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Investigating solvents and treatment methods on a matte pigment inkjet print

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Abstract

This study investigates the influence of various solvents and application methods on an aqueous pigment ink matte microporous Hahnemühle PhotoRag inkjet print, aiming to ascertain the susceptibility towards solvent treatment of inkjet prints meant for the fine art market. Thirteen solvents commonly employed by conservators are subjected to assessment through three distinct application methods: drop application, damp cotton swab application with various amounts of friction applied, and a subset underwent exposure in vapour chambers. These tests are complemented by comprehensive photo documentation (normal, raking, and UV-radiation), spectrophotometer measurements, and HIROX microscopy to determine changes to the objects. Alongside these experiments liquid chromatography-mass spectrometry, paper-spray mass spectrometry, and Fourier-transform infrared spectroscopy were employed for identifying ink components and to assess the solvent's dissolving capabilities. The outcomes emphasise that the method of solvent introduction significantly influences the impact on these types of photographic media. Application with friction, especially in combination with water-containing solutions, results in displacement of the colourants. Therefore, the choice of solvent still has an impact as certain solvents induce alterations in either ink and, or the additives in the paper support than other solvents.

Keywords: inkjet photography; aqueous pigment ink; matte microporous coating; solvent treatment; chemical composition.

Introduction

The introduction of digital inkjet technology for the fine art market dates back to 1991 (Wilhelm, 2000), which in its early stage were predominantly aqueous inks utilising dyes and a paper support. Since then, the industry has witnessed remarkable expansion, both in terms of the variety of materials available and the number of companies offering them. The combinations of ink and media, however, influence not only the aesthetics but also the long-term stability of the resulting photographic object. Fortunately, with this realisation emerged an understanding of the susceptibility of inkjet prints to factors like light, humidity, temperature, and air pollutants, leading to the establishment of preservation guidelines (Fischer, 2007). However, the treatment of fine art inkjet prints remains underexplored. This can be attributed to several factors; firstly, the relative novelty of inkjet printing as a photographic process, leading to limited treatment research; and secondly, the rapid evolution of formulations and the multitude of companies supplying materials for inkjet printing, making comprehensive research a complex undertaking.

Notwithstanding these challenges, a few articles have shed light on the impact of solvents on inkjet prints such as Gadomski (2009) and Ploye (2011). Both studies were published over a decade ago and considering the likelihood of changes in ink formulation and substrate composition, the behaviour of inkjet prints towards solvents might differ now. Therefore, this research aims to address this

knowledge gap and provide further insight in contemporary inkjet material by investigating and differentiating the effects of solvents and mechanical action when used for conservation treatment. The effectiveness of solvents, for example to remove dirt or adhesives, was not part of the scope of this research and hence not assessed.

Methodology

Material of the samples

The selection of the print material was based on a brief survey conducted among five fine art printing studios asking what their most common paper support used by photographers was at the time (December 2022). Therefore the research focused on one particular type of inkjet print: Hahnemühle PhotoRag paper where a target image made of colour gradient blocks cyan, magenta, yellow, and black was printed on. According to Hahnemühle, PhotoRag paper has a matte micro-porous image-receiving layer (IRL), consisting out of polymeric binder and inorganic pigments (Wexler and Reczek, 2012) on a substrate made of pure cotton and is acid- and lignin-free (Hahnemühle website, 2024).

The printing was carried out using the Epson SureColor P20000 printer, a piezo inkjet printer employing aqueous pigment ink. This printer model is compatible with both Epson Ultrachrome Pro ink and Epson Ultrachrome K3 ink, and for this research a combination of these ink series was collected based on availability for analysing. Liquid ink samples were retrieved directly from those cartridges that were donated by two local printmaking studio's. The composition information of the specific cartridges from the Safety Data Sheet (SDS) is given in Table 1.

Epson Ultrachrome Pro T8002 Cyan Ink	**Epson Ultrachrome Pro T8005 Light Cyan Ink**
65%~80% water 10%~12.5% glycerol 1%~3% triethanolamine	65%~80% water 10%~12.5% glycerol 1%~3% triethanolamine
Epson Ultrachrome K3 T5914 Yellow Ink	
50%~65% water 12.5%~15% glycerol 0.5%~1% triethanolamine <0.05% 1,2-benzisothiazoline-3-one 3%~5% ethylene glycol	
Epson Ultrachrome K3 T5913 Vivid Magenta Ink	**Epson Ultrachrome Pro T8006 Vivid Light Magenta Ink**
50%~65% water 15%~20% glycerol 1%~3% triethanolamine <0.05% 1,2-benzisothiazoline-3-one 1%~3% triethylene glycol monobutyl ether	65%~80% water 10%~12.5% glycerol 1%~3% triethanolamine 0.1%~0.25% 2-pyrrolidone 0.0015%~0.05% 1,2-benzisothiazolin-3-one

Table 1 - Overview of the composition information obtained from their respective safety data sheets of the examined ink cartridges in the analytical research part. All SDS consulted on the website https://www.epson.eu/safety-data-sheets on 10-05-2023.

