moisture, dirt and atmospheric pollutants into the substrate. ¹⁵

Blanching, a result of exposure to damp conditions, and uneven absorption of the varnish, which is a common feature resulting from applying a natural resin to a porous substrate, may also contribute to an

altered ap coating w

4 Potent

Whilst it avents rare has been during clacause of the layer of presented to increase

5 Oil Me

Traditional inks were collinseed, saft The old robe the oil extreme the hazardous other method or ozone²⁰. celerated the

¹⁰ The shift towards greater polarity is due to the incorporation of oxygen and is reported to occur within a 10–20 year period. Phenix (1998), p. 111.

¹¹ Feller et al. (1985), pp. 57-62

¹² de la Rie (1988)

¹³ The presence of varnish was reported to be a major contributing factor in the deterioration of many oil sketches on paper in the British Museum resulting in major changes in appearance and physical strength. Kosek/Green (1992)

¹⁴ See Keck (1969) for a comprehensive account of causes and appearance of varnish cracks.

¹⁵ Gaskell (2000)

¹⁶ Dacus Hai

¹⁷ Dacus Hai

¹⁸ Also referi

¹⁹ Exposure t ish green f proximatel odour. Lee

²⁰ Schräder a action of o and Co. pa

altered appearance. Under such conditions a proposition to remove the coating with organic solvents may be justified.

4 Potential Effects of Solvents on Printed Media

Whilst it can be argued that removing varnish from a print with solvents rarely has the complications associated with easel paintings, it has been reported that "the same solvents which affect oil paintings during cleaning, must also affect linseed oil-based printing inks because of their similar composition. In fact the exposure of the very thin layer of printing ink and the absorbent nature of the paper would seem to increase the dangers of solvent exposure to the ink".16

5 Oil Medium

Traditionally the principle ingredients of intaglio and planographic inks were carbon black and a processed drying oil, ¹⁷ commonly poppy, linseed, safflower and walnut oil, known in the trade as "varnish". ¹⁸

The old method of preparing printers' or lithographic varnish was to heat the oil to a very high temperature until ignited, a process far more extreme than that used in the preparation of oil painting medium. This hazardous procedure was largely replaced in the 19th century when other methods were introduced such as boiling or exposure to oxygen or ozone 20. All processes however had the same result in that they accelerated the decomposition or polymerisation of the oil to produce a

¹⁶ Dacus Hamm (1992)

¹⁷ Dacus Hamm (1992)

¹⁸ Also referred to as typographic varnish, burnt oil or heat-bodied oil.

¹⁹ Exposure to oxygen resulted in a pale coloured varnish that was free from the brownish green fluorescence exhibited by ordinary lithographic varnishes. It contains approximately ten times as much free acid as other methods and has an unpleasant odour. Leeds (1894)

²⁰ Schräder and Dumcke patented a procedure that produced varnish rapidly by the action of ozone on raw oil. The oil was then bleached following the Germany Graf and Co. patent. Various other variations and patents followed during the early 20th

viscous medium capable of rapidly drying during print production. Oxidation polymerisation processes in the oil film promote the formation of three-dimensional networks.²¹ As a result the sensitivity of the print film to solvents decreases but swelling and leaching may occur.

Linseed oil consists of a polymeric binder phase plus a mobile, low molecular weight phase which has the potential to be extracted (leached) from the film by liquid solvents. Leaching is essentially a secondary process that occurs as a consequence of the solvent being absorbed into and swelling the oil film.²²

The simple loss of this organic binder mass, the abundance and type of which vary according to the age and thickness of the film and the polarity of the solvent used, could lead to an increase in roughness of the surface resulting in a matt, less saturated appearance. Whilst in the majority of cases this phenomenon may go unnoticed, high gloss inks containing excess oil due to the use of "fat" techniques²³ and the fashion for raised print lines²⁴ may be significantly affected. Further, these low molecular weight volatiles are thought to have a plasticising effect on the film; therefore removal may result in embrittlement of the film and a propensity to fracture.

According to Phenix,²⁵ leaching has much more significance in relation to longevity than the single action of one treatment step involving var-

signif Rising so This : inks s

solvei

nish 1

6 Pi

From

costly tallic s in the its into it mor much natura potent Anil er blac becaus

century for example Rosenblum and Rideal, British patent No 9529 (1897) and Ramage, British Patent No 7242 (1901).

