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Disinfection of Photographic Materials with Ethanol Vapours: Preliminary Evaluation of the Effects on Chromogenic Prints

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The biodeterioration of photographic collections by mould is a recurring problem. In 2017, Lucas et al. demonstrated that exposing photographs to 70:30 (v/v) ethanol-water vapours for two hours kills five of the most common fungal species found in photographic collections. The goal of this project was to evaluate any side effects of this treatment on chromogenic prints. Sixty non-mouldy historic photographs, grouped by decade from the 1940s through to the 2000s, were exposed in small chambers to the ethanol-water vapour treatment. Treatment effects were evaluated by a combination of spectrophotometric measurements and visual observations of colour, surface sheen and planarity. The measurements indicated colour change on a majority of the treated samples. The magnitude of colour change varied with sample date of production. Samples from the 1980s and 2000s exhibited the highest percentage of significant alteration by treatment (89%), with significant colorimetric change and, in most cases, colour changes visible to the eye (67%). Samples from earlier decades were less affected by the treatment both in the percentage of affected samples and in the magnitude of the colour change.

La biodégradation des collections photographiques par les moisissures est un problème récurrent. En 2017, Lucas et al. ont démontré que l'exposition de photographies à des vapeurs d'éthanol-eau (70:30 v/v) pendant deux heures tue cinq des espèces fongiques les plus répandues dans les collections photographiques. Le but de ce projet était d'évaluer les éventuels effets secondaires de ce traitement sur les tirages à développement chromogène. Soixante photographies historiques non moisies, réparties par décennie des années 1940 aux années 2000, ont été exposées aux vapeurs d'éthanol-eau dans de petites chambres de solvants. Les effets du traitement ont été évalués au moyen de mesures spectrophotométriques et d'observations visuelles de la couleur, de la brillance de surface et de la planéité. Les mesures ont indiqué un changement de couleur sur la majorité des échantillons traités. L'ampleur du changement de couleur variait en fonction de la date de production de l'échantillon. Les échantillons des années 1980 et 2000 présentaient le pourcentage d'altération après traitement le plus élevé (89 %), avec un changement de couleur significatif et, dans la plupart des cas, des changements de couleur visibles à l'œil nu (67 %). Les échantillons des décennies précédentes ont été moins affectés par le traitement, tant en ce qui concerne le pourcentage d'échantillons affectés que l'ampleur du changement de couleur.

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INTRODUCTION

Biodeterioration of Photographic Materials

Several types of microorganisms can develop and grow on photographic materials. The most commonly found microorganisms are mould,[1] a common term used to designate several filamentous fungal species belonging to the Fungi kingdom. Mould-induced biodeterioration of photographic collections is a recurring problem that can result in partial or total loss of the photographic image. Damage can be caused by the secretion of metabolic products, such as pigments, or by the reaction of these products with the constitutive object materials, due to enzymatic hydrolysis or oxidation.[2,3] Most photographs serve as a substrate for mould growth because they are composed of hygroscopic proteins and polysaccharides, such as gelatin, albumen and cellulose. Mould-induced damage can be minimized with strict control of the storage environment;[2] however, mould remediation treatments are still often necessary for objects or collections where storage conditions are less controlled or where disasters have resulted in exposure to water or high humidity.

Mould Remediation for Photographic Materials

The first remediation step is to deactivate the mould by drying the affected photographs. Most hydrated hyphae will die when dried, while spores, the reproductive cell of some types of fungi, have the potential to remain viable. Spores can become dormant when external conditions are unfavourable for growth, meaning their metabolic activity is at its lowest in order to avoid germinating.[2]

Dry cleaning permits removal of loose mould structures, such as hyphae, hyphal fragments or spores, from the surface of the photograph. It is, however, a partial solution as mould structures (viable or non-viable) may remain embedded within the porous materials. As a result, mechanical removal will only reduce the amount of mould present on the object. Embedded mould spores may remain viable and can activate, germinate and develop once the external conditions are favourable.[2] Furthermore, previously mould-damaged objects are more prone to fungal growth and will be contaminated more easily than undamaged objects.[4]

Disinfection provides an additional level of protection to the object by rendering the mould spores non-viable (fungicidal effect), as opposed to being deactivated but still viable (fungistatic effect). In the context of heritage collections, killing all living spores with a sterilization treatment is not the goal as collections are not stored in a sterile environment. Disinfection aims at lowering the amount of viable fungal spores on a photograph to a level similar to the ones present in clean collection space.

The use of alcohol as a biocide is widespread in the health and food sectors. Research has shown that ethanol used alone has no antifungal action and that it is necessary to use it mixed with water to allow its penetration into the fungal cell.[4,5] Depending on the ethanol-water ratio, the ethanol treatment can result in a fungistatic or a fungicidal effect. Though other ratios are possible, 70:30 (v/v) ethanol-water mixture has been demonstrated to have a strong fungicidal effect;[4] it is often recommended by studies on written heritage collections.[4,6-8] Our previous research has demonstrated that exposing mould-affected silver gelatin prints to vapours from a 70:30 (v/v) solution of absolute ethanol and demineralised water for two hours kills five mould species from four different genera commonly associated with photographic materials.[9,10] Although this method has been shown to successfully disinfect mould on photographs, its short- and long-term effects on their constituent materials is less well understood.

Effects of Ethanol-Water Solutions on Photographic Materials

Previous studies have described the effects of ethanol on paper and photographs, including their primary support, binder and image-forming materials.

Primary supports

Paper supports do not seem to be adversely affected by treatment with an alcohol-water solution. Sequeira et al. and Weiß showed that immersion of paper samples in 70% ethanol does not modify colour or mechanical properties of the tested paper.[4,11] Similar results were obtained by Lucas et al. for paper samples treated with absolute ethanol-demineralised water (70:30 v/v) vapours for two hours.[10] Tomsŏvá and Ďurovič showed that exposure of baryta paper without an emulsion to 96% butanol vapours does not induce colour changes.[12] Cellulose acetate supports, however, may be damaged. Thyss reported that the immersion of Ektachrome films in an ethanol-water (70:30 v/v) solution created strong and irreversible planar distortions.[13]

Binders

Gelatin binders are potentially more sensitive to treatment with an alcohol-water solution. Tomsŏvá et al. evaluated the effects of 96% butanol vapours on gelatin. This treatment caused some modifications in the gelatin structure in that the amino acid chains were shortened and the degree of polymerization decreased, resulting in a lower gelatin viscosity.[14] Several authors have noted a change in surface appearance or gloss after application with a cotton swab of alcohols (ethanol or isopropanol), pure or mixed with water.[13,15,16]

Image materials

Image materials pose the area of greatest potential concern. Martin documented modification of the silver image density, reddish coloration and yellowing on developing-out silver gelatin prints after exposure to ethanol-water vapours (50:50 and 95:5 v/v) for 21 days at 45°C. The damage was interpreted as being caused by redox reactions and further catalyzed by heat and a higher ratio of water in the solution.[17] Tomsŏvá and Ďurovič exposed developing-out silver gelatin prints to 96% butanol vapours for two days, at 26°C. The samples showed no colour change after treatment; however, treated samples were more faded and yellowed after aging than untreated samples.[12]

Quintric showed that the immersion of contemporary chromogenic prints on resin-coated paper in an ethanol-water (50:50 v/v) solution caused partial dissolution of the dyes, inducing a colour change observed on the samples; the extent of the damage depended on the amount of solution (drop or immersion) and the contact time.[16] Similar results were reported by Thyss for the immersion of Ektachrome films in an ethanol-water (70:30 v/v) solution; however, the same solution applied with a cotton swab did not induce any colour change.[13] The Eastman Kodak Company described several types of damage to their chromogenic print dyes caused by the use of materials containing butyl or isopropyl alcohols for post-processing treatments, such as lacquering. They also indicated that the effects varied widely depending on type of treatment and its implementation.[18]

Although these previous studies indicate that the treatment tested in this investigation – two-hour exposure to 70:30 (v/v) ethanol-water vapour at room temperature – is unlikely to damage the primary paper support, changes to silver- and dye-based photographic images are possible. Previous research has also shown that the solvent application method (cotton swab, immersion, vapour) and contact time influence the effect of the treatment on image materials.[13,16,17]

Scope of the Project

The purpose of this project was to build on earlier research on the use of ethanol vapours on photographs and paper [9,10] and evaluate the effects of the treatment on photographic materials common in collections. Testing was limited to chromogenic prints.[19] This colour printing technique was selected for two reasons:

1. It was widely used in commercial printing for the general public and by artists during the 20th century. As a result, chromogenic prints are very common in archival and fine art photographic collections.
2. The dyes composing the image are very sensitive to solvents. Indeed, the effects of aqueous solutions of alcohols on chromogenic photographic materials varies and seems to depend on the water ratio, contact time, application method and the emulsion itself.[13,16] As a result, chromogenic prints are among the photographic printing processes most likely to be damaged by ethanol vapour treatment.

As changes to the image forming materials were of greatest concern, the changes caused by treatment were quantified using colour measurement on the emulsion as well as visual comparison.

METHODS

Sample Selection and Preparation

The effect of solvent treatment on chromogenic dyes depends on the brand, the production year and the solvent application method.[13,16] Thus, historical print samples were selected for this project from six different decades: the 1940s, 1950s, 1960s, 1970s, 1980s and 2000s.[20]

As historical prints are all different, ten samples were obtained to represent each decade (**Figure 1**).[21] The earlier samples from the 1940s and 1950s were purchased on eBay. Samples from the 1960s, 1970s, 1980s and 2000s were selected from a didactic collection maintained by Greg Hill at the Canadian Conservation Institute. Prints were dated using either information on the print (backprint, stamp, inscriptions) or knowledge of the subject represented (for samples from the 1980s and 2000s). The samples were selected to be as representative as possible of the diversity of materials available for each decade, varying the brand, type of print (printed from a negative or a transparency), type of support and provenance of the samples. Information about the prints is contained in **Appendix I**.