Testing and Analysis

Common solvents and solvent mixtures frequently employed by photograph conservators were selected: demineralised water (demi-water), 50:50 demi-water ethanol, 30:70 demi-water ethanol, ethanol (Merck, Absolute Ethanol for analysis), iso-propanol (2-propanol Biosolve Chimie SARL, LC-MS grade), acetone (VWR Chemicals, technical grade), ethyl acetate (Acro Organics, 99,5+% for HPLC), methyl ethyl ketone (2-butanone Sigma-Aldrich, ACS >99%), hexane (VWR Chemicals,

AR 99.3%), heptane (VWR Chemicals, AR 99.3%), iso-octane (Merck, AR grade), benzene (Sigma-Aldrich, for HPLC ≥99.9%) toluene (Acros Organics, 99%+), xylene (Fischer, AR grade), and Kodak Photo-Flo 200 (1:200 surfactant, propylene glycol and octylphenoxypolyethoxyethanol, in water). Applying the solvents to the inkjet prints was done via two distinct methods: directly as a drop onto the surface where the solvent could naturally evaporate, and with cotton swabs. While applying drops directly onto the surface of a photographic object is not a frequent practice due to its aggressive nature, it was chosen to distinguish between solvent interaction and mechanical action, aiding in a more comprehensive understanding of the results. In the cotton swab test, two different application techniques were employed: firstly, the damp cotton swab was gently dragged along the surface of the ink in a linear manner while rotating the swab; and secondly, the damp cotton swab was used in a three-times circular motion within a 1x1 cm square area similar to the method described by Morrison (2005).

Lastly, a subset of inkjet prints was exposed to vapours of the following solutions: demi-water, 30:70 demi-water ethanol, ethanol, iso-propanol, and ethyl acetate. These solvents were chosen due to their common use in practices such as flattening, mould disinfection, and adhesive removal. Each print was placed within a vapour chamber for a duration of two hours and afterwards left unrestricted while drying. The time duration of this vapour chamber experiment was based on research conducted in the field of mould treatment for photographic objects (Lucas, Déniel and Dantigny, 2017).

The impact of the solvents and their application on the ink and support was assessed via CIE Lab spectrophotometry using a Konica Minolta Spectrophotometer (CM-26000d, SCI M/I+E, UV 100%, 10°/D65). Photo documentation was performed using a Nikon digital camera D750 to capture images under normal and raking light, and UV-radiation. Moreover, HIROX microscopy was also employed to observe ink and, or surface alterations.

Adjacent to this research, analytical research was conducted to determine dissolving capabilities of the solvents and to identify ink components. Fourier transform infrared spectroscopy (FTIR), liquid chromatography coupled with a photodiode array and mass spectrometer (LC-PDA-MS), and paper-spray mass spectrometry (PS-MS) were used for this purpose. FTIR and LC-PDA-MS techniques were used to analyse liquid ink from the collected ink cartridges. Cut-outs were made from the inkjet print and functioned as physical samples for PS-MS to analyse the interaction between solvents, printed ink, and IRL. The specific methodology for the respective analytical techniques as well as more detailed descriptions and discussions about these experiments can be found in the thesis (Maillette de Buy Wenniger, 2023). Below a shortened version of the methodology is given.

Parameters

FTIR: Pike GladiATR coupled to a PerkinElmer Frontier FTIR was used and IR spectra collected with Perkin Elmer Spectrum software. After an air background, spectra were obtained with the parameters 4 cm^{-1} resolution, 4000-400 cm^{-1} scanning range, and one scan per sample using liquid ink samples from the cartridges.

UV-VIS: a Varian Cary 50 Bio UV-Visible Spectrophotometer with baseline correction was employed to obtain UV-Vis spectra. A quartz cuvette (4 mL, dimension 1x1 cm) was first used to measure a blank (Milli-Q water), and afterwards for the liquid ink samples scanning between 200-700 nm. The Yellow, Cyan, and Magenta were diluted 10x1000 and the Light Cyan and Light Magenta diluted to 10x200 with Milli-Q water.