²¹ A complex process in which hydroxyperoxides and diacids (e.g. azelaic), the abundance of which is often during analysis taken as a marker of aged drying oils, are formed resulting in chain cleavage, hydrolysis and deterioration of the ester bond network known as deesterification. As oxidation and hydrolysis increases ionic carboxyl groups are formed and fatty acids and glycerol are liberated. This results in fatigue, stiffness, loss in binding capacity and an increased affinity for aqueous liquids and solvents.

²² Phenix (1998)

²³ Excess ink left on the surface during controlled wiping of the plate produces soft muted effects of infinite, subtle variety. Whistler used this technique to great effect in his Nocturnes.

²⁴ A characteristic technique used by many of the painter/etchers of the late 19th early 20th centuries and in particularly Seymour Hayden. Reports claimed that rather than press his prints in a traditional manner he preferred to dry them attached boards with gum tape.

²⁵ Phenix (1998)

²⁶ Keck

²⁷ Duri was serve short

²⁸ Wide

²⁹ Wins

³⁰ USA adde

nish removal. The cumulative effects of post treatments may contribute significantly to the artefact's long term visual and physical deterioration.

Risks are believed to be further increased if polar and fast evaporating solvents are used²⁶ and if there is a previous history of cleaning. This may explain the published and unpublished reports of printing inks softening, lifting, cracking and changing in appearance after post solvent treatment.²⁷

6 Pigmentation

From the 1880's on a variety of "blacks" were introduced to replace the costly lamp black. Gas black, which is formed from the deposits on a metallic surface of soot from gas burning, was used extensively, particularly in the USA due to the abundance there of natural gas. Characterised by its intensity of tone and glossy appearance, its granular texture made it more difficult to incorporate into the medium and required twice as much oil varnish to form the right consistency. Higher oil ratios and the natural tendency of gas black to be sensitive to water increases the ink's potential vulnerability to solvent and post aqueous cleaning.

Aniline dyes added to even the highest grade intaglio inks,²⁸ and other black pigment substitutes such as asphalt²⁹ and pitch³⁰ are also at risk because of their solubility in some solvents.

²⁶ Keck (1969)

²⁷ During solvent tests on 4-year-old naturally aged print samples, acetone and ethanol was reported to leave fissures in the ink film. An absence of wrinkles was also observed which the author attributed to the swelling of the film and/or the leaching of short chain fatty acids. Dacus Hamm (1992)

²⁸ Widespread use from the 1860's onwards. Andés (1889), p. 236

²⁹ Winship, British patent No 334, 370 (1930)

³⁰ USA patent No 741, 726 (1903): During the 19th century pitches, rosins and tars were added to inks for cheaper applications: Mills/White (1987), p. 43.

7 Additives and Adulterants

In an attempt to improve the working performance and costs associated with commercial and fine art printing, the use of additives and adulterants was a common feature of the late 19th and early 20th centuries.

Driers, typically litharge, iron sulphate, manganese acetate and lead acetate, were regularly added to prevent smearing and aid in the drying of drying oils and semi drying oils.³¹ Also mixtures including non-drying oils were sometimes added as adulterants.

Driers catalyse the oxidative polymerisation of the oil medium but may exacerbate leaching. The presence of metal driers will form metal soaps in the oil further increasing the sensitivity of the ink to cleaning reagents.

Other potentially sensitive components include waxes,³² spirit varnishes made from natural resins³³ and certain thinners such as paraffin and turpentine,³⁴ all of which were variously added to either retard or increase the drying of the ink during high speed production.

8 Hand-colouring

According to Wilder,³⁵ nearly all prints from the 19th century were intended for hand colouring. Hand colouring was either completed by contracted out-workers or more commonly in-house in large publishing houses such as Rudolf Ackerman or the American firm of lithographers Currier and Ives. A largely female workforce who worked on

what co prints in A lim prints a and org ficulties the disc Furthe to organ produce ing fron renderin white sp

9 Pape

Solvents solvent r spheric r some wo dration³⁹ structure vents ho

³¹ Semi-drying oils include cottonseed, maize, soya bean and menhaden oil and were used extensively in the USA either on their own or mixed with the more costly linseed oil. Non drying oils dry by absorption into the porous substrate and by loss of volatile dilutants. Driers were also often added to speed up the process. Mitchell (1937), p. 244