Each print was cut into two pieces, to create an untreated control sample and a treated sample. The control sample was stored and kept in the dark in an archival folder.

Disinfection Treatment

The concentration of ethanol-water vapour in the headspace of the vapour chamber depends on the size of the chamber, the quantity of porous materials inside and how they are arranged. To standardize the conditions of exposure, sample treatment took place in ten identical vapour chambers, with one sample per chamber. Each chamber assembly was composed of a polypropylene container with a silicone gasket-sealed lid (15 x 15 x 7 cm; 1,575 cm^3 volume) into which the ethanol-water solution was poured. An upside-down polystyrene weighing dish (6.5 cm diameter) was used as a support for a 10 x 10 cm polystyrene grid, with a layer of non-woven polyester placed on top (**Figure 2**).

The 70:30 (v/v) ethanol-water stock solution was prepared using absolute ethanol and reverse osmosis water.[22] A volume of 54 mL of solution was calculated as required in each chamber to provide the same solution to chamber volume ratio as used previously (350 mL for a 10,200 cm^3 chamber).[9] To ensure an excess concentration of the ethanol-water solution, 60 mL of solution was pipetted from the stock solution into each chamber. The ethanol-water solution was replaced for each sample, in order to minimize the variation induced by the different evaporation rates of ethanol and water in the chamber while samples were being switched. Personal protective equipment was worn to prepare and manipulate the solutions as absolute ethanol can cause irritation of the skin, eyes and airway.[23]

Each treated sample was processed as follows:

1. The 70:30 (v/v) ethanol-water solution was poured into the chamber.
2. The sample was placed in the chamber, emulsion facing up, above the solution.
3. The chamber was closed and sealed for two hours.
4. The sample was removed from the chamber and dried in a blotter stack for one week.

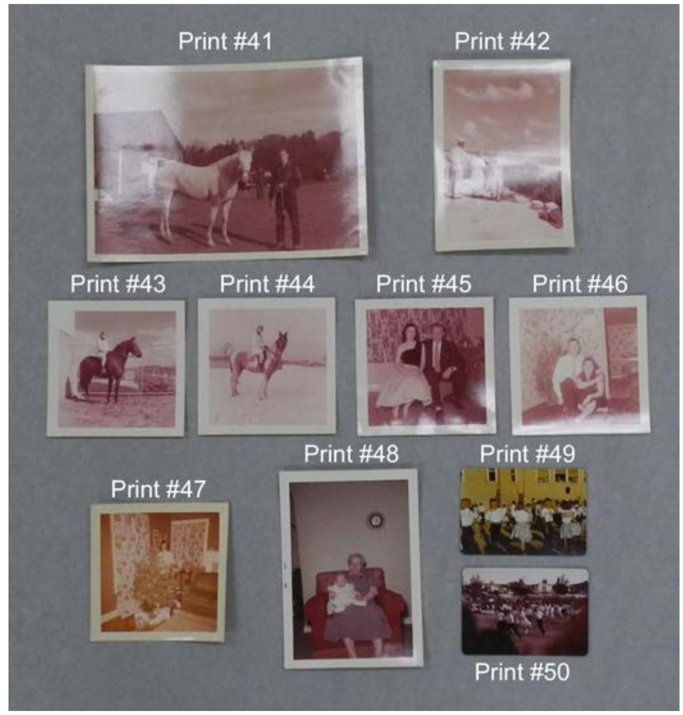

Figure 1. Example of ten samples for the 1950s. #41 to #48 are fiber-based prints printed from colour negatives, mostly from Kodak (#41 to #47). #49 and #50 are Kodachrome prints on pigmented acetate.

Drying

The water in the solution increases the relative humidity in the vapour chamber,[24] which acts to humidify the sample. Depending on its constituent materials and specific sensitivity, the print sample will be more or less relaxed after two hours in the vapour chamber. If left out to air dry, the samples typically show planar distortions after treatment; thus, it was decided to dry the samples in a weighted blotter stack to limit planar distortions.

Samples were placed in the drying stack, emulsion down, between two non-woven polyester sheets, then placed between two blotters, under a poly(methyl methacrylate) (PMMA) sheet and 14.5 kg of weight (**Figure 3**) for one week, then stored with untreated samples.

Visual Examination

Each treated sample was visually assessed to determine if the treatment caused changes to the colour, surface sheen and planarity relative to control samples and to before-treatment observations (**Appendix II**). Visual examination of samples was carried out with a white folder stock background in CCI's paper conservation lab under ambient room lighting (indirect natural light supplemented with daylight fluorescent lamp). Control and treated samples were placed directly adjacent for comparison.

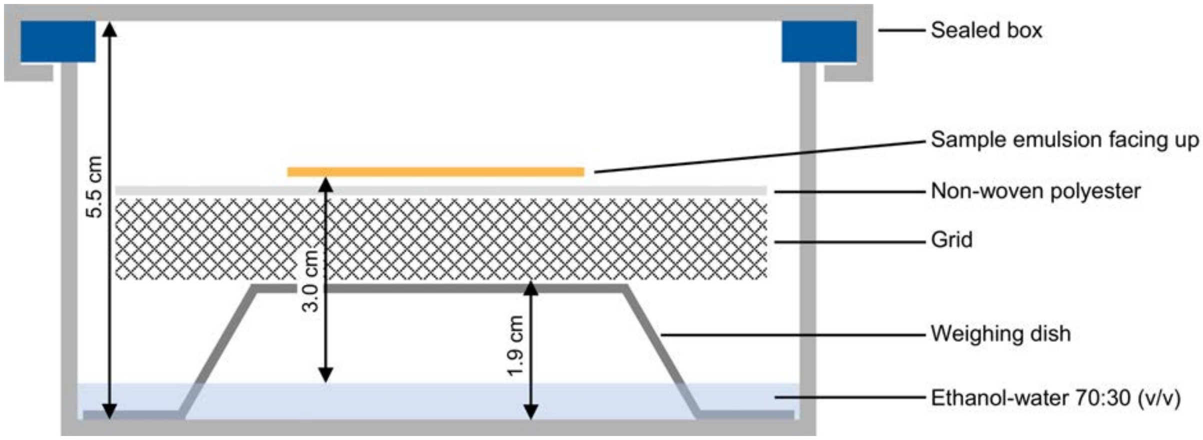

Figure 2. Vapour chamber configuration.

Colour Measurement

The print colour was measured before and after treatment to determine if exposure to vapours of the ethanol-water solution had altered the dyes forming the image. Reflectance colour was measured with a Konica Minolta CM700d spectrophotometer with diffuse illumination, 8° viewing geometry (d/8), specular component excluded, and a 3 mm diameter circular measurement area. The device was calibrated prior to measurement with a white ceramic tile standard (CM-A177/01498/70011840) and a Zero Calibration Box (CM-A32).

Polyester sheet templates were made for each print sample to allow reproducible positioning of the spectrophotometer's targeting mask (**Figure 4**). Two circles were drawn around each target: the larger circle was used to place the targeting mask while the smaller circle was cut out slightly larger than the instrument's 3 mm diameter specimen measuring port, to allow direct measurement on the print surface, unimpeded by the reflective surface of the polyester. A beige 4-ply matboard was used as a standard backing in case prints were not entirely opaque. A polyester-encapsulated metal plate was used as a support to hold the samples, templates and standard backing in place with magnets.

For each print, measurements were carried out on target pairs: one on the control sample and the other on the treated sample, chosen in visually similar and uniform colours. When possible, additional targets were selected; up to ten per sample, varying colour and density. Each location was given a unique identifying number (**Figure 5**).

Each target on both treated and control samples was measured three times, lifting up and replacing the spectrophotometer, which was held in the same orientation relative to the metal plate, between each measurement. The template was not repositioned between measurements but checked for accurate positioning. Both treated and control samples were placed under the template for measurements.

The measurements were taken by one person to minimize operator error, with a second person operating the computer for direct spectrophotometer-to-computer downloading of data. Before-treatment measurements were taken one week before treatment, and after-treatment measurements were taken shortly after drying.[25]

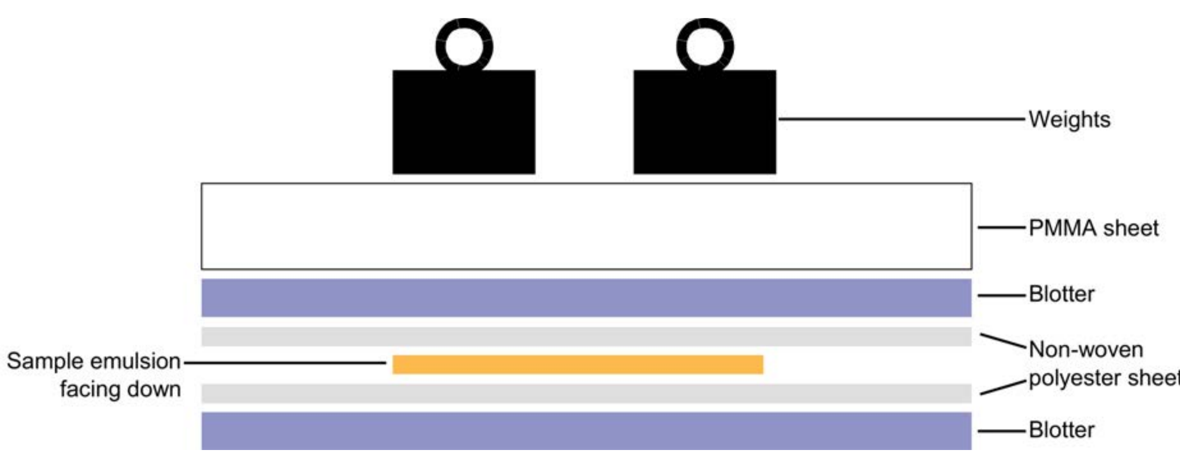

Figure 3. Drying stack configuration.

