Watercolour Pencils: Composition and Conservation Concerns

ABSTRACT

This work examines the composition of a variety of commercially available artists’ watercolour pencils (from Derwent, STAEDTLER™, and Reeves®), and the reactions of the pencils to aqueous and solvent immersion, non-contact humidification, and mechanical smudging. Both artificially aged and un-aged samples were tested. Fourier Transform Infrared (FTIR) spectroscopy was used to identify the composition of the pencils, spectrophotometry was used to quantify any colour shift following the experiment, and ImageJ software was used to compare the effects of smudging.

Despite many similarities to traditional watercolour paints in how they are used, the pencils differ greatly from their traditional counterparts in composition. All of the watercolour pencils analysed were found to contain colourants, clays, a polysaccharide binder, and modified polyethylene glycol. The results of the immersion, humidification and smudging tests provide a basis to inform the treatment of works containing watercolour pencils but also illuminate the need for further investigation in this and other related media types emerging on the market.

INTRODUCTION

Within the last century watercolour pencils (WCPs) have become more prevalent as a multidisciplinary artistic medium. Watercolour pencils can be used wet or dry to achieve a multitude of colours, textures, and artistic effects. Little information is available in the art conservation literature regarding their general composition, aging characteristics, or the risks associated with their treatment.

A review of the paper conservation literature finds many references concerned with the care and treatment of works composed with watercolours. Published topics have involved direct studies of specific artists’ materials, as well as overviews of individual pigments, and more technical analyses of watercolour aging parameters. Since the early twentieth century, however, watercolours (WC) have been made commercially available to artists in the form of pencils, offering an additional method of application and a new area of study.

WCPs can be used dry, as a typical pencil in terms of drawing or writing, or they can be used wet, either by dipping the pencil lead in water prior to application or by applying water with a brush after dry application to create a wash. Unlike traditional watercolour half-pans or tubes, the WCP leads must be soft enough to deposit media on the surface of a substrate with gentle pressure while also retaining enough strength to withstand the heavy mechanical pressures associated with sharpening, and more vigorous application. WCPs are not regarded as permanent, in the sense that re-wetting the medium may result in additional flow even after the application of a watercolour pencil has been allowed to dry on a paper substrate. The range of working properties that these WCPs are able to achieve comes with a corresponding change in composition, and aging characteristics. This paper seeks to investigate the nature of WCPs and the potential concerns they may pose for the paper conservator.

At this point, the issue of terminology must be addressed. In advertisements and artist material catalogues, watercolour pencils have been described and marketed in a variety of different ways. Generally, they are referred to with one term referencing the medium’s interaction with water (i.e. aquarell(e), water-soluble, and water-thinned), and a second term to reference to the form of application (i.e. pencil, crayon, and stick). For the purposes of this study, the term watercolour pencil will be used to describe what can broadly be understood as a soft, coloured, water-soluble “lead” within a wooden case.

HISTORICAL BACKGROUND

The copy pencil is generally considered to be the predecessor of the WCP in terms of working properties. Copy pencils were introduced in the 1870s, and were used in letterpress
copying and as a more indelible alternative to traditional graphite pencils. The lead of a copy pencil was composed of graphite, clay and a colourant which was usually dye-based. Mordants, such as alumina, as well as binding agents like dextrin, gum tragacanth, albumen, or wax were also added. These pencils would be moistened before being applied to a paper substrate.

The earliest available reference to a product akin to WCPs was provided by an archival specialist at STAEDTLER™. It is a catalogue description for oil-pastel pencils from 1928:

These [...] artist pencils are used with STAEDTLER colouring instrument No. 7720 for a colouring process which combines the advantages of coloured pencils with water-colour paint. By blending the colours with the instrument dipped in water or with a paint brush or with the finger, unknown effects can be achieved. They can be used on plain paper, oiled paper, tracing cloth, etc. and combined with water paints or tempera.

It is possible that similar products manufactured by other artists’ suppliers were available at a slightly earlier date, however no such evidence was found at the time of this publication.

One of the few detailed accounts of historical uses of WCPs comes from Margaret Holben Ellis’s review of Jackson Pollock’s works of art on paper. In his early works, Pollock appears to have used WCPs more as a dry drawing tool. In his later years, Pollock’s use of WCPs seems to be more closely aligned with their intended use, “suggesting a fully realized familiarity with them”.