³² Schweitzers' recipe for lithographic ink included a considerable amount of wax and resins for example, 80 lb bleached beeswax, 20 lbs shellac, 20 lb white grain tallow soap (from mutton), 20–30 lbs lamp black. Many English recipes of the period also contained substantial quantities of additives as given: Mastic 60 lbs, shellac 300 lbs and unspecified amounts of gum lac, tallow soap, yellow wax and rosin. Mitchell (1937), p. 266

³³ Rosin, copal, mastic and shellac

³⁴ Mitchell (1937), p. 98

³⁵ Wilder (1969), p. 19

³⁶ An intr provide from lo applied the girls finest que resistant

³⁷ Carlyle

³⁸ Arney/F

³⁹ James et

⁴⁰ Correcte yellowis papers) a

what could be described as a production line processed thousands of prints in this way.³⁶

A limited range of pigments was generally used for hand colouring prints and several, including gamboge, Vandyke brown and synthetic and organic lake pigments, are known to be sensitive to alcohols. Difficulties also arise in deciphering the location of these pigments as often the discoloured varnish masks the transparent, delicate tones.

Further, additives in certain watercolour ranges may also be reactive to organic solvents. Carlyle describes a range of water-soluble paints produced by Reeves and Company called Moist Watercolour's and dating from the 1850's. They contained relatively large quantities of wax rendering them potentially sensitive to solvents of low polarity such as white spirit.³⁷

9 Paper

Solvents appear to have very little impact on paper. Dehydration and solvent retention is believed to be a temporary phenomenon as atmospheric moisture soon replaces water lost during treatment.³⁸ Even so, some workers have voiced concerns regarding solvent retention, dehydration³⁹ and the formation of certain complexes within the cellulose structure to which the short and long term effects are unknown. Solvents however may affect resin coated or corrected⁴⁰ papers or rosin

ociat-

adul-

ries.

d lead

e dry-

g non-

at may soaps

igents.

it vararaffin ard or

ere inted by

ıblish-

lithogced on

³⁶ An intriguing account of the Currier and Ives studio during the mid 19th century is provided. Twelve young women, mainly of German decent and training, worked from long tables where a model was set up, visible to all to copy. Each colourist applied one colour then passed it on to another. The Finisher, who also managed the girls, would check the end results and touch up where necessary. Colours of the finest quality were imported from Austria and valued especially for their reported resistance to light. Wilder (1969), p. 171

³⁷ Carlyle (2002), pp. 421-422

³⁸ Arney/Pollack (1980)

³⁹ James et al. (1997), p. 262

⁴⁰ Corrected paper is described as white paper with blue or red dyes added to modify yellowish cast. Azo, aniline dyes and later stilbene derivatives (common in poster papers) are potentially solvent sensitive.

nd were / linseed volatile /, p. 244 wax and ow soap ontained unspeci-

based sizing agents, resulting in either a reduction in tensile strength or changes to the surface characteristics of the support.

10 The Benefits of Removing Aged Varnishes

Although the potential risks associated with varnish removal are cause for concern, the benefits in regard to appearance and in halting hydrolysis and depolymerisation are substantial. The presence of an inflexible, impermeable coating may cause significant internal stresses to the paper during fluctuations in temperature and humidity and also constricts any further treatment that might be necessary in regard to cleaning and structural conservation or restoration. It could also be argued that the existence of a varnish is more a statement on historic display techniques rather than respect for artist intension.

11 Traditional Varnish Removal Techniques

The two traditional approaches to removing degraded varnishes from paper are either immersing in or swabbing with a variety of solvents. The success of these techniques varies considerably depending on the conservators understanding of the complex issues associated with solubility and the response of the coating to treatment. An immediate disadvantage of both of these techniques is that they can increase penetration of the varnish into the paper leaving appreciable residues behind. This may result in a changed appearance or may induce blanching⁴¹ particularly if followed by aqueous treatments to reduce the effects of acidity.

More recently techniques involving solvent poultices and gels that work by restricting capillary flow appear to offer additional advantages and provide the conservator with increased control. 12 Sol

Poultic which range f hydrate pressur solvent porous be clea niques. Fullers

13 Solv

Pioneer gels hav cleaninş mendat 1986 su

⁴¹ Blanching is particularly prevalent when fast evaporating solvents such as acetone are used. Removal of blanching once formed usually requires either more rigorous cleaning or exposure to alcohol fumes or a light spray over several days/weeks, known as reforming.