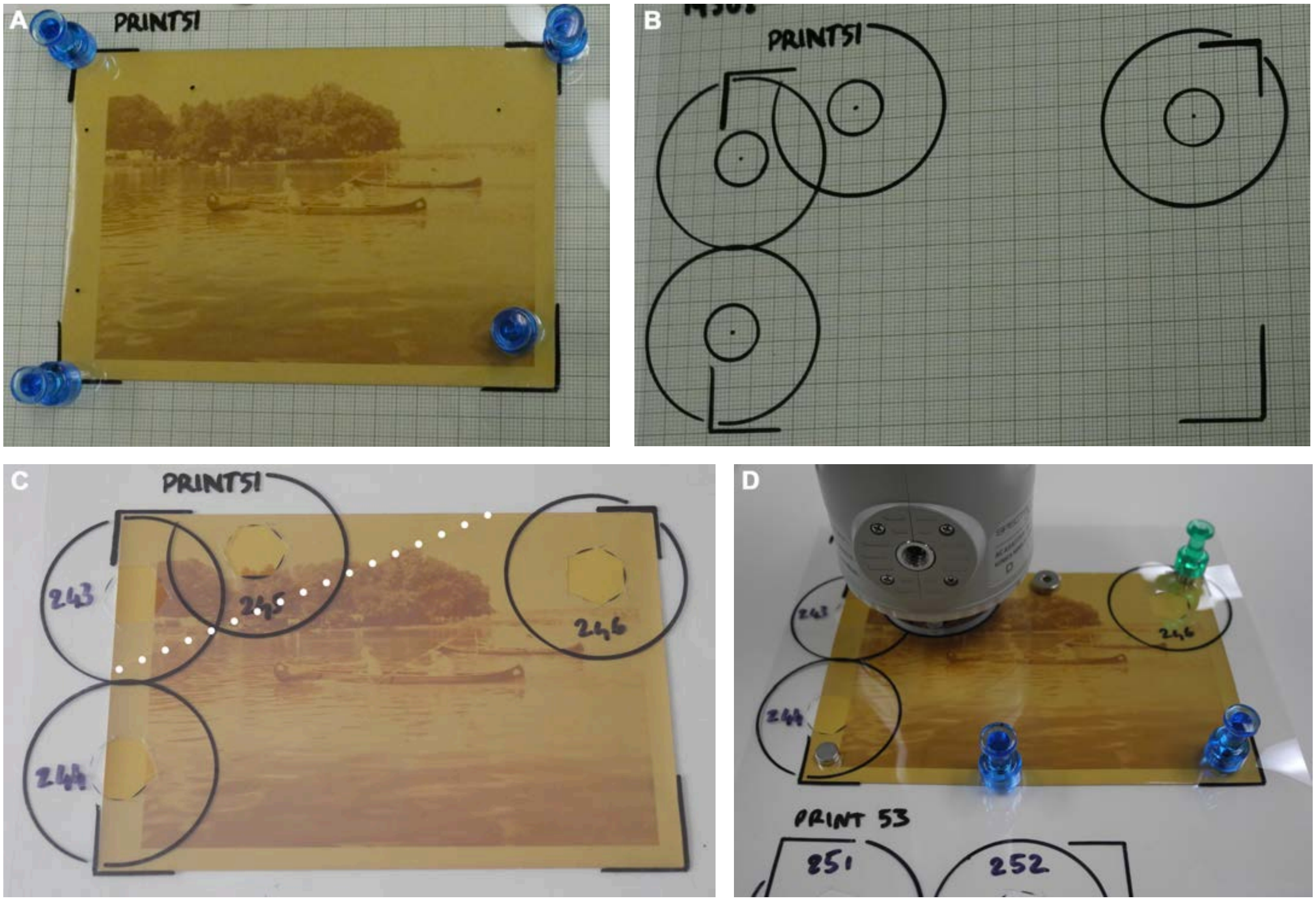

Figure 4. Colour measurement template used for Print #51. A) The four corners and targets were marked on the template. Graph paper was used to help with positioning of the prints under the template. B) Two circles were drawn around each target. C) The inside of the smaller circle was cut out to produce a hole in the template. The dotted line designates the cut line between the control sample (targets #243 and #245) and treated sample (targets #244 and #246). D) The larger circle was used to place the targeting mask.

Colour measurements were downloaded from the spectrophotometer to Konica Minolta SpectraMagic NX software. Data, in the form of CIE (1976) L*a*b* values, were transferred to a customized Microsoft Excel spreadsheet where data processing was carried out using standard colorimetric formulas. The average and standard deviation of L*, a* and b* values were calculated from the set of three measurements taken for each target.[26] The average L*, a* and b* values before and after treatment were used to calculate ΔE* (CIE 1976) for each target.[27] The ΔE* values indicate the degree of colour difference before and after treatment of targets on treated samples. The same calculations were made for control targets to distinguish treatment effects from variations due to the measurement technique.

Reproducibility of measurements

The reproducibility of colour measurements depends on instrumental and operator error. Thresholds for acceptable repeatability were defined relative to a measure of instrument repeatability as defined by the manufacturer.[28] To define the measurement error, the standard deviation (SD) of the L*, a* and b* values was determined for each set of three target measurements. When $SD > 0.1$ for at least one of the values, template alignment was verified and targets remeasured, up to four times, to obtain a set of three target measurements with a lower standard deviation. When $0.1 \leq SD < 0.2$ for all four replicates, the set that gave the lowest standard deviation was used in calculations. When $SD \geq 0.2$ for all four replicates, the target data was excluded due to its low reliability.

The effect of operator error – from the placement of the sample under the template and the placement of the device to take the measurement – on the reproducibility of colour change values was evaluated by measuring targets #13 to #17 on Print #4 a second time before treatment. For each target, the ΔE* between the first and second set of measurements was calculated. The results fell within the range $0.15 \leq \Delta E^* \leq 0.3$; therefore values of $\Delta E^* \leq 0.3$ are not considered significant.

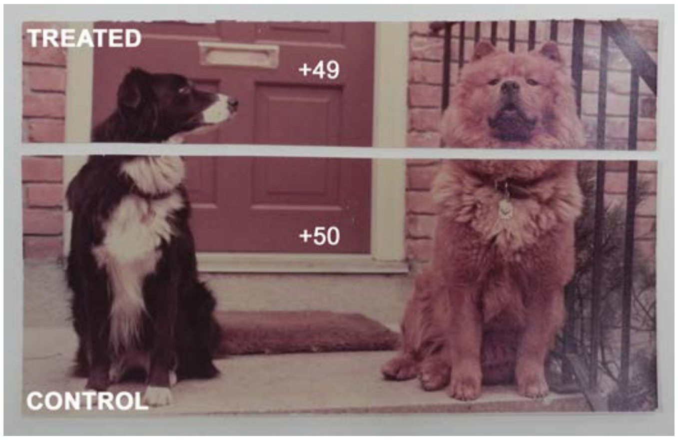

Figure 5. Example of target locations on Print #11. The centre of each 3 mm diameter circular target is indicated by a "+" next to the corresponding unique identifying number.

Figure 6. An example of colour difference between the treated and control samples (separated by a dotted line) that was visible to the eye (Print #13). The treated sample showed a greener hue (-Δa*).

Threshold for significant colour change

The perception of a specific colour depends on several factors: the object, the light source, the observer and the surrounding colours.[29] The compounding of factors that influence colour perception makes determining a ΔE* threshold for significant colour change complicated. Furthermore, a change in colour, as indicated by ΔE*, will not be perceived the same way depending on its location in the CIE (1976) L*a*b* colour space. For example, the human eye is more sensitive to a change in chromaticity (Δa* or Δb*) than in lightness (ΔL*).[30]

For the purpose of this research, we use ΔE* = 1.0 as the threshold for significant colour change. This corresponds to the minimum level at which colour change is noticed by an experienced observer, based on the ΔE*1976 categories for perceptible colour change described by Mokrzycki and Tatol.[29] By the same categories, colour change is perceptible to in-experienced viewers only when ΔE* > 2. These thresholds were adopted for the purpose of classifying colour change results for treated targets into three perceptibility categories: ΔE* < 1.0 (not perceptible), 1.0 ≤ ΔE* < 2.0 (just noticeable) and ΔE* ≥ 2.0 (perceptible).

RESULTS AND DISCUSSION

Visual Examination

Sample by sample results from the visual examination before and after treatment are presented in **Appendix II**, recorded as change in colour visible to the eye, in surface sheen and in planar distortion.

Changes in colour visible to the eye

Colour change was visible to the eye on 10% of the 1960s samples (1 of 10), 55% of the 1980s samples (5 of 9) and 78% of the 2000s samples (7 of 9) (**Figure 6**). No colour change was observed on samples from the 1970s, 1950s or 1940s.

Comparing visual observations with instrumental data revealed no consistent relationship. All but one of the visibly different samples showed at least one treated target with ΔE* ≥ 2.0 (perceptible); the remaining sample (Print #8) had one of two treated targets with 1.0 ≤ ΔE* < 2.0 (just noticeable). However, similar ΔE* values were calculated for other samples where colour changes were not distinguishable to the eye. Various combinations of factors can explain this observation. Overall colour change might not be perceptible if:

- Only some, not all, of the targets on an individual sample had ΔE* ≥ 2.0.
- High specular gloss interfered with visual comparison (Prints #49 and #50).
- The samples already exhibited an overall shift in colour. For instance, colour change was difficult to observe in samples from the 1940s that had an overall shift toward yellow.
- The colour change was comprised of change in several axis directions (ΔL*, Δa*, Δb*), rather than a larger change in one specific direction.[29]

Figure 7. Surface sheen difference between treated and control samples (Print #38).