Pollock’s diverse exploitation of the working properties of WCPs provides a perfect case study of issues that WCPs pose for the conservator. When used dry, the waxy nature of WCPs can be easily confused with other waxy drawing media such as crayons, coloured pencils, or pastels. This makes precise identification of the medium difficult, if not impossible, with visual examination alone. Similarly, when used wet, WCPs could reasonably be misidentified as traditional watercolours or ink. In either case, misidentification of the media could lead the conservator to grossly underestimate the potential solubility concerns associated with WCPs.

Despite the use of WCPs by notable artists in the 1940s/50s, the published knowledge on WCPs remains sparse in the decades following. It is not until the 1990s that artist manuals on the uses and techniques associated with WCPs were contacted. STAEDTLER™ communicated that:

The colored leads contain…binding agents based on cellulose, filling agents such as Talcum or Kaolin (natural products), coloring pigments which are according to the EN 71 standard, [and] slip additives such as fat, natural and synthetic waxes and emulsifying agents...

The company’s manufacturing method for WCPs is similar to that of standard pencil crayons. It involves mixing the raw materials into a homogeneous substance and pressing the finished mix into cylindrical blocks. These blocks are then passed through a hydraulic press to make a ‘rope,’ which is then cut to individual 185mm pieces. The flexible leads are put into metal tins and dried for eight hours at temperatures between 60–120°C. After drying, the leads for standard coloured pencils are ready to be glued into the pencil slat. At this point, WCP leads go through an additional working cycle where they are impregnated with a wax that diffuses into the lead and makes them “water-colourable”.

Compositional analysis was carried out to see if there were any great differences in composition between different brands of WCPs (STAEDTLER™, Derwent and Reeves®) and within different lines of WCPs produced by the same manufacturer (STAEDTLER™ karat aquarelle and STAEDTLER™ ergosoft).

To investigate the effects of typical conservation treatments, the experimental procedure followed the method outlined by Liz Dube (1998) during her investigation of the solubility parameters of historic copy pencils. Drawn lines of WCPs were exposed to several distinct treatment conditions including humidification, smudging, and immersion in aqueous and solvent baths. In this study, both artificially aged and un-aged samples were submitted to all of the test conditions.

CHEMICAL ANALYSIS
Small samples of the leads were taken directly from the pencil and liquid-liquid separation was used to separate the components. Isolated components of the pencil leads were analysed by mid-IR spectroscopy using a Nicolet Avatar™ 320 Fournier Transform Infrared (FT-IR) spectrometer equipped with a Nicolet SMART™ Golden Gate attenuated total reflectance (ATR) accessory (Thermo Instruments, Canada). The spectra were collected with 32 scans at a 4 cm⁻¹ resolution, with background correction. Data was collected and analysed using EZ Omnìc® 5.2 software.

SAMPLE PREPARATION
Samples were prepared by drawing horizontal lines with select WCPs by hand onto Winsor & Newton Watercolour Pen and Ink paper (mould made, 140lb. 100% cotton rag, acid free, neutral pH, internal and surface sizing). This
Daniels found that aging traditional watercolour samples at 100°C and 50% RH for 96 hours rendered them water-insoluble. Here the aging parameters were emulated as closely as possible to see if the same effect would be observed in WCPs.

Once all samples were fully prepared, a pairing of one aged and one un-aged sample was subjected to a variety of tests. The test conditions are described in Table 1.

After testing, samples subjected to solvent immersions were allowed to evaporate in a fume hood and samples treated aqueously were allowed to dry at ambient laboratory conditions for 24 hours prior to analysis. After drying, the effects of each method were observed under magnification and analysed.

SPECTROPHOTOMETRY

Colour changes in the media, before and after immersion and humidity testing, were determined with a Minolta ChromaMeter (CR-700d). The Chroma Meter was calibrated before the collection of each data set. The smallest aperture (5mm) of the spectrophotometer was selected however this aperture was still greater than the thickness of the lines produced by the pencil (~2mm). Given this discrepancy, any measured colour change would be dominated by the degree of bleeding into the surrounding paper, not by the change in the colour of the line itself.