⁴² Cleari medit mater case o

⁴³ Fuller other

⁴⁴ Kiesel white

⁴⁵ Lapon lloidal hold it associa directl of Lap py, Res (2003)

⁴⁶ Wolbe

gth or

cause
nydroinflexto the
o concleanrgued
isplay

s from lvents. on the th solite disenetraehind. ching⁴¹ ects of

ls that ntages

acetone rigorous s/weeks,

12 Solvent Poultices

Poultices are essentially composed of an inert porous substrate to which solvents or other reagents can be added. The substrates can range from macerated paper pulp fibres through to synthetic or natural hydrated silicates. Traditionally used in conjunction with adhesive and pressure sensitive tape removal, poultices work by releasing an active solvent. The dissolved material is then drawn back into the poultices porous substrate after evaporation of the solvent. The dry material can be cleared using a variety of mechanical, swabbing or aqueous techniques. ⁴² Materials which make for the best poultice substrates include Fullers earth ⁴³, Kieselgur ⁴⁴ or Laponite ⁶⁹ ⁴⁵.

13 Solvent Gels

Pioneered by Richard Wolbers, ⁴⁶ at the University of Delaware, solvent gels have been considered a valuable addition to techniques used in the cleaning of paintings and varnish removal since the late 1980's. Recommendations for use on paper artefacts are however few. Hartwell in 1986 suggested using gels as an alternative to liquid solvents for the

⁴² Clearing is made more effective if the poultice is applied over an isolating layer of medium weight Japanese or rayon paper. Lens tissue and many non-woven polyester materials are not recommended as they either inhibit capillary movement or in the case of lens tissue leave appreciable residues behind.

⁴³ Fuller's earth is formed from hydrated silicates of magnesium, calcium aluminium or other metals. Its pale grey brown colour is a drawback.

⁴⁴ Kieselgur (diatomaceous earth) is hydrated silica from diatom plant skeletons. It is whiter than Fullers earth but less cohesive.

⁴⁵ Laponite® is a synthetic inorganic clay silicate which forms a viscous thixotropic colloidal gel with water to which solvents can be added. Its high viscosity enables it to hold its shape well in a poultice thus reducing lateral movement, strike through and associated local staining. Tests have shown that Laponite also works well if applied directly to a surface in dry powder form to which solvent is then added. Residues of Laponite under UV, appears dark purple yet fluoresce white under UV microscopy, Residues detected under the microscope under X polars were anisotropic. Totten (2003)

⁴⁶ Wolbers (1992)

removal of pressure sensitive tapes⁴⁷ and Petukova in 1992 presented a case study regarding the removal of an unspecified organic resin varnish from a series of 19th century maps using an ethanol based gel.⁴⁸

Gels⁴⁹ have much greater potential over poultices in concentrating the cleaning action of an admixture of miscible or immiscible solvents and reagents due to their highly viscous and cohesive nature. This serves to focus capillary action in one phase thus decreasing lateral migration and strike through. The decrease in penetration is in contrast to the action of a poultice, which forms two distinct phases, firstly facilitating the penetration of the solvent into the substrate and then re-absorbing the mobilized products through capillarity.⁵⁰

The inclusion of water in the gel, which in itself is highly polar, retards the evaporation of the volatile components and increases the dissolution of polar coating systems thus leading to a decrease in contact time and exposure to harmful chemicals. The important advantages include the capacity of a gel to "unpack" or remove the upper most layers of a discoloured varnish whilst leaving the lower layers intact, to act as a saturating layer limiting the effects of blanching and to provide lubricating qualities that have been reported to decrease the negative effects of abrasion during the clearing process. The use of gel formulations for cleaning easel paintings has recently been reviewed. These authors have also offered a new type of reversible gel based on polyethyleneimine and its reaction with carbon dioxide to produce an ammonium carbamate gel form (PEICO₂). This gel can quickly and

easi of a rem

14 (

Conc the p Lapo ment have for the

demo

ide) i

rectly

resid

15 Rc

Remo

tants move tions water is diff diffici

cause as infi

⁴⁷ Hartwell (1986)

⁴⁸ Petukhova (1992)

⁴⁹ Solvent gels are essentially composed of Carbopol (thickening agent) and Ethomeen (surfactant) which form a thixotropic clear gel in the presence of water to which a variety of polar, non-polar solvents and reagents can be added to target very specific solubility parameters.