- The colour change was located in very saturated colours where change is less perceptible.[30]
- The colour change was located in black or dark coloured areas, where change is less perceptible because it does not impact the overall white balance of the image.[31]

Changes in surface sheen

A slight change in surface sheen was observed only on samples from the 1960s. All affected samples (4 of 10 from that decade) were Kodak Ektacolor, printed between 1961 and 1971. These samples had a "semi-reflective toward glossy" surface before treatment, which was slightly less glossy after treatment (**Figure 7**).

Changes in planar distortion

A change in planarity was observed on 44% of samples (26 of 58). Two types of planar distortions were observed: curling (24 samples) and cockling (2 samples). Curling occurred on samples from the 1940s to the 1980s (**Figure 8**). It was more common on fibre-based prints (16 samples) than on resin-coated prints (8 samples). Of those prints that exhibited change in planarity after treatment, only the four 1940s samples did not have any planar distortion before treatment.

Cockling only occurred on prints on pigmented acetate (Prints #49 and #50). These two samples showed significant distortions immediately after vapour treatment, which were reduced after drying the samples in the blotter stack (**Figure 9**).

Figure 8. Difference in planarity (strong curling) between treated and control samples (Print #55).

Colour Measurement

ΔL*, Δa*, Δb* and ΔE* values[27] for each target are listed in **Appendix III**. One treated target measurement was excluded from analysis because of a high standard deviation (SD ≥ 0.2) on all four sets of measurements (#255, Print #53, 1940s).

Results per decade

The distribution of treated targets within each perceptibility category for each decade is summarized in **Table I** and plotted in **Figure 10**. The details of category distribution for each sample can be found in **Appendix IV.**

The samples showing the most significant change in colour are the more recent ones. Indeed, the samples from the 1970s, 1980s and 2000s show a ΔE* ≥ 1.0 for 56% or more of the treated targets (combined percentage for 1.0 ≤ ΔE* < 2.0 and ΔE* ≥ 2.0), which corresponds to 7 of 10, 8 of 9 and 8 of 9 samples respectively. This proportion progressively decreases for earlier decades, down to 18–20% of targets for the 1940s and 1950s samples, many of which already exhibited colour shift before treatment.

The amount of colour change for samples from the 1980s and 2000s is significantly higher than for earlier prints. The largest proportion of treated targets from the 1980s and 2000s samples showed perceptible colour change with ΔE* ≥ 2.0, whereas those from the 1960s and 1970s have a larger proportion of areas with 1.0 ≤ ΔE* < 2.0. This ratio evens out for the 1940s and 1950s, where the percentage of areas showing 1.0 ≤ ΔE* < 2.0 is similar to the percentage of areas with ΔE* ≥ 2.0. It is interesting to note, however, that the distribution of treated targets with a perceptible change in colour is not the same for the 1940s and 1950s. Although the overall percentage is the same, the targets are distributed over 4 of 10 samples for the 1940s but only 2 of 10 samples for the 1950s (**Appendix IV**).

No trend in colour change (ΔL*, Δa*, Δb*) based on target colour was identified. As well, no association could be made between the colour changes observed on samples and

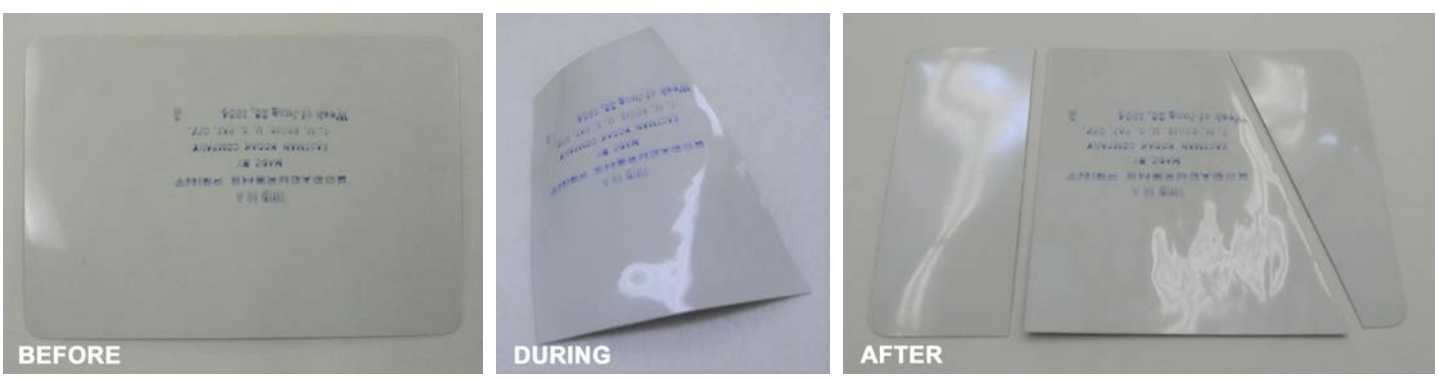

Figure 9. Print #49 before, during (after vapour treatment) and after treatment (after drying). The distortions are highlighted by the specular reflection of light on the print.

Table I. Distribution of treated targets within each perceptibility category, per decade.

		ΔE* < 1.0		1.0 ≤ ΔE* < 2.0		ΔE* ≥ 2.0	
Decade	**Total number of targets**	**Number of targets**	**%**	**Number of targets**	**%**	**Number of targets**	**%**
1940s	25[§]	20	80%	3	12%	2	8%
1950s	28	23	82%	3	11%	2	7%
1960s	25	14	56%	8	32%	3	12%
1970s	25	11	44%	14	56%	0	0%
1980s	16	6	38%	0	0%	10	62%
2000s	22	4	18%	8	36%	10	45%

[§]One of the original 26 targets (#255, Print #53) was excluded due to a high standard deviation.

their brand, paper type or date, with the exception of the two Kodachrome samples on pigmented acetate (Prints #49 and #50). It is important to note that they were the only two samples printed from a transparency, rather than a negative. As a result, their internal structure is different: for Kodachrome prints the order of coloured layers is yellow, magenta, cyan (from outer to inner layer), compared to cyan, magenta, yellow for chromogenic photographs printed from a negative after the mid-1950s.[32,33]

Anomalous results on control targets

Some of the control targets (10 of 142) showed anomalous results with ΔE* > 1.0. This was unexpected given that controls should not exhibit any change beyond instrumental/operator error. The following observations can be made:

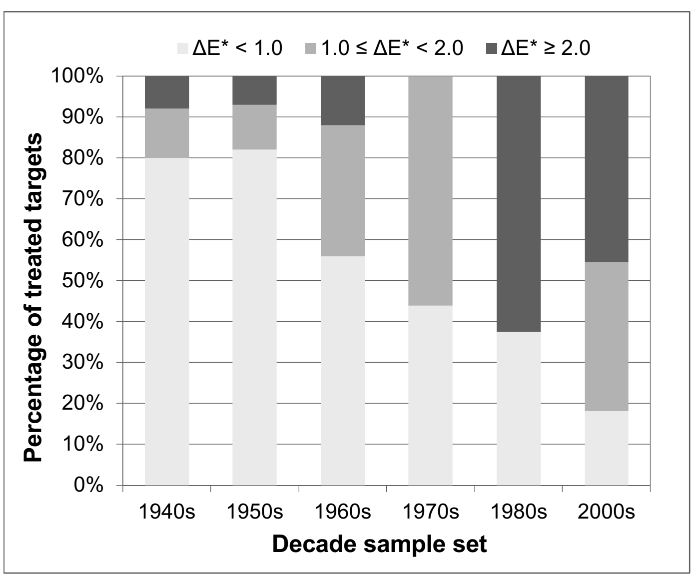

Figure 10. Distribution of treated targets within each perceptibility category, per decade.

- The majority of affected targets were located on samples from the 1980s (2 of 9 prints) and 2000s (3 of 9 prints). Only one target came from an older print, from the 1950s (1 of 10 prints).
- The gloss of affected samples ranged from semi-reflective to glossy.
- More than half of affected targets (6 of 10) were black or dark colours.
- More than half of affected targets (6 of 10) showed an increase in lightness (+ΔL*).
- All affected samples showed a similar or larger colour change in the control than their paired treated targets. Thus, the change observed in the treated targets may not be due to the treatment.

CONCLUSION

The use of ethanol-water vapours to treat mould-deteriorated photographic prints has been previously proven to be effective on five mould species most commonly found in collections.[9,10] It is important to verify that new treatment options do not damage the collections prior to using them. A treatment consisting of exposure to saturated vapours of 70:30 (v/v) absolute ethanol and reverse osmosis water for two hours was previously shown not to damage paper. This investigation tested whether the dyes forming the image would be damaged by evaluating the effects of the ethanol-water vapour treatment on historic chromogenic print samples from six different decades, the 1940s to the 2000s.

Colour measurements were taken on the emulsion before and after treatment to determine if the treatment induced colour changes to the dyes. Visual comparisons of control and treated samples assessed the treatment's effects on visible colour change, surface sheen and planarity. Comparison of the results of colour measurements and visual colour assessments indicated whether instrumental readings corresponded to visually perceptible change.

The results showed that this disinfection treatment may cause colour change of the dyes that form the image in some samples. The colour changes were more likely and more significant for more recent prints. The treatment also induced planar distortion and slight change of surface sheen in some samples.