To eliminate this source of error, all the samples were analyzed using a template made from matte black cardstock laminated with Marvelseal™ with a measured 2mm slit in the centre. This slit was aligned with the WCP line to prevent

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Table 1. Test Conditions of Sample Pairings

<table>
<thead>
<tr>
<th>Sample Pairing</th>
<th>Test Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Control (no treatment)</td>
</tr>
<tr>
<td>2</td>
<td>Aqueous immersion for 5 minutes</td>
</tr>
<tr>
<td>3</td>
<td>Solvent immersion (ethanol) for 5 minutes</td>
</tr>
<tr>
<td>4</td>
<td>Solvent immersion (acetone) for 5 minutes</td>
</tr>
<tr>
<td>5</td>
<td>Solvent immersion (toluene) for 5 minutes</td>
</tr>
<tr>
<td>6</td>
<td>Humidification at 100% RH for 60 minutes (non-contact)</td>
</tr>
<tr>
<td>7</td>
<td>Smudging: a paper pastel smudge stick was quickly passed once over the entire sample from top to bottom with even manual pressure</td>
</tr>
</tbody>
</table>

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Fig. 1. Example of a WCP test strip with the following colours/brands:
1. Derwent Ivory Black 67
2. Reeves Black
3. Staedtler karat aquarell Art. Nr. 125-9 Schwarz Black
4. Staedtler ergosoft Art. Nr. 156-9
5. Derwent Gunmetal 69
6. Staedtler karat aquarell Art. Nr. 125-80 Dove grey
7. Derwent Prussian Blue 35
8. Reeves Dark Blue
9. Staedtler karat aquarell Art. Nr. 125-3 Blue
10. Staedtler ergosoft Art. Nr. 156-3
11. Derwent Deep Vermillion 14
12. Reeves Dark Vermillion

Fig. 2. Spectrophotometer
any transmission of extra light and to prevent smudging of the samples (fig. 2). This set-up was found to produce a highly linear offset in the L*, a*, and b* components of the colour measurement that could be easily be compensated for to determine the CIELAB coordinates of the watercolour line alone. Three locations on each sample line were measured and average values for L*, a* and b* were determined. Using the CIELAB 2000 system, the average \( \Delta E_{00} \) values were calculated.

**Computational Image Analysis**

To be able to compare the aged and un-aged sample sets in the smudge test, photomicrographs were taken of each smudged line. The photomicrographs were imported into ImageJ, an open-source software originally developed by Rasband for the American National Institutes of Health for computational image analysis. Using this software, the images were automatically translated into 8-bit greyscale in order to produce histograms. These histograms were imported into Excel in order to make qualitative comparisons.

**Results and Discussion**

**Compositional Analysis**

The overall composition was fairly consistent between each of the samples analyzed (fig. 3). All of the WCP leads were found to contain the same four materials: clay, a water-soluble wax, a polysaccharide binder, and colourants. The colourants used by each brand were not identified by pigment index numbers. Throughout the course of analysis it became apparent that dyes were also used in conjunction with pigments for some pencils. While all of the WCP leads examined

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**Fig. 3. Mid IR Spectra of white WCPs by brand.**

**Fig. 4. FT-IR spectrum of isolated wax component in Reeves white WCP which was extracted through liquid-liquid separation between distilled water and acetone in the acetone phase along with a reference spectrum of polyethylene glycol (PEG).**
contained polysaccharide binders, the binder in each sample was functionally different. Some spectra suggested the presence of agar, while others appeared more similar to a cellulose gum. While traditional watercolour cakes usually contain gum arabic, this did not seem to be the primary binder in any of the WCP leads tested.

The waxy component in the WCP samples was found to be a polyethylene glycol (fig. 4). The peaks at 2925 cm\(^{-1}\) and 1360 cm\(^{-1}\) both indicate the common presence of methyl groups, suggesting that the wax component—or at least part of it—is likely a methoxypolyethylene glycol, or mPEG. mPEG is a water-soluble, linear polymer and is commercially available from Dow Chemicals under the trade name Carbowax™. When the methyl stretching modes, are considered along with the carboxylic functionality around 1700 cm\(^{-1}\) and a notable lack of hydroxyl bending around 3200 cm\(^{-1}\), it seems likely that the waxy component is actually a mixture of mPEG, CarboxylPEG and Carboxyl-methyl PEG.

AQUEOUS AND SOLVENT IMMERION

As expected with water-active materials, the immersion bath in distilled water resulted in an immediately obvious visible change of the unaged samples (fig. 5). However, the aged WCP samples in this experiment also experienced significant bleeding. This is contrary to what might be expected if one is assuming similarity between traditional watercolours and WCPs when emulating Daniels’ aging conditions. This discrepancy can be partially explained by the compositional analysis previously discussed.