⁵⁰ Cremonesi et al. (2000); Cremonesi (2004)

⁵¹ Burnstock/Learner (1992)

⁵² Erardt/Bischoff (1993) and also in Fronek (1987)

⁵³ Ford/Byrne (1991)

⁵⁴ Carretti/Dei (2006)

⁵⁵ Carretti et al. (2008)

⁵⁶ Tott 57 Wai

easily be transformed into a much less viscous liquid by the addition of a weak acid that displaces the carbon dioxide. This affords easier removal. The use of gels for the cleaning of works of art on paper has not, however, been so extensively investigated.

14 Concerns Regarding Gel Residues on Paper

Concerns associated with the clearance of solvent poultices and gels and the potential long-term effects of residues on paper cannot be dismissed. Laponite® has been shown to considerably darken with age on parchment under artificial ageing. Fagarose, Carbopol, and Laponite® gels have recently been evaluated as alternatives to cellulose ether poultices for the local removal of moisture-sensitive adhesives on paper. In this study by Warda et al, visual and ultraviolet examination techniques demonstrated that both Carbopol (pH adjusted with sodium hydroxide) and Laponite® caused discolouration on paper when applied directly and that a barrier tissue was effective at blocking the deposition of residues. Agarose did not, however, show any adverse effects.

15 Removal of Gel Residues from Works of Art

Removal of gelling-agent and surfactant residues in a process known as "clearing" is a complicated issue, especially with regard to surfactants which, by their nature, tend to adhere to surfaces and not be removed by solvents or aqueous washes. There are many recommendations ranging from mechanical removal to swabbing with deionised water and a series of organic solvents. The success of these treatments is difficult to assess because gelling-agent and surfactant residues are difficult to detect using conventional analytical equipment either because of their low concentrations, making insensitive techniques such as infra-red spectroscopy ineffective, or because of their low volatility

⁵⁶ Totten (2003)

⁵⁷ Warda et al. (2007)

preventing successful analysis by gas chromatography. However several groups of workers embarked on an extensive programme to investigate gel residues left on works of art after cleaning with solvent gels, resulting in a collective publication.⁵⁸

In the case of the surfactant Ethomeen C12, residues have been detected on oil paint surfaces by derivatisation with 3-trifluorphenyl trimethyl ammonium hydroxide followed by gas chromatography – mass spectroscopy.⁵⁹

However pyrolysis-gas chromatography – mass spectroscopy has been successful in detecting very small concentrations of surfactant residues such as Ethomeen C25 on oil paint surfaces. ⁶⁰ A detection limit of 1 µg of surfactant was established during this study.

Thus while studies on the gel residues left on easel paintings and polychrome sculptures have been carried out, there is little published information regarding the detection of such residues in paper.

However in two preliminary studies⁶¹ carried out by our group, onemicrolitre samples of five known concentrations of solutions of Ethomeen C12 ranging from 4.2×10⁻⁴ g·ml⁻¹ to 8.4×10⁻³ g·ml⁻¹ were placed directly, without derivatisation, on the platinum ribbon filament of a Pyrola 2000 pyrolyser attached to a thermo focus gas chromatogram fitted with a DSQ II mass spectrometer. A series of peaks, all of which showed an ion of m/z: 100 Daltons in their fragmentation pattern, were characteristic of Ethomeen C12. The largest of these was selected and its peak area measured in each case. Examination and extrapolation of the peak areas indicated a detection limit of approximately 1 microgram. A similar experiment carried out with samples of Ethomeen C25 at concentrations ranging from 3.7×10⁻⁴ g·ml⁻¹ to 7.5×10⁻³ g·ml⁻¹ gave a series of peaks, all of which showed ions of m/z: 41, 43, 53, 69, 70 and 83 Daltons in their fragmentation patterns, and were characteristic of Ethomeen C25. A detection limit of approximately 5 micrograms was indicated. In the next stage of the studies, solvent gels containing Ethomeen C12,

Xylene, wa or reduce and aged a Some sam solvent ge with a dry a scalpel fi were searc able amou with water were only a residue nary resul Ethomeen research in residues o a future da

Acknowle

Acknowle lowing per Dr. Joyc London; I from the N versity; an tion Institu

⁵⁸ Stulik et al. (2004)

⁵⁹ Carlson/Petersen (2004)

⁶⁰ Khandekar (2004)