Can an ethanol vapour treatment be safely used for mould remediation treatments on chromogenic prints? The results obtained only allow us to draw one general conclusion: there is a risk of colour change to chromogenic prints. As a result, this treatment should not be used to treat a collection as a whole without taking into account the varying risks to different types of chromogenic materials. If the visual aesthetic aspect of the print is a crucial value for the object, as it would be for fine art photographs, the treatment should not be undertaken. In the context of archival collections, the treatment might be considered after accounting for the balance between the risk of not treating the mould infestation and the risk of some visual damage to the print. The choice between treatment and no treatment will depend on each specific situation. The treatment should not be used on Kodachrome prints on pigmented acetate, which showed visually significant colour changes and cockling after treatment in this study.

More research is needed to confirm the results of this study and to further increase our understanding of the impact of disinfection treatment on chromogenic photographs. This project assessed a limited number and variety of samples, which do not fully represent the diversity of chromogenic materials. The results also include some anomalous colour change values for control samples that are not fully explained. More tests on modern samples of a uniform colour (medium grey, cyan, magenta and yellow) could help determine the effect of the treatment on each dye and whether the print's structure (layer order) has an influence. Such tests might also probe whether prints that already exhibit colour shift are less vulnerable to change with this technique. Tests on fungi-inoculated samples could also be interesting as the mould-damaged emulsion may provide better access to the dyes and influence the results.

Mould development on photographic material is a common problem encountered in many collections. If the need for a conservation treatment exists, it should not preclude the primary need for preventive measures, namely, control of the humidity levels in collection facilities to prevent any mould from developing in the first place. Ethanol-water vapour treatment has been shown to be effective in killing moulds embedded in the object material; however, it does not remove the potential health and safety issues caused by some mould species,[3,4] and it does not prevent the documents from becoming mouldy again.

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MATERIALS

Absolute ethanol, anhydrous: GreenField Global Inc., 6985 Financial Drive, Suite 501, Mississauga, Ontario L5N 0G3, Canada; Tel.: 905-790-4575; Website: <https://greenfield.com/>

Blotters, unbuffered cotton blotting paper: Carr McLean, 461 Horner Avenue, Toronto, Ontario M8W 4X2, Canada; Tel.: 1-800-268-2123; Website: <www.carrmclean.ca/>

Matboard, Rising Buffered Museum Board, Antique White, 4-ply: Talas, 330 Morgan Avenue, Brooklyn, New York 11211, USA; Tel.: 212-219-0770; Website: <www.talasonline.com/>

Non-woven polyester, Reemay, 71 gsm: Talas, 330 Morgan Avenue, Brooklyn, New York 11211, USA; Tel.: 212-219-0770; Website: <www.talasonline.com/>

Polyester sheet, Mylar, 4 mil: Talas, 330 Morgan Avenue, Brooklyn, New York 11211, USA; Tel.: 212-219-0770; Website: <www.talasonline.com/>

Polypropylene food container, IKEA 365+: IKEA, 2685 Iris Street, Ottawa, Ontario K2C 3S4, Canada; Tel.: 1-866-866-4532; Website: <www.ikea.com/ca/>

Polystyrene weighing dish: Fisher Scientific, 112 Colonnade Road, Ottawa, Ontario K2E 7L6, Canada; Tel.: 1-800-234-7437; Website: <www.fishersci.ca/>

Polystyrene grid: Home Depot, 1616 Cyrville Road, Ottawa, Ontario K1B 3L8, Canada; Tel.: 613-744-1700; Website: <www.homedepot.ca/>

Reverse osmosis water made from tap water purified an EMD Millipore Milli-Q Direct 8 reverse osmosis water purification system: MilliporeSigma, Canada, Sigma-Aldrich Canada, 2149 Winston Park Drive, Oakville, Ontario L6H 6J8, Canada: Tel.: 1-800-565-1400; Website: <https://www.emdmillipore.com/CA/en/product/Milli-Q-Direct-8-Water-Purification-System,MM_NF-ZR0Q008WW>

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24 The relative humidity in the box depends on the temperature, the size of the box, and the quantity of porous materials in the box. Previous empirical observations and tests showed the relative humidity reaches 80% within the first 30 minutes of the treatment.

25 After-treatment measurements for the 1980s and 2000s samples were taken respectively three and four days after drying. After-treatment measurements for all other samples were taken right after drying.

26 L* is the lightness variable with values between 0 (black) and 100 (white). a* and b* are the chromaticity coordinates, with a* values between −100 (green) and 100 (red), and b* values between −100 (blue) and 100 (yellow). The standard deviation indicates the dispersion of the dataset.

27 ΔE* (CIE 1976) is defined by the following equation: $\Delta E^*_{1976} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$ where ΔL*, Δa*, Δb* are the differences in L*, a* and b* values between the before and after treatment colour for the same target. See Konica Minolta, *Precise Color Communication: Color Control from Perception to Interpretation* (Tokyo: Konica Minolta, 2007), <https://www.konicaminolta.com/instruments/knowledge/color/pdf/color_communication.pdf>. Accessed March 2020.

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Appendix I. Sample information.

Sample number	Date	Brand	Paper name	Primary support	Optical brightener	Dimensions (cm)
Samples from the 2000s						
1	2000-2006 (backprint)	Kodak	Ektacolor Edge 8 Paper (backprint)	Resin-coated	Yes	10 x 15
2	2000-2006 (backprint)	Kodak	Ektacolor Edge 8 Paper (backprint)	Resin-coated	Yes	10 x 15
3	2000-2006 (backprint)	Kodak	Ektacolor Edge 8 Paper (backprint)	Resin-coated	Yes	10 x 15
4	2000-2006 (backprint)	Kodak	Ektacolor Edge 8 Paper (backprint)	Resin-coated	Yes	10 x 15
5	Unknown	Fuji	Fujicolor Crystal Archive Paper	Resin-coated	Yes	9 x 12
6	Unknown	Fuji	Fujicolor Crystal Archive Paper	Resin-coated	Yes	10 x 10
7	Unknown	Fuji	Fujicolor Crystal Archive Paper	Resin-coated	Yes	10 x 12
8	Unknown	Fuji	Fujicolor Crystal Archive Paper	Resin-coated	Yes	10 x 15
16	2000-2005 (backprint)	Kodak	Ektacolor Royal (backprint)	Resin-coated	Yes	10 x 15
Samples from the 1980s						
11	Unknown	Unknown	Unknown	Resin-coated	Yes	10 x 17
12	1981	Kodak	Ektacolor (backprint)	Resin-coated	Yes	9 x 9
13	1988	Kodak	Ektacolor (backprint)	Resin-coated	Yes	9 x 12
14	1982	Kodak	Ektacolor (backprint)	Resin-coated	Yes	9 x 12
15	1984	Unknown	Unknown	Resin-coated	Yes	10 x 15
17	Unknown	Unknown	Unknown	Resin-coated	Yes	10 x 15
18	1989	Mitsubichi	Mitsubichi Color Paper (backprint)	Resin-coated	Yes	9 x 12
19	Unknown	Fuji	Fujichrome Paper (backprint)	Resin-coated	Yes	9 x 12
20	Unknown	Fuji	Fujicolor Paper (backprint)	Resin-coated	Yes	13 x 18
Samples from the 1970s						
21	June 1973	Kodak	Ektacolor print (backprint)	Resin-coated	No	9 x 12
22	Unknown	Kodak	Ektacolor print (backprint)	Resin-coated	Yes	9 x 12
23	Unknown	Kodak	Ektacolor print (backprint)	Resin-coated	Yes	9 x 9
24	Unknown	Kodak	Ektacolor print (backprint)	Resin-coated	Yes	9 x 9
25	1968-1971 (backprint)	Kodak	Ektacolor print (backprint)	Resin-coated	No	9 x 9
26	1974	Kodak	Ektacolor print (backprint)	Resin-coated	No	9 x 12
27	Sept 1978	Kodak (?)	Unknown	Resin-coated	Yes	9 x 9
28	Unknown	Unknown	Unknown	Resin-coated	Yes	9 x 9
29	Unknown	Fuji	Fujicolor Paper (backprint)	Resin-coated	Yes	10 x 15
30	1979	Fuji	Fujichrome Paper (backprint)	Resin-coated	Yes	9 x 12

Appendix I. Sample information (cont'd).

Sample number	Date	Brand	Paper name	Primary support	Optical brightener	Dimensions (cm)
Samples from the 1960s						
31	Unknown	Unknown	Unknown	Fiber-based	Yes	9 x 9
32	1967	Unknown	Unknown	Fiber-based	No	9 x 9
33	Unknown	Unknown	Unknown	Fiber-based	Yes	9 x 9
34	Unknown	Unknown	Unknown	Fiber-based	Yes	9 x 9
35	1964	Kodak	Kodacolor print (stamp) / Ektacolor print (backprint)	Fiber-based	No	9 x 9
36	1961-1971 (backprint)	Kodak	Ektacolor print (backprint)	Fiber-based	No	9 x 9
37	1961-1971 (backprint)	Kodak	Ektacolor print (backprint)	Fiber-based	No	9 x 12
38	1961-1971 (backprint)	Kodak	Ektacolor print (backprint)	Fiber-based	No	9 x 9
39	1961-1971 (backprint)	Kodak	Ektacolor print (backprint)	Fiber-based	No	9 x 9
40	1961-1971 (backprint)	Kodak	Ektacolor print (backprint)	Fiber-based	No	13 x 18
Samples from the 1950s						
41	1954	Kodak	Kodacolor print	Fiber-based	No	13 x 18
42	1955	Kodak	Kodacolor print	Fiber-based	No	9 x 12
43	1956	Kodak	Kodacolor print	Fiber-based	No	9 x 9
44	1956	Kodak	Kodacolor print	Fiber-based	No	9 x 9
45	1956	Kodak	Kodacolor print	Fiber-based	No	9 x 9
46	1957	Kodak	Kodacolor print	Fiber-based	No	9 x 9
47	1958	Technicolor	Technicolor print	Fiber-based	No	9 x 9
48	1959	Unknown	Unknown	Fiber-based	No	9 x 12
49	1954	Kodak	Kodachrome print	Pigmented acetate	No	6 x 8
50	1956	Kodak	Kodachrome print	Pigmented acetate	No	6 x 8
Samples from the 1940s						
51	14 Aug 1944	Kodak	Kodacolor print	Fiber-based	No	9 x 12
52	14 Aug 1944	Kodak	Kodacolor print	Fiber-based	No	9 x 12
53	26 Oct 1945	Kodak	Kodacolor print	Fiber-based	No	8 x 14
54	27 Oct 1945	Kodak	Kodacolor print	Fiber-based	No	8 x 14
55	23 Oct 1945	Kodak	Kodacolor print	Fiber-based	No	8 x 14
56	27 Aug 1947	Kodak	Kodacolor print	Fiber-based	No	8 x 14
57	30 Jan 1948	Kodak	Kodacolor print	Fiber-based	No	9 x 9
58	30 Jan 1948	Kodak	Kodacolor print	Fiber-based	No	9 x 9
59	3 May 1949	Kodak	Kodacolor print	Fiber-based	No	9 x 12
60	27 Feb 1950 (week of)	Kodak	Kodacolor print	Fiber-based	No	9 x 12

Appendix II. Properties of samples before and after ethanol vapour treatment.