LC-PDA-MS: a UPLC Waters Acquity H-class system equipped with a PDA detector (configured to scan between 200 and 800 nm) was coupled to a Thermo Scientific Q Exactive Focus Orbitrap mass

spectrometer (set in MS/MS mode). The LC system used a 150x2.1 mm Zorbax Eclipse Plus C18 column with 1.8 µm particles in combination with a mobile phase gradually going from mobile phase A (aqueous) to B (organic) in 60 minutes. The method was based on Astefanei *et al.* (paper submitted).

PS-MS: a Thermo Scientific LTQ Velos mass spectrometer with an Orbitrap coupled to a Velox360 Prosolia sample dispenser set to dispense 10 µL per run was used. Acquisition time set to 1 minute (6 sec. 0V, 48 sec. 4000V, 6 sec. 0V), scanning between 100-2000 m/z, normalized collision energy 34 eV, and capillary temperature set to 200°C.

Results and Discussion

Composition of the inkjet print

A comprehensive understanding of the ink's composition was achieved using a combination of LC-PDA-MS, FTIR, and PS-MS techniques. Using the liquid samples obtained from the cartridges with ATR-FTIR revealed the specific pigments employed in the ink formulation: Pigment Yellow 74 was identified in the T5914 (K3) Yellow ink, while either Pigment Red 122 or Pigment Violet 19, both quinacridone pigments, was found in the T5913 (K3) Vivid Magenta, and T8002 (Pro) Cyan contained a variant of the phthalocyanine pigment (Pigment Blue 15). Identification of the pigment for the light cyan and light magenta inks was not possible via FTIR, but the two FTIR spectra are almost identical to each other, suggesting that even though the pigments are different, their composition is identical. Fortunately, UV-Vis spectroscopy confirmed that the same pigment for T8006 (Pro) Vivid Light Magenta ink is used as T5913 (K3) Vivid Magenta ink, and for T8005 (Pro) Light Cyan ink the same pigment blue 15 as T8002 (Pro) Cyan ink is used. Moreover, through the UV-Vis spectra it is shown that the colour difference between a standard and its respective light ink (e.g. cyan and light cyan ink) results from pigment concentration, which for the light ink was calculated to be 5-6x more diluted (Fig. 1). Only the pigment utilised in the Yellow ink cartridge could be confirmed and identified through LC-PDA-MS, eluting at 39.7 and 58.2 minutes with an absorption peak around 413 nm (Fig. 2). The chosen LC method was not suitable for the magenta and cyan pigments as they are too hydrophobic for the selected mobile phase. Fortunately, the mentioned additives in SDS could be confirmed with LC-PDA-MS. The biocide, triethylene glycol monobutyl

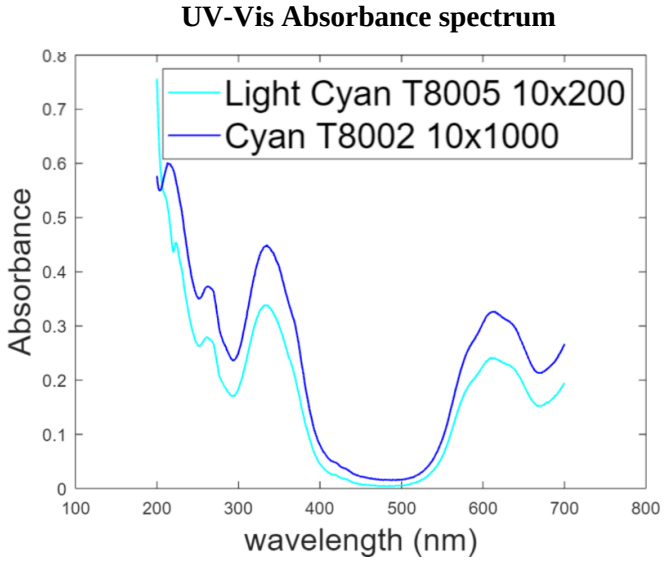

Fig. 1 - UV-Vis spectrum comparing Epson Ultrachrome Pro T8002 Cyan ink (10x1000 times diluted in Mili Q water) and T8005 Light Cyan ink (10x200 diluted in Mili Q water). The absorption spectra of the two inks are identical except below 250 nm where the water in the light cyan takes over. The similarity between the two spectra signifies the same pigment is added to the cyan and its respective light cyan ink.

ether eluting at 13 minutes, was identifiable via the PDA spectrum while the other additives could only be verified through the MS spectrum (Fig. 2).