⁶¹ Coles (2008), pp. 104–106; Fleming (2008), pp. 148–151

⁶² Coles (20

⁶³ Fleming

⁶⁴ Coles (20

⁶⁵ Fleming

Xylene, water and Carbopol were formulated and were used to remove or reduce both rosin varnish62 and rubber adhesive residues63 from new and aged archival paper⁶⁴ and from Whatmans number 1 filter paper⁶⁵. Some samples were left "uncleared" while others were "cleared" of the solvent gel in various ways including washing with water and removal with a dry swab. Two-by-two millimetre squares of paper were cut with a scalpel from the various samples and were pyrolysed. The pyrograms were searched for the peaks characteristic of Ethomeen C12. A detectable amount of Ethomeen C12 residue was left in each case, but washing with water appeared to be most effective at clearing the residues which were only present in quantities close to the detection limit representing a residue of approximately 3×10⁻⁷ g·mm⁻² on the paper. Thus preliminary results appear to be encouraging in regard to the low retention of Ethomeen C12 residues and the effectiveness of clearing techniques. The research into the retention of both Ethomeen C12 and Ethomeen C25 residues on paper is ongoing and will be published in greater detail at a future date.

Acknowledgements

Acknowledgements and a great deal of thanks are extended to the following people for their valuable help, advice and use of source material:

Dr. Joyce Townsend, Senior Conservation Scientist at Tate Britain, London; Hye Jung Yum, Louisa Coles and Shona Fleming graduates from the MA Conservation of Fine Art Programme Northumbria University; and Rachel Rivenc, Research assistant at The Getty Conservation Institute, Los Angeles, California.

⁶² Coles (2008), pp. 111-113

⁶³ Fleming (2008), pp. 104-106

⁶⁴ Coles (2008), pp. 148-151

⁶⁵ Fleming (2008), pp. 111-113

Bibliography		Coles
Andés (1889)	Andés, Louis Edgar: Oel- und Buchdruckfarben. Praktisches Handbuch für Firniß- u. Farbenfabrikanten, Wien/Pest/ Leipzig (1889) : as quoted in Mitchell (1937), p. 259	
Arney/Pollack (1980)	Arney, Jonathan S.; Pollack, L. B.: The retention of organic solvents in paper. In: <i>Journal of the American Institute of Conservation</i> 19 (1980), pp. 69–74	Crema
Burnstock/Learner (1992)	Burnstock, Aviva; Learner, Tom: Changes in the surface characteristics of artificially aged mastic varnishes after cleaning using alkaline reagents. In: <i>Studies in Conservation</i> 37 (1992), pp. 165–184	Cremo
Carlson/Petersen (2004)	Carlson, Janice; Petersen, W. Christian: Aging Characteristics of Surfactants' Appendix: Interaction of MethPrep with Surfactants. In: Solvent Gels for the Cleaning of Works of Art – The Residue Question, Valerie Dorge (Ed.), Los Angeles, California: The Getty Conservation Institute (2004), pp. 110–115	Dacus
Carlyle (2002)	Carlyle, Leslie: The Artist Assistant: Oil Painting Instruction Manuals and Handbooks in Britain 1800–1900: With Reference to Selected eighteenth-century Sources, London 2002	de la R
Carretti/Dei (2006)	Carretti, Emiliano; Dei, Luigi: Gels as Cleaning Agents in Cultural Heritage Conservation. In: <i>Molecular Gels, Materials with Self-Assembled Fibrillar Networks</i> , Richard G. Weiss and Pierre Terech (Eds.), Netherlands (2006), pp. 929–936	Desaint
Carretti et al. (2008)	Carretti, Emiliano; Dei, Luigi; Weiss, Richard; Baglioni, Piero: A new class of gels for the conservation of painted surfaces. In: <i>The Journal of Cultural Heritage</i> 9, Issue 4 (2008), pp. 386–393	Erardt/I