	Properties before treatment		Change in in property after vapour treatment		
Sample number	Surface sheen	Planar distortion	Surface sheen	Planar distortion	Colour (visible to the eye)
Samples from the 2000s					
1	Semi-reflective towards glossy	None	No	No	Yes
2	Semi-reflective towards glossy	None	No	No	Yes
3	Semi-reflective towards glossy	None	No	No	Yes
4	Glossy	Slight curling	No	No	No
5	Glossy	None	No	No	No
6	Glossy	None	No	No	Yes
7	Glossy	None	No	No	Yes
8	Glossy	None	No	No	Yes
16	Semi-reflective towards glossy	None	No	No	Yes
Samples from the 1980s					
11	Semi-reflective towards matte	None	No	Slight curling	No
12	Semi-reflective towards matte	None	No	Slight curling	Yes
13	Semi-reflective	None	No	No	Yes
14	Semi-reflective towards matte	None	No	No	Yes
15	Semi-reflective towards matte	None	No	No	No
17	Semi-reflective towards matte	None	No	No	No
18	Semi-reflective towards glossy	None	No	No	Yes
19	Semi-reflective towards glossy	Slight curling	No	No	No
20	Semi-reflective	None	No	No	Yes
Samples from the 1970s					
21	Semi-reflective towards matte	Slight curling	No	No	No
22	Semi-reflective towards glossy	Slight curling	No	No	No
23	Semi-reflective towards matte	None	No	Slight curling	No
24	Semi-reflective towards matte	Slight curling	No	No	No
25	Semi-reflective towards glossy	None	No	Slight curling	No
26	Semi-reflective towards glossy	None	No	Slight curling	No
27	Semi-reflective towards matte	Slight curling	No	Slight curling	No
28	Semi-reflective towards matte	None	No	Slight curling	No
29	Semi-reflective	Slight curling	No	Medium curling	No
30	Semi-reflective	Slight curling	No	No	No

Appendix II. Properties of samples before and after ethanol vapour treatment (cont'd).

	Properties before treatment		Change in in property after vapour treatment		
Sample number	Surface sheen	Planar distortion	Surface sheen	Planar distortion	Colour (visible to the eye)
Samples from the 1960s					
31	Semi-reflective towards glossy	Slight curling	No	No	No
32	Semi-reflective towards glossy	None	No	No	No
33	Semi-reflective towards glossy	None	No	Slight curling	No
34	Semi-reflective towards glossy	Slight curling	No	No	No
35	Semi-reflective towards glossy	None	Slightly less glossy	Slight curling	No
36	Semi-reflective towards glossy	None	No	Slight curling	No
37	Semi-reflective towards glossy	None	Slightly less glossy	No	No
38	Semi-reflective towards glossy	None	Slightly less glossy	Slight curling	No
39	Semi-reflective towards glossy	None	Slightly less glossy	Slight curling	Yes
40	Semi-reflective	None	No	Slight curling	No
Samples from the 1950s					
41	Semi-reflective	None	No	Medium curling	No
42	Semi-reflective	Slight curling	No	No	No
43	Semi-reflective	None	No	Medium curling	No
44	Semi-reflective	None	No	Medium curling	No
45	Semi-reflective	None	No	Medium curling	No
46	Semi-reflective	None	No	Medium curling	No
47	Semi-reflective	None	No	No	No
48	Semi-reflective	None	No	Slight curling	No
49	Glossy	None	No	Slight cockling	No
50	Glossy	None	No	Very slight cockling	No
Samples from the 1940s					
51	Semi-reflective	Strong curling	No	No	No
52	Semi-reflective	Strong curling	No	No	No
53	Semi-reflective	None	No	Medium curling	No
54	Semi-reflective	None	No	Strong curling	No
55	Semi-reflective	None	No	Strong curling	No
56	Semi-reflective	None	No	Medium curling	No
57	Semi-reflective	Slight curling	No	No	No
58	Semi-reflective	Slight curling	No	No	No
59	Semi-reflective	Slight curling	No	No	No
60	Semi-reflective	Slight curling	No	No	No

Appendix III. Results of colorimetric measurements: white = not perceptible, light grey = just noticeable, dark grey = perceptible.

Sample number	Target**	Colour of area	Control/Treated	ΔL*	Δa*	Δb*	ΔE*
Samples from the 2000s							
1	1	Black	Treated	-1.1	-1.1	3.1	3.5
	2	Black	Control	-0.1	-0.1	0.1	0.2
	3	Black	Treated	-1.1	-1.0	1.1	1.9
	4	Black	Control	0.9	0.1	0.0	0.9
2	6	Medium grey	Treated	-0.2	-0.7	3.7	3.8
	5	Medium grey	Control	0.3	0.1	0.1	0.3
	7	Dark blue	Treated	-0.3	-2.8	4.2	5.0
	8	Dark blue	Control	0.0	0.3	-0.3	0.4
3	10	Medium grey	Treated	-0.1	-1.5	4.6	4.8
	9	Medium grey	Control	0.2	0.0	0.0	0.2
	11	Black	Treated	-0.2	-1.9	3.5	4.0
	12	Black	Control	-0.1	0.0	0.1	0.1
4	13	Off white	Treated	0.5	0.0	-0.2	0.5
	15	Off white	Control	-0.1	-0.1	0.4	0.4
	14	Dark green	Treated	0.1	-0.3	-0.1	0.3
	17	Dark green	Control	-0.6	0.4	0.7	1.1
	16	Light green	Treated	0.2	0.1	-0.2	0.3
	18	Light green	Control	-0.7	0.3	0.7	1.1
5	20	Magenta pink	Treated	-0.4	-1.0	-0.5	1.2
	19	Magenta pink	Control	0.6	-1.1	0.5	1.3
	21	Blue	Treated	-0.4	1.3	-1.7	2.2
	22	Blue	Control	0.7	-0.3	0.0	0.8
	24	Black	Treated	0.5	-1.0	-0.8	1.4
	23	Black	Control	2.5	-0.1	0.0	2.5
	25	Green	Treated	-0.3	0.2	-1.7	1.8
	26	Green	Control	0.7	1.2	-1.2	1.9
6	27	Dark blue	Treated	-0.4	-0.2	1.1	1.1
	28	Dark blue	Control	1.1	0.1	0.4	1.2
	30	Black	Treated	1.6	-0.5	0.1	1.7
	29	Black	Control	1.8	0.2	0.2	1.9
	31	Yellow	Treated	-1.2	0.5	-2.7	3.0
	32	Yellow	Control	0.3	0.0	-0.6	0.7
7	33	Black	Treated	2.1	-0.7	-0.1	2.2
	34	Black	Control	0.1	0.0	0.0	0.1
8	35	Yellow	Treated	-0.7	-0.5	1.1	1.4
	36	Yellow	Control	-0.1	0.1	0.2	0.3
	37	Off white – grey tint	Treated	-0.2	-0.1	-0.3	0.4
	38	Off white – grey tint	Control	0.0	0.0	0.1	0.2
16	61	White	Treated	-0.1	0.2	1.1	1.1
	62	White	Control	0.1	0.0	0.0	0.1
	64	Red	Treated	-0.8	0.4	4.2	4.3
	63	Red	Control	0.1	-0.1	-0.2	0.2
	66	Red	Treated	-0.8	0.7	4.8	5.0
	65	Red	Control	0.3	-0.3	-0.3	0.5

**Target pairs in visually similar colours are listed one after the other. Treated targets are followed by their paired control targets.

Appendix III. Results of colorimetric measurements: white = not perceptible, light grey = just noticeable, dark grey = perceptible (cont'd).