Daniels (1993) identified the reason for traditional watercolours being rendered water-insoluble after aging was due to the irreversible dehydration of the gum arabic binder. Compositional analysis of WCP leads revealed that, while a polysaccharide binder existed in each of the WCP leads, gum arabic was not among them. This poses the question of whether or not these other binding agents undergo the same mechanism for achieving water-insolubility. If so, it could be concluded that the polysaccharide binder(s) present in the WCP leads either did not consistently undergo this same process of irreversible dehydration to the critical point where it renders the media water-insoluble—either because the aging conditions were not sufficient or because the presence of other materials in the leads inhibited this reaction— or the binder(s) did undergo dehydration to the critical point of insolubility but were not present in a high enough concentration to fully protect the colourants in the media. Further research is required to fully understand these initial results.

As for the solvent immersions, most of the WCP samples were not significantly altered by ethanol, acetone or toluene except for the red samples. All of the red samples experienced colour change, making them an interesting case study. Figure 6 shows the cumulative colour change of the sample media and paper after being submerged in an aqueous or solvent bath. The colour shift in the paper is fairly substantial which is significant given that the opacity of watercolour pencil media varies with dilution.

Most of the colour shift in the paper pertained to the L* coordinates (see Appendix). This suggested that the paper is darkening after submersion in each of the baths. This could be due to the solubilisation or displacement of additives in the paper.

Focussing on the change in a* and b* values is subsequently of greater interest. For the relatively non-polar solvents, toluene and acetone, the results for the red WCP media show that artificial aging had no statistically significant effect on colour change within the a* and b* coordinates (fig. 7). The change in colour may be attributed to high sensitivity of the dye-based colourants, which likely remain constant before and after aging. This is further confirmed by the negative a* values which indicate a shift away from red and therefore, a loss of colourant.
It should be noted also that while all of the red samples were affected by toluene, only one was affected by acetone. This explains why the averaged magnitude of change is lower with the acetone samples but the standard deviation is higher.

As for immersion in relatively polar solvents, ethanol and water, artificial aging caused a statistically significant change in colour in the red samples (fig. 8). However, the colour shift between aged and un-aged samples immersed in water was visibly and statistically more noticeable than that of ethanol.

The overall change in b* is most significant in the case of the water and ethanol. The change in b* is positive for un-aged samples and negative for aged samples in both water and ethanol. This means that un-aged samples became more yellow and aged became less yellow.

This result may, once again, have to do with the influence of the colour change of the paper. Washing aged papers is most often done to try to remove acidic by-products in the paper, thus making the paper less yellow. By contrast, un-aged papers are likely to have alkaline buffers and other additives removed by an aqueous or ethanol bath, making them less bright.

If this theory is correct, the change in b could initially be understood as a source of error however, as previously touched upon, the opacity of WCP media varies with dilution, therefore, if these results speak more to the change in the colour of the paper they may also simultaneously speak to an increasing lack of opacity which could be interpreted as solubilisation—or partial solubilisation—of the media in question.

However, somewhat contradictory to the last supposition is that all samples immersed in ethanol and water experience a positive shift in a* values which is a shift towards red. This could be the result of partial solubilisation of the binder, resulting in a more consistent film on the surface of the paper and more saturation of the colourants however, at this time; we cannot concretely confirm or deny this interpretation of the data.

NON-CONTACT HUMIDIFICATION
Humidification was not found to produce any observable effect on any of the WCP media tested. Given that humidification is often employed to aid in flattening, it is worth stressing the fact that humidification was carried out in a chamber and drying was not constricted and did not involve any pressing afterwards.

SMUDGING
Mechanical smudging marred all the WCP media examined, both un-aged and artificially aged. Examining the value histograms of each photomicrograph, the peaks due to the colourant of each WCP line were more skewed to higher colour values in the un-aged samples than the aged samples (fig. 9). The colourants are therefore more thinly spread across a larger surface area of the paper in the un-aged samples, indicating a higher degree of smudging. When aged,
the degree of mechanical damage to the media is significantly lower. From this it can be understood that damage to WCP media will be progressively less likely to occur as a work ages, possibly due to the crosslinking of the media to the substrate or from the migration of the soft modified PEG components away from the surface.