Coles (2008)	Coles, Louisa: Historical Context, Conservation Treatment and Structural Repair of a Relief Model on Paper of the Siege of Ladysmith (c1900) Incorporating a Discussion of the Use of Solvent Gels to Remove Organic Varnish Films from Pa- per, Dissertation at the University of Northumbria 2008
Cremonesi et al. (2000)	Cremonesi, Paulo; Curti, Alessandra; Fallarini, Laura; Raio, Silvia: Preparazione e utilizzo di Solvent Gels, reagenti per la pulitura di opere policrome. In: <i>Progetto Restauro</i> 15, Padova (2000), pp. 25–33
Cremonesi (2004)	Cremonesi, Paulo: L'Uso di Tensiaottivi e Chelanti nella Pulitura di Opere Policrome. In: <i>I Talenti – Metodologie, Tecniche e Formazione nel Mondo del Restauro</i> 10, 2 nd Edition, Padova (2004), pp. I–112
Dacus Hamm (1992)	Dacus Hamm, Patricia: A history of the manufacture of printing ink from 1500–1900: With notes for the conservator. In: <i>The Manchester Conference Papers</i> , 1 st –4 th April 1992, S. Fairbrass (Ed.), The Institute of Paper Conservation (1992), pp. 30–34
de la Rie (1988)	de la Rie, E. René: Photochemical and thermal degradation of films of dammar resin. In: <i>Studies in Conservation</i> 33 (1988), pp. 53–70
Desaint (1913)	Desaint, Andre: Trucs d'Atelier, 2000 formules, procédés ou tours de mains pour le peintre en bâtiments. Dourdan, Paris 1913 : as quoted by Hiler (1934), p. 243
Erardt/Bischoff (1993)	Erardt, David; Bischoff, Judith J.: Resin soaps and solvents in the cleaning of paintings: similarities and differences. In: <i>ICOM committee for conservation</i> , Janet Bridgland (Ed.), 10 th triennial meeting, Washington DC, 22 th –27 th August, Preprints 1, ICOM Committee for Conservation 1993, pp. 141–146

Khai

Kose

Leed

Mills

Mills

Mitcl

Petul

Phen

Feller et al. (1985)	Feller, Robert L.; Stowlow, Nathan; Jones, Elizabeth: On Pic-
	ture Varnishes and their Solvents, 3 rd Edition, Washington 1985
Fleming (2008)	Fleming, Shona: The conservation and art historical study of an 18th century "Harlequinade" entitled The Fairy King: accompanied by scientific research on the detection of Ethomeen residues in paper using Py-GC-MS, following the application of solvent gel to remove degraded pressure sensitive tape. Dissertation at the University of Northumbria 2008
Ford/Byrne (1991)	Ford, Bruce; Byrne, Allan: The lipid stripping potential of resin soap gels used for cleaning oil paintings. In: <i>AICCM Bulletin</i> 17 (1991), pp. 51–60
Fronek (1987)	Fronek, Joe: LACMA experiments with Cleaning Systems. In: WAAC Newsletter 9, no. 1 (1987), pp. 9–10
Gaskell (2000)	Gaskell, Claire: The conservation of a scrap screen from Carlyle's House, London. In: <i>The Paper Conservator</i> 24 (2000), pp. 1–11
Hartwell (1986)	Hartwell, Dare: Cleaning Natural Resin Varnishes. In: <i>WAAC</i> Newsletter 8, no. 2 (1986), pp. 4–6
Hiler (1934)	Hiler, Hilaire: Notes on the Techniques of Painting, London 1934
James et al. (1997)	James, Carlo; Corrigan, Caroline; Enshaian, Marie C.; Greca, Marie R.: Old Master Prints and Drawings. In: <i>A Guide to Preservation and Conservation</i> , translated and edited by Marjorie B. Cohn, Amsterdam 1997
Keck (1969)	Keck, Sheldon: Mechanical alteration of the paint film. In: Studies in Conservation 14 (1969), pp. 9–30

lu On Dia		When I have North and the state of the state
h: On Pic-	Khandekar (2004)	Khandekar, Narayan: Detection of Residues on the Surfaces
ashington		of Museum Objects Previously Cleaned with Aqueous Gels.
		In: Solvent Gels for the Cleaning of Works of Art – The Residue
ical study		Question, Valerie Dorge (Ed.), Los Angeles, California: The
ical study		Getty Conservation Institute (2004), pp. 116–130
airy King:	K 1/C (1002)	Karah Iranas Cara I. B. C. H. Latin I.
n of Etho-	Kosek/Green (1992)	Kosek, Joanna; Green, Lorna R.: Survey oil painting and
ng the ap-		sketching on paper in the collection of the British Museum
ure sensi-		- An assessment of stability. In: Manchester IPC. Conference
nbria 2008		papers, Institute of Paper Conservation (1992), pp. 96-102
tential of	L do (1904)	Londo E. A. Matanan Lithannahi
n: AICCM	Leeds (1894)	Leeds, F. A.: Notes on Lithographie varnish. In: Journal of the
I. AICCM		Society of Chemical Industry 13 (1894), p. 203 : as quoted by
		Mitchell (1937) p. 236
Systems.	Mills/White (1987)	Mills, John S.; White, Raymond: The Organic Chemistry of
, bystema:	Willis, Willie (1967)	Museum Objects, 1st Edition, London 1987
		Museum Cojects, 1 Edition, Edition 1967
from Car-	Mills/White (1994)	Mills, John S.; White, Raymond: The Organic Chemistry of
24 (2000),		Museum Objects, 2 nd Edition, Oxford 1994
	Mitchell (1937)	Mitchell, C. Ainsworth: Inks their Composition and Manu-
In: WAAC		facture: Including methods of examination and a full List of
		British Patents, 4th Edition, London 1937
z, London	Petukhova (1992)	Petukhova, Tatyana: Removal of Varnish from Paper Artifacts.
		In: The 1992 Book and Paper Group Annual, American Institute
		of Conservation of Historic and Artistic Works, Vol. II, Robert
C.; Greca,		Espinosa (Ed.), (1992), pp. 136-140
1 Guide to		
d by Mar-	Phenix (1998)	Phenix, Alan: The Science and Technology of the Cleaning of
		Pictures: Past, Present and Future. In: Proceedings of 25th anni-
		versary conference, School of Conservation, K. Borchersen (Ed.),
t film. In:		Copenhagen 1998, pp. 109-119