Sample number	Target**	Colour of area	Control/Treated	ΔL*	Δa*	Δb*	ΔE*
Samples from the 1980s							
11	49	Brown – red tint	Treated	0.5	-0.3	0.0	0.6
	50	Brown – red tint	Control	0.1	0.0	0.0	0.1
12	52	Brown – red tint	Treated	0.6	-2.4	-0.1	2.4
	51	Brown – red tint	Control	0.0	0.1	0.2	0.2
13	53	Dark grey	Treated	-0.6	-4.2	0.0	4.2
	54	Dark grey	Control	0.0	0.0	0.1	0.1
	55	Dark grey	Treated	-0.4	-4.3	-0.5	4.4
	56	Dark grey	Control	0.2	0.1	-0.2	0.3
14	58	Black	Treated	0.5	-2.6	1.1	2.9
	57	Black	Control	0.8	-0.2	-0.2	0.8
15	60	Black	Treated	2.3	-1.4	-0.7	2.8
	59	Black	Control	1.8	-0.3	-0.5	1.9
17	68	Light tan	Treated	0.0	-0.2	0.0	0.2
	67	Light tan	Control	0.1	0.0	-0.3	0.3
	69	Black	Treated	1.6	-2.7	0.2	3.1
	70	Black	Control	0.1	0.0	0.1	0.1
18	72	Off white	Treated	-0.1	-1.7	2.7	3.2
	71	Off white	Control	0.4	0.1	0.0	0.5
19	73	Medium grey	Treated	-0.5	0.3	-0.7	0.9
	74	Medium grey	Control	0.3	0.0	-0.1	0.3
	75	Off white – pink tint	Treated	0.2	0.5	-0.2	0.6
	76	Off white – pink tint	Control	0.1	-0.1	0.0	0.2
	77	Beige	Treated	-0.1	0.5	-0.2	0.6
	78	Beige	Control	0.0	0.0	0.0	0.1
	79	Beige	Treated	0.2	0.3	-0.3	0.5
	80	Beige	Control	-0.1	-0.1	-0.2	0.2
	82	Black	Treated	1.0	-1.8	0.3	2.1
	81	Black	Control	2.2	-0.5	-0.2	2.3
20	84	Medium grey – yellow tint	Treated	-0.6	-2.9	-0.7	3.0
	83	Medium grey – yellow tint	Control	0.4	0.0	-0.1	0.4
	86	Beige	Treated	-1.2	-2.5	0.4	2.8
	85	Beige	Control	0.2	0.1	-0.1	0.3

**Target pairs in visually similar colours are listed one after the other. Treated targets are followed by their paired control targets.

Appendix III. Results of colorimetric measurements: white = not perceptible, light grey = just noticeable, dark grey = perceptible (cont'd).

Sample number	Target**	Colour of area	Control/Treated	ΔL*	Δa*	Δb*	ΔE*
Samples from the 1970s							
21	87	Off-white	Treated	0.1	-0.4	-0.3	0.5
	88	Off-white	Control	0.0	0.0	-0.2	0.3
	90	Tan	Treated	0.1	-0.7	-0.4	0.7
	89	Tan	Control	-0.1	0.0	-0.2	0.2
	92	Tan	Treated	0.1	-1.3	-0.1	1.3
	91	Tan	Control	0.1	0.0	-0.2	0.3
22	94	Dark brown	Treated	0.0	-0.1	1.4	1.4
	93	Dark brown	Control	0.4	-0.2	-0.6	0.8
	96	Beige – pink tint	Treated	0.2	0.0	-0.1	0.2
	95	Beige – pink tint	Control	0.1	-0.1	-0.2	0.2
	97	Brown – red tint	Treated	0.0	-0.3	1.0	1.0
	98	Brown – red tint	Control	-0.1	0.3	0.2	0.4
23	99	Light blue	Treated	0.1	-0.3	0.0	0.4
	100	Light blue	Control	0.3	0.0	0.0	0.3
	101	Light blue	Treated	0.2	-0.3	0.0	0.3
	102	Light blue	Control	0.3	0.0	-0.1	0.3
24	103	Dark brown	Treated	0.1	-0.7	0.4	0.8
	104	Dark brown	Control	0.1	-0.1	0.0	0.2
25	105	Beige	Treated	-0.1	0.0	-0.6	0.6
	106	Beige	Control	0.0	0.0	-0.1	0.1
	107	Off white – grey tint	Treated	0.1	-0.2	0.2	0.3
	108	Off white – grey tint	Control	0.0	-0.1	-0.1	0.2
	109	Dark blue – green tint	Treated	0.3	-0.6	0.3	0.8
	110	Dark blue – green tint	Control	0.4	-0.1	0.0	0.5
26	112	Dark brown – red tint	Treated	1.0	-0.6	0.1	1.2
	111	Dark brown – red tint	Control	0.0	-0.2	0.2	0.3
	113	Dark brown – red tint	Treated	-0.4	-0.4	0.1	0.6
	114	Dark brown – red tint	Control	0.7	-0.5	-0.3	0.9
	116	Brown – red tint	Treated	0.9	-0.9	-0.2	1.3
	115	Brown – red tint	Control	0.2	-0.4	-0.2	0.5
27	118	Brown – red tint	Treated	-0.2	-1.4	0.8	1.6
	117	Brown – red tint	Control	0.7	-0.2	-0.2	0.8
	120	Light blue	Treated	-0.5	-1.2	0.6	1.4
	119	Light blue	Control	0.2	-0.2	-0.2	0.3
	121	Light purple	Treated	-0.3	-0.9	0.0	1.0
	122	Light purple	Control	-0.2	0.0	-0.2	0.3
28	124	Off white – blue tint	Treated	0.0	-0.4	0.3	0.5
	123	Off white – blue tint	Control	-0.2	0.0	-0.2	0.3
	126	Light grey	Treated	0.7	-0.6	0.6	1.1
	125	Light grey	Control	-0.3	0.2	0.2	0.4
29	128	Brown - red tint	Treated	-0.7	-1.2	-0.6	1.5
	127	Brown - red tint	Control	0.0	0.3	0.3	0.5
	130	Off-white – yellow tint	Treated	0.2	0.1	-1.1	1.2
	129	Off-white – yellow tint	Control	0.2	0.0	-0.2	0.3
	131	Dark brown	Treated	-0.9	-1.3	-0.3	1.6
	132	Dark brown	Control	0.1	0.0	0.1	0.1
30	134	Black	Treated	-0.1	-0.2	1.1	1.1
	133	Black	Control	-0.1	0.0	-0.1	0.1
	135	Black	Treated	0.2	-0.3	1.2	1.3
	136	Black	Control	0.4	-0.1	-0.4	0.6

**Target pairs in visually similar colours are listed one after the other. Treated targets are followed by their paired control targets.

Appendix III. Results of colorimetric measurements: white = not perceptible, light grey = just noticeable, dark grey = perceptible (cont'd).

Sample number	Target**	Colour of area	Control/Treated	ΔL*	Δa*	Δb*	ΔE*
Samples from the 1960s							
31	138	Light blue	Treated	0.0	-0.3	0.3	0.4
	137	Light blue	Control	0.0	0.0	0.0	0.1
32	140	Tan	Treated	-0.9	-0.4	0.3	1.0
	139	Tan	Control	0.0	0.0	-0.2	0.2
	142	Tan	Treated	-0.8	-0.2	1.1	1.4
	141	Tan	Control	0.1	0.0	0.0	0.1
33	144	Dark blue – grey tint	Treated	-0.2	-0.2	-0.4	0.5
	143	Dark blue – grey tint	Control	0.3	-0.1	-0.3	0.4
	145	Off white – red tint	Treated	-0.2	-0.1	-0.2	0.4
	146	Off white – red tint	Control	0.0	0.0	-0.3	0.3
34	148	Light pink	Treated	-0.2	-0.1	-0.2	0.3
	147	Light pink	Control	-0.1	0.0	-0.5	0.5
	150	Light pink – blue tint	Treated	-0.1	-0.3	-0.2	0.4
	149	Light pink – blue tint	Control	0.2	-0.1	-0.2	0.3
	151	Light pink – blue tint	Treated	-0.2	-0.2	-0.2	0.3
	152	Light pink – blue tint	Control	0.0	0.1	0.0	0.1
35	153	Off-white	Treated	-0.4	-0.4	0.5	0.7
	154	Off-white	Control	0.1	-0.1	-0.1	0.2
	156	Medium grey – red tint	Treated	-1.2	-1.0	-1.2	1.9
	155	Medium grey – red tint	Control	0.3	-0.1	-0.1	0.3
	158	Medium grey – red tint	Treated	-0.5	-1.8	-0.2	1.9
	157	Medium grey – red tint	Control	0.0	0.0	-0.2	0.2
36	159	Light blue	Treated	-0.4	-0.2	0.1	0.5
	160	Light blue	Control	-0.1	0.0	-0.1	0.1
	161	Light blue	Treated	-0.3	-0.1	0.1	0.3
	162	Light blue	Control	-0.1	0.0	-0.1	0.2
37	163	White	Treated	-0.2	-0.4	0.9	1.0
	164	White	Control	0.0	-0.1	0.0	0.1
	165	Medium grey	Treated	-0.5	-1.9	0.0	2.0§
	166	Medium grey	Control	-0.1	0.0	0.0	0.1
38	167	Light blue – grey tint	Treated	-0.7	0.0	0.6	0.9
	168	Light blue – grey tint	Control	0.3	0.0	-0.1	0.3
	169	Medium grey	Treated	-0.9	0.1	0.6	1.1
	170	Medium grey	Control	0.4	-0.1	-0.2	0.5
39	171	Dark purple	Treated	-0.7	-2.1	-0.5	2.3
	172	Dark purple	Control	0.4	-0.3	0.0	0.5
	174	Purple	Treated	-1.6	-1.7	-1.6	2.8
	173	Purple	Control	0.1	-0.1	-0.1	0.2
	176	Medium grey – purple tint	Treated	9.6	0.2	-1.8	9.8
	175	Medium grey – purple tint	Control	0.2	-0.2	0.0	0.3
	178	Beige - pink tint	Treated	-0.4	-0.5	-0.2	0.7
	177	Beige - pink tint	Control	0.1	-0.1	0.0	0.1
40	180	Off white – green tint	Treated	-0.2	-0.2	0.1	0.3
	179	Off white – green tint	Control	0.0	0.0	-0.1	0.1
	182	Light green	Treated	-0.3	-0.2	0.5	0.6
	181	Light green	Control	0.1	0.1	0.0	0.1
	184	Dark grey – purple tint	Treated	-0.2	-0.3	0.5	0.6
	183	Dark grey – purple tint	Control	0.3	-0.1	0.0	0.3
	185	Dark blue – green tint	Treated	1.0	0.2	0.2	1.1
	186	Dark blue – green tint	Control	0.1	0.1	0.1	0.2

**Target pairs in visually similar colours are listed one after the other. Treated targets are followed by their paired control targets.
§The ΔE for this target is categorized as just noticeable (light grey) since its value, 1.96, rounds up to but is under 2.0.