Pigments are per definition insoluble in water and to employ pigments in aqueous inks the manufacturer exploits polymeric dispersants that, according to patents, will be film forming once printed (Miyabayashi *et al.*, 2001). The polymeric dispersant is stated to microencapsulate the pigments. However, in the material safety data sheets of the inks no molecule or polymer is listed that would function as a polymeric dispersant. The analysis conducted via LC-PDA-MS uncovered the presence of four distinct polymers eluting between 5 to 35 minutes within all the examined ink cartridges. Patents discussing micro-encapsulated pigments often refer to polymeric binders composed of styrene and acrylates in their examples (Sano *et al.*, 2001; Miyabayashi, 2007), which are monomers with a larger molecular mass than the identified 44 mass-to-charge (m/z) monomer (Fig. 2). Nevertheless, this 44 m/z monomer was present across all analysed ink cartridges, whether belonging to the Ultrachrome Pro or K3 ink series, in both LC-PDA-MS and PS-MS analyses, suggesting a different polymer being used as the dispersant. Moreover, PS-MS results indicated again a monomer of 44 m/z of the binder within the IRL of the Hahnemühle PhotoRag paper which in this case would likely be polyvinyl alcohol when referencing literature (Lee, 2004). More research is required to obtain a more in-depth identification of the polymers both found in the ink and IRL.

Dissolving capabilities of the solvents

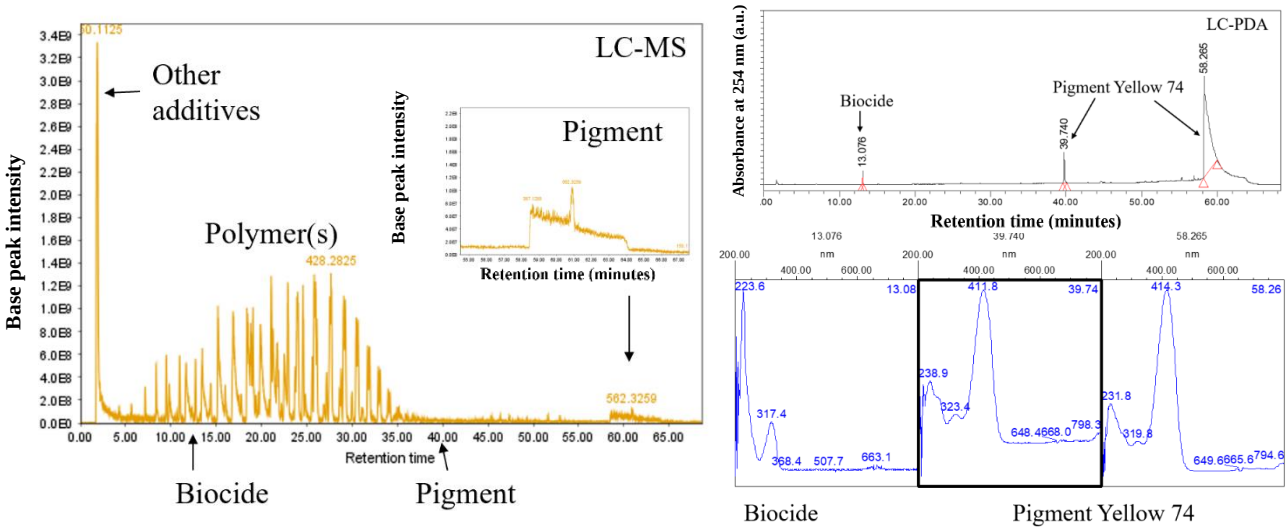

Fig. 2 – LC-MS (left) and LC-PDA (both on the right) spectra for Epson Ultrachrome K3 T5914 Yellow ink. The combination of both techniques resulted in confirmation of the additives, biocide, pigment, and polymers.

Even though full identification of all ink components was not achieved, the solvent sensitivities of individual liquid ink components could be deduced by the LC-PDA-MS elution time (Fig. 2). As expected, the additives, encompassing surfactants and biocides, exhibited a highly hydrophilic nature, while the pigments demonstrated very hydrophobic tendencies indicated by their retention time. The polymer's character was established through its elution gradient spanning in between the environmental change within the column from 80% aqueous (A) and 20% organic (B) mobile phase to 40% A and 60% B mobile phase. This suggests its potential for solubility in more hydrophilic solutions.