Riffault (1843) Riffault, Vergnaud: Nouveau Manuel complet du Peintre en

Bâtiments, du Fabricant de Colleures, du Doreur, du vernisseur, du vitrier et de l'argenteur, contenant tout ce qui a rapport à ces différents, etc. Nouv. éd. ent. refonde, et cons. aug.,

Paris 1843: as quoted by Hiler (1934)

Stulik et al. (2004) Stulik, Dusan; Miller, David: Resarch into Solvent Gel Resi-

due. In: Solvent Gels for the Cleaning of Works of Art – The Residue Question, Valerie Dorge (Ed.), Los Angeles, California:

The Getty Conservation Institute (2004), pp. 18-65

Tingry (1804) Tingry, Pierre Françoise: The Painter and Varnisher's Guide.

Dedicated to the Society at Geneva for the Encouragement of the Arts, Agriculture, and Commerce. Illustrated with En-

gravings 1804

The Young Artists' (1877) The Young Artists' Guide Containing Instructions for a Be-

ginner, London/Glasgow 1877

Totten (2003) Totten, Andrea M.: Laponite Residues on Paper and Parch-

ment. In: The Paper Conservator 27 (2003), pp. 23-34

Warda et al. (2007) Warda, J.; Brückle, Irene; Bezúr. A.; Kushel, D.: Analysis of

Agarose, Carbopol and Laponite Gel Poultices in Paper Conservation. In: Journal of the American Institute for Conservation

46, Issue 3 (2007), pp. 263-279

Wilder (1969) Wilder, Frank L.: How to Identify Old Prints, London 1969

Wolbers (1992) Wolbers, Richard: Recent Developments in the use of Gel For-

mulations for the Cleaning of Paintings. In: Preprints to the conference Restoration '92: conservation, training, materials and techniques, latest developments, V. Todd et al. (Eds.), Amsterdam,

October 20th-22th, IIC, London (1992), pp. 74-75

Research in Book and Paper Conservation in Europe – a State of the Art –

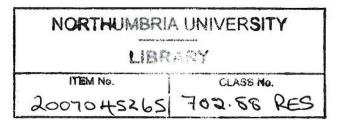
edited by Patricia Engel

B Verlag Berger Horn/Wien Gefördert

vom Bundesministerium für Wissenschaft und Forschung in Wien, dem Bundesministerium für Unterricht, Kunst und Kultur in Wien und durch den Verein Buchstadt Horn – das Buch im Zentrum.

Bibliographic information published by Die Deutsche Bibliothek Die Deutsche Bibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data is available on the Internet at http://dnb.ddb.de.

British Library and Library of Congress Cataloguing-in-Publication Data: A catalogue record for the book is available from The British Library, Great Britain, and from the Library of Congress, USA.



Impressum

© Verlag Berger, Horn/Wien

Alle Rechte vorbehalten – Printed in Austria

Bildrechte den Autoren vorbehalten

Umschlag/Layout: Ingolf Schwan

Gesamtherstellung: Druckerei Berger, Wiener Straße 80, A-3580 Horn

ISBN: 978-3-85028-490-5

To th

The pr servati The tion ac tions, a and ar and co Whi protec Europ tention Yet, owns reflect of their as cas births these richer standi Apa sure c Hoy are in perfo: equal

contra

good

pages

canno

other

tectin

Stil