CONCLUSIONS

The overall composition of the WCPs was found to be fairly consistent among the brands tested. Each contained the same four major components: clay, a modified PEG, a polysaccharide binder and the colourants. To be more specific and more quantitative, a more precise method of analysis such as gas chromatography with mass spectrometry (GC-MS) would be required; however this is beyond the scope of this project.

The aim of the accelerated thermal aging was to determine whether or not the WCPs would become insoluble in water over time just as traditional watercolours have been shown to do. In this experiment, the WCP media was not rendered fully water-insoluble however the possibility that WCPs can become increasingly resistant to moisture in time, cannot be fully disregarded either; further study of the potential mechanisms for rendering WCP media water-insoluble and it’s relation to thermal aging parameters is required.

Further investigation is also required to determine the types of PEG used in the pencils and their aging characteristics. Conservation literature pertaining to the use and stability of polyethers so far is largely focussed on the use of PEG as a consolidant for archaeological wood. Notable concerns include rapid oxidation due to chain scissioning, which is accelerated by light, as well as acidic degradation, which occurs in the presence of metals.\(^9\) These concerns may carry over to their use in WCPs. Photo-oxidation of PEG could have detrimental effects on the stability of WCP media, as could acidic degradation catalyzed by the presence of metal ions in wash water, metal inclusions in paper, and metallic pigments in the pencils themselves.

In the solvent testing, ethanol was found to cause the least amount of colour shift in the 14 un-aged and aged samples tested and visibly caused the least amount of bleeding. Acetone and toluene both had less-than-desirable effects on the dye-based components in some of the pencil samples, however, did not appear to cause detrimental effects on any of the other colours in our experiment.

Non-contact humidification proved to be harmless to the samples tested, however both aged and un-aged samples proved to be very susceptible to damage by abrasion. In light of these discoveries, it is recommended that humidification only be carried out in a non-contact enclosure like a humidification dome as opposed to a Gore-Tex® sandwich and that flattening be carried out with dutiful consideration of the softness or the media. In terms of storage, drawings with dryly-applied WCPs should be treated similar to that of other waxy media, insomuch that any direct contact with the surface is very likely to result in abrasion, smudging and subsequent distortion of the image.

WCPs offer the amateur and artist an exciting new avenue for creative expression, which correspondingly, creates new avenues of research for the conservator and conservation scientist. The considerations expressed here are not limited to works of art carried out in WCPs; they also extend to conservators seeking a medium for toning and inpainting. Issues of solubility and lightfastness have yet to be fully understood however it is hoped that this research has provoked curiosity,
which may inspire further inquiry into this and other related products that are emerging on the market.

In recent years, Winsor & Newton have introduced lines of watercolour sticks and watercolour markers. Derwent has released their Artbar range of watercolour bars as well as their Inktense range of dye-based pencils and bars, and Caran d’Aché has introduced their Neocolor® range of water-soluble crayons. Clearly watercolour drafting is an artistic medium that is gaining prominence, and therefore, one deserving of the conservator’s attention.

ACKNOWLEDGEMENTS

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NOTES

1. Dube: 1988, 2
2. pers. comm. Staedtler, 2015
3. Ellis: 2005, 129
4. Ellis: 2005, 129
5. EN-71 is a European Union Standard specifying safety requirements for toys
6. pers. comm. Staedtler, 2015
7. pers. comm. Staedtler, 2015

APPENDIX

See chart below.

<table>
<thead>
<tr>
<th>Treatment (compared to Un-aged)</th>
<th>Control L<em>a</em>b*</th>
<th>Average dL* (0° -100 Lightness)</th>
<th>Average da* (+red, -green)</th>
<th>Average db* (+yellow, -blue)</th>
<th>dE2000</th>
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<tr>
<td>Water Un-aged</td>
<td>Paper</td>
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<td>0.33</td>
<td>0.54</td>
<td>1.94</td>
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<td>1.09</td>
<td>0.47</td>
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<td></td>
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<td>7.39</td>
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<td>0.26</td>
<td>3.48</td>
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<td>Acetone Un-aged</td>
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Each L*a*b* change was calculated individually with all three data sets. Average dL*, da*, db* calculated by averaging the three data sets from individual calculation and the resulting standard deviation is also reported. dE2000 values were calculated by first averaging the three data sets of coordinates for each of the treated and control samples, aged and un-aged.
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SOURCE OF MATERIALS

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Wallack’s Art Supply Store
290 Princess Street
Kingston, ON K7L 1B5
Phone: (613) 549-5806