Incorporating the PS-MS technique further enriched our understanding of the behaviour of the inkjet towards solvents. The data generated from this experiment offered indications on the solvent´s ability to affect the printed ink, IRL, or both by dissolution. This information can be deduced from this analytical technique as a solvent is directly applied on to the physical print sample, the inkjet with ink and IRL cut to a sharp point (Fig. 3), that is facing directly the injector port. The sharp point of the paper sample and an applied voltag e cause the solvent to go towards the port and form stable ion droplets. If the solvent was able to dissolve a component of the sample it will be present in this ion droplet and can be detected. The summarized results, presented in Table 2, highlight instances where a stable ion droplet was formed due to the solubilisation of a component or when no signal was detected, meaning that nothing was dissolved. Not all solvents mentioned in the methodology could be used during this experiment due to the correct purity grade (MS grade) not being available. Interestingly, pure ethanol exhibited the ability to dissolve both the IRL and the ink binder. Furthermore, a visual observation emerged in relation to the yellow inkjet print samples exposed to toluene and 2-butanone, following two runs a definite disappearance of the yellow colourant was observed that was not reflected in the gathered spectrum.

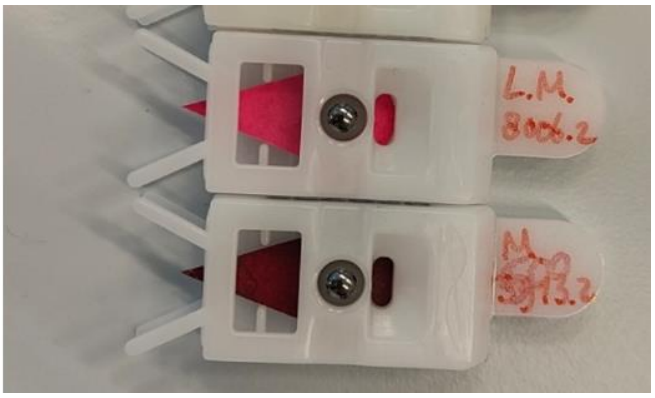

Fig 3 – Cut outs of Whatman filter paper to correct size and shape for PS-MS. The paper is loaded with ink from the cartridges, creating samples with only ink components present.

No Signal	**Signal**
Water	Ethanol (IRL and ink)
Water:ethanol solutions (50:50 and 30:70)	Iso-propanol (IRL)
Heptane	Ethyl acetate (IRL)
Toluene	2-butanone (IRL)

Table 2 - Summarised results of the paper spray mass spectrometry experiments.

Fig. 4 - Verso as seen under UV-radiation. Bright circular spots can be seen that can be contributed to the effects of 50:50 water ethanol solution affecting the OBAs in the paper support.

Solvent Introduction

Solvent drop test

The examination through photo documentation utilising UV-radiation accentuated the impact of solvents on the optical brightening agents (OBAs) within the paper. This impact was particularly prominent in the form of luminous circles observed from the verso (Fig. 4). These luminous circles were only observed in areas that came into contact with water-ethanol solutions. On the other hand, the influence of iso-propanol, acetone, 2-butanone, xylene, and ethyl acetate was irregular and presented itself as darker circles with the most pronounced effects observed on the yellow colour blocks.

Cotton swab test

Unlike the drop test with water-ethanol solutions, no prominent bright spots were observed under UV-radiation after application of the swab tests. However, distinctive darker areas were visible, particularly evident with the combination of 2-butanone, ethyl acetate, or toluene on yellow ink areas. When looking into detail via spectrophotometry at an applied solvent to a specific ink (magenta, yellow, and cyan), no pattern can be established that would indicate a distinct different behaviour of one solvent or one colour.

Comparing circular versus linear movement of the cotton swab demonstrated that a gentler motion makes a significant difference. Subjecting the print to increased friction (circular motion) tends to lead to abrasion where the pigments themselves are displaced rather than being dissolved (Fig. 5). Notably, water containing-solutions (water, water-ethanol mixtures, and Kodak Photo-Flo 200) and to a lesser degree ethanol caused displacement of the ink.