Appendix III. Results of colorimetric measurements: white = not perceptible, light grey = just noticeable, dark grey = perceptible (cont'd).

Sample number	Target**	Colour of area	Control/Treated	ΔL*	Δa*	Δb*	ΔE*
Samples from the 1950s							
41	187	Light grey – pink tint	Treated	0.1	0.0	-0.3	0.3
	188	Light grey – pink tint	Control	0.0	-0.1	-0.4	0.4
	190	Brown – red tint	Treated	0.4	-0.1	-0.5	0.6
	189	Brown – red tint	Control	0.9	-0.7	-0.5	1.3
	191	Grey – pink tint	Treated	0.3	0.0	-0.3	0.4
	192	Grey – pink tint	Control	0.3	-0.2	-0.4	0.5
42	193	Grey – pink tint	Treated	0.0	0.1	0.0	0.1
	194	Grey – pink tint	Control	0.2	-0.1	-0.2	0.3
	195	Light pink – grey tint	Treated	0.3	-0.1	-0.2	0.4
	196	Light pink – grey tint	Control	0.0	0.0	-0.1	0.1
	197	Light pink	Treated	-0.3	0.1	0.1	0.3
	198	Light pink	Control	0.0	0.0	-0.2	0.2
43	200	Off-white	Treated	-0.2	0.0	0.2	0.3
	199	Off-white	Control	-0.2	0.0	0.0	0.2
	202	Light pink – grey tint	Treated	0.0	0.0	0.2	0.2
	201	Light pink – grey tint	Control	0.1	0.0	-0.1	0.2
44	203	Light pink	Treated	0.0	0.0	0.2	0.2
	204	Light pink	Control	0.0	0.0	0.0	0.0
	205	Off-white	Treated	-0.3	0.1	0.3	0.4
	206	Off-white	Control	0.0	0.0	0.0	0.0
	207	Light pink	Treated	0.0	0.0	0.3	0.3
	208	Light pink	Control	0.0	0.0	0.0	0.0
45	209	Off-white	Treated	-0.3	0.0	0.1	0.3
	210	Off-white	Control	0.1	0.0	0.0	0.1
	212	Light pink – grey tint	Treated	0.2	-0.2	0.1	0.3
	211	Light pink – grey tint	Control	0.0	0.0	-0.1	0.1
	214	Pink – grey tint	Treated	-0.1	0.3	0.3	0.4
	213	Pink – grey tint	Control	0.3	-0.3	-0.3	0.5
	215	Dark pink – grey tint	Treated	0.0	0.1	0.2	0.2
	216	Dark pink – grey tint	Control	0.0	0.1	0.0	0.1
46	218	Off-white – yellow tint	Treated	-0.1	0.0	-0.2	0.3
	217	Off-white – yellow tint	Control	-0.2	0.0	-0.2	0.3
	219	Brown – orange tint	Treated	0.1	0.0	0.1	0.1
	220	Brown – orange tint	Control	0.3	-0.2	-0.3	0.4
47	222	Light brown – orange tint	Treated	-0.3	0.0	0.0	0.3
	221	Light brown – orange tint	Control	-0.1	0.0	0.1	0.1
	224	Brown – orange tint	Treated	-0.6	0.3	0.1	0.7
	223	Brown – orange tint	Control	-0.3	0.1	0.0	0.3
48	226	Grey – red tone	Treated	0.2	-0.1	0.2	0.3
	225	Grey – red tone	Control	0.4	-0.1	-0.3	0.5
	228	Light grey – red tone	Treated	0.0	0.3	0.3	0.4
	227	Light grey – red tone	Control	-0.1	0.0	-0.1	0.1
	230	Red	Treated	-0.3	0.3	0.4	0.6
	229	Red	Control	0.0	-0.1	-0.1	0.1
49	232	Yellow	Treated	-0.5	0.2	-0.8	1.0
	231	Yellow	Control	0.1	-0.1	-0.2	0.3
	234	Black	Treated	-0.1	0.4	-0.9	1.0
	233	Black	Control	-0.4	0.1	0.3	0.5
	235	Black	Treated	0.7	0.4	-1.9	2.1
	236	Black	Control	0.2	-0.1	-0.5	0.6
50	238	Off-white – blue tint	Treated	0.1	-0.1	0.0	0.2
	237	Off-white – blue tint	Control	-0.3	0.2	-0.2	0.4
	239	Black	Treated	-0.3	0.5	0.8	1.0
	240	Black	Control	0.0	-0.1	0.1	0.1
	242	Dark brown – red tint	Treated	-0.8	1.1	2.1	2.5
	241	Dark brown – red tint	Control	0.2	0.2	0.0	0.3

**Target pairs in visually similar colours are listed one after the other. Treated targets are followed by their paired control targets.

Appendix III. Results of colorimetric measurements: white = not perceptible, light grey = just noticeable, dark grey = perceptible (cont'd).

Sample number	Target**	Colour of area	Control/Treated	ΔL*	Δa*	Δb*	ΔE*
Samples from the 1940s							
51	244	Yellow	Treated	-0.1	0.5	0.8	0.9
	243	Yellow	Control	0.3	-0.1	-0.5	0.6
	246	Yellow	Treated	-0.1	0.0	0.2	0.2
	245	Yellow	Control	-0.1	0.0	-0.3	0.3
52	248	Dark yellow	Treated	0.2	0.0	0.4	0.4
	247	Dark yellow	Control	0.2	-0.1	0.1	0.2
	250	Yellow	Treated	-0.1	0.1	0.0	0.1
	249	Yellow	Control	0.2	-0.1	-0.6	0.6
53	251	Light blue – yellow tint	Treated	1.8	-0.3	1.2	2.2
	252	Light blue – yellow tint	Control	0.0	0.0	0.0	0.0
	253	Light blue – yellow tint	Treated	0.5	-0.3	0.0	0.6
	254	Light blue – yellow tint	Control	0.1	0.0	0.0	0.1
	255	Beige – yellow tint	Treated	Very high standard deviation – excluded from analysis.			
	256	Beige – yellow tint	Control	0.1	-0.1	-0.1	0.2
54	258	Blue – yellow tint	Treated	0.6	-0.3	0.6	0.9
	257	Blue – yellow tint	Control	0.1	0.0	-0.1	0.2
	259	Blue – yellow tint	Treated	1.2	-0.3	1.1	1.7
	260	Blue – yellow tint	Control	0.0	0.1	-0.2	0.2
55	261	Yellow – brown tint	Treated	0.9	-1.6	2.6	3.1
	262	Yellow – brown tint	Control	0.0	0.0	0.0	0.0
	263	Yellow	Treated	0.1	-1.1	-0.5	1.2
	264	Yellow	Control	0.0	-0.1	-0.1	0.2
56	266	Grey – yellow tint	Treated	-0.3	0.1	0.8	0.9
	265	Grey – yellow tint	Control	0.2	0.0	-0.5	0.5
	268	Beige – yellow tint	Treated	-0.3	0.0	0.4	0.5
	267	Beige – yellow tint	Control	0.0	0.1	0.1	0.1
	270	Beige – yellow tint	Treated	-0.2	0.0	0.3	0.4
	269	Beige – yellow tint	Control	0.2	-0.1	-0.2	0.3
57	272	Yellow	Treated	0.2	-0.1	-0.2	0.3
	271	Yellow	Control	-0.1	-0.1	-0.3	0.4
	274	Yellow	Treated	0.2	0.0	-0.4	0.5
	273	Yellow	Control	0.4	-0.1	-0.3	0.5
	276	Yellow	Treated	-0.1	0.0	0.0	0.1
	275	Yellow	Control	0.1	0.0	-0.3	0.4
58	278	Yellow	Treated	0.0	-0.2	-0.5	0.6
	277	Yellow	Control	0.2	0.0	-0.6	0.6
	281	Yellow	Treated	0.0	0.1	-0.1	0.1
	279	Yellow	Control	0.1	0.0	-0.1	0.1
	282	Yellow	Treated	0.1	0.0	-0.2	0.2
	280	Yellow	Control	0.3	-0.1	-0.3	0.4
59	284	Yellow	Treated	-0.1	-0.1	0.1	0.2
	283	Yellow	Control	-0.1	-0.1	-0.1	0.2
	286	Yellow	Treated	-0.4	-0.1	0.5	0.6
	285	Yellow	Control	0.0	0.0	-0.1	0.1
	288	Yellow	Treated	-0.5	0.1	0.7	0.9
	287	Yellow	Control	0.0	0.0	-0.2	0.2
60	290	Yellow	Treated	-0.4	0.2	0.3	0.6
	289	Yellow	Control	0.0	0.1	0.2	0.2
	292	Light brown – yellow tint	Treated	-0.8	0.4	1.0	1.3
	291	Light brown – yellow tint	Control	0.4	-0.2	0.1	0.4
	294	Beige – yellow tint	Treated	-0.1	0.0	0.3	0.3
	293	Beige – yellow tint	Control	0.0	0.1	0.2	0.3

**Target pairs in visually similar colours are listed one after the other. Treated targets are followed by their paired control targets.

Appendix IV: Distribution of treated targets (%) within each ΔE* category per sample.