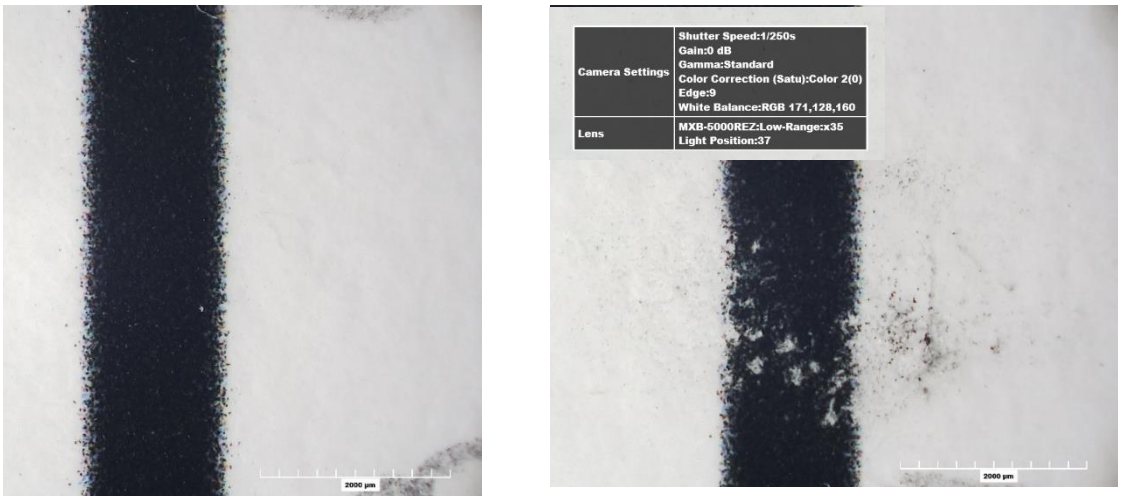

Fig. 5- Linear rotation (left image) and circular rotation (right image) using Kodak Photo-Flo 200 images demonstrating the effect of friction. Increased friction results in displacement of the pigment. Image made with HIROX microscopy, Bright field, 35x magnification lens.

Vapour chamber test

The results from the vapour chamber experiments reiterated that employing a more delicate application method when introducing solvents tends to preserve the colourants, OBAs, and planarity of the prints. No change to the surface texture and sheen, OBAs, ink, and overall colour was observed while examining these prints. Comparative spectrophotometer measurements between the application experiments mirrored the findings. According to the CIE Lab theory, deviations exceeding 2 ΔE units could be perceivable by an untrained observer (Mokrzycki and Tatol, 2011), however, in this study, calculated ΔE values surpassing 2 did not correspond to noticeable differences.

Conclusion

The experiments regarding solvent and application method indicated that for a matte micro-porous fine art inkjet print the introduction method of the solvent is the primary factor when considering treatment options. Applying friction will cause major alteration to the surface and the pigment ink, especially with Kodak Photo-Flo 200 and to a lesser degree other water-based solutions, causing ink displacement rather than dissolution. Using less friction such as linear rolling or using drops of solvent affects primarily the OBAs with most of the tested solvents, creating either luminous or dark circles which was only observable under UV-radiation. This occurrence, however, happened irregularly. The inkjet prints from the vapour chamber test showed no alterations. Thusly, reducing the amount of solvent and mechanical action seems to be the right course of action for treating fine art matte inkjet prints.

The experiments and the analytical research indicated that each component in an inkjet print (IRL binder, OBAs, colourant, polymeric ink binder, and additives) can be impacted by a solvent. However, the behaviour of each component in an inkjet print toward solvents is influenced by their function within the photographic object. For example, the ability of the IRL to carry water away from the surface indicates interaction with water and thus a certain sensitivity, which is reflected in the cotton swab results, but the pigments, chosen for their lightfastness, are very hydrophobic and so no significant interaction with water will occur. Therefore, as expected no universal solvent could be deduced from this research that would not influence any of the components. On the other hand, 2-butanone and toluene are suspected to have a more pronounced influence on the yellow ink then on cyan or magenta.

More research is required as this research could only investigate a small sample size and one type of inkjet print as well as limited solvent application methods. Furthermore, during this research the effectiveness of the solvents and cleaning method was not considered. Nevertheless, the comparison with previous research gives a more general indication of the behaviour of fine art inkjet prints towards solvents and treatment. A gentle approach towards treatment or the introduction of solvents will reduce the risk of damage significantly, but the choice of solvent does have an impact. For instance, from this research it has become evident when considering dirt or adhesive removal with a cotton swab using ethanol brings a considerable risk of dissolving the polymeric ink binder, IRL binder, or affecting the OBAs in the print.

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