PAINT ANALYSIS OF SAMPLES FROM RYAN PREMISES NHS, NEWFOUNDLAND

Despoina Kavousanaki

Conservation Science, Parks Canada

In the current study, 11 paint samples from the exterior walls of 5 buildings (Table 1) that exist at the Ryan Premises National Historic Site were sent to the Conservation Science laboratory of Parks Canada for scientific analysis. The latter includes both the determination of the color of the finish used at a particular time in the building's history and the identification of the paint's components (pigment, binder, filler). However, due to a very tight deadline, we currently present the color matching results together with the analytical results of the top white finish only. The reason for the chemical identification of both the white pigment and the binder lies in the tendency of all architectural paints to discolor with age[1], a fact that is particularly apparent for bright whites[2]. The factors that play the most significant role in the degradation of the white paint layer, which would eventually affect the color matching results, are the yellowing of oil mediums, fading and/or darkening of light-sensitive pigments, air pollution and continuous oxidation reactions[1]. So, the identification of the ingredients used in the original paint will help us define the degree of yellowing and consequently the potential alteration of the original colour to the current one.

Furthermore, we would like to address that in order to determine the color of the coats with some degree of precision[1], a relatively large area of each individual coat has to be exposed[3] so the color can be analysed in situ by a spectrophotometer or using the Munsell color code. The analysis of small samples in the laboratory lacks a degree of precision, especially for the inner layers, since their color match has to be done in the sample's mounted cross section. This is due to the fact that the inner layers cannot be exposed[4], so as the color can be perceived with the naked eye. Therefore, their exposure has to be carried out in a cross section of the sample mounted in an acrylic resin (Bio-Plastic). The exposure is in turn accomplished through grinding and polishing of the samples. The resulted mounted cross sections acquire the whole paint layers sequence however the layers' fine thicknesses complicate their color matching. The latter has been carried out to the mounted cross sections using the Munsell color chips under the stereomicroscope with an illumination of an artificial light simulating natural north light.

---

[1] https://books.google.ca/books?id=U8a7JhAnLzkC&pg=PA9&lpg=PA9&dq=color+matching+munsell+chips+for+historical+purposes&source=bl&ots=Sf0M04VQCO&sig=gXiyAsRoyaRYJBi0B1xePvwwutI&hl=el&sa=X&ved=0ahUKEwj4lNGtxZPOAhWI6IMKHU09A5kQ6AEIWDAI#v=onepage&q=color%20matching%20munsell%20chips%20for%20historical%20purposes&f=false

[2] file:///U:/GoogleChrome/Downloads/RF_TechSheet_-_Yellowing_Of_Whites%20(1).pdf

[3] https://books.google.ca/books?id=c9Gh5sdH_tkC&pg=SA5-PA10&lpg=SA5-PA10&dq=color+matching+munsell+chips+for+historical+purposes&source=bl&ots=5Sp70I4G2R&sig=aAf5n0nQqXI8EO0vETJNwlD1IQs&hl=el&sa=X&ved=0ahUKEwj4lNGtxZPOAhWI6IMKHU09A5kQ6AEIRzAF#v=onepage&q=color%20matching%20munsell%20chips%20for%20historical%20purposes&f=false

[4] The removal of the top layer was carried out in two red samples both manually and chemically. However both practices resulted in the destruction of the samples.

North light is essential in order to render the colors accurately without the effects of the yellow spectrum of direct sunlight[5]. Of course this technique lacks a certain degree of precision (small thickness of the paint layer, mixture of colours, discoloration of the inner layers due to aging). However, due to the similarity of the results from both the spectrophotometer (expressed in Munsell parameters) and the comparison of the Munsell color chips with the color of the top finish layer in the mounted cross sections, the above practice was eventually performed.

Table 1: Description of samples

Building No.	1	1	2	2	3	3	4	4	5	5	5
Sample No.	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10	#11
Colour (top finish)	White	Red	white	red	white	red	white	red	white	red	yellow

Analytical results

The top white finish of samples 1, 3, 5, 7 and 9 was analysed by spectroscopic techniques (Raman and ATR-FTIR) resulting in the identification of both the pigment and the binder. The former is rutile (titanium dioxide) (Figure 1) and the latter is linseed oil (Figure 2), a historically popular material to cover wood (Garvin 2002). The resulting composition indicates that a potential alteration of the initial colour is derived from the yellowing of the drying oil medium and not from a mutation of the white pigment. Rutile's form of titanium dioxide is considered as one of the most colorfast of all pigments[6,7]. Furthermore, it is chemically inert and does not react with airborne pollutants, organic solvents or other pigments as well as it exhibits increased weather resistance[6]. On the contrary, the yellowing of drying oils has been known qualitatively for centuries (Levison 1985). Among them, linseed oil has the tendency to yellow the most (Dorge and Howlett 1998). However, this yellowing occurs more readily in the dark and can be at least partially reversed by exposure to light (Dorge and Howlett 1998). This means that exterior paints are affected less by the condensation reactions that lead to yellowing of linseed oil which in turn impacts on the preserved colour of the top finish. Furthermore, the yellowing of linseed oil in titanium dioxide white is caused by the tendency of the oil to migrate and form a thin film on the paint surface[5], a fact that can be hindered by the addition of zinc white[5]. Bearing in mind that for cost reasons, titanium dioxide is seldom used as the sole ingredient in paint pigment (Garvin 2002), we can assume that zinc white may have been used[8] as a component in the original paint mixture which limits further the yellowing result.

[5] https://en.wikipedia.org/wiki/Historic_paint_analysis
[6] file:///U:/GoogleChrome/Downloads/RF_TechSheet_-_Yellowing_Of_Whites%20(1).pdf
[7] www.naturalpigments.com/titanium-dioxide-pigment.html
[8] In order to confirm the presence of zinc white, further analysis is needed.

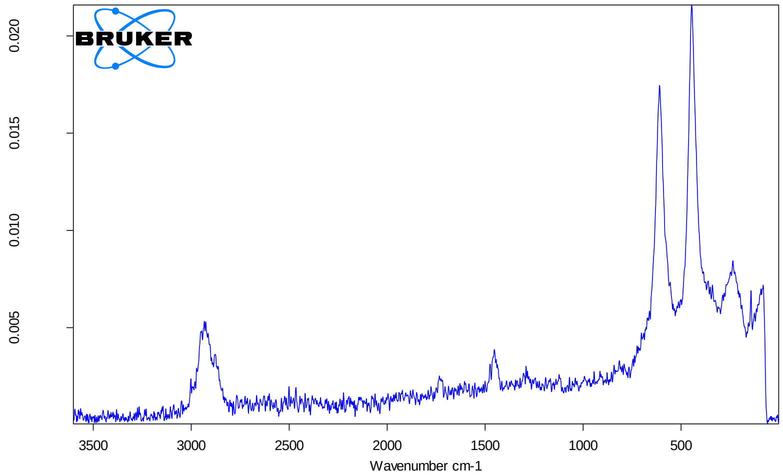


Figure 1: Raman spectrum of the white top finish of Sample #1 - Building 1. Characteristic peaks of rutile: 446(s) cm^{-1}, 611(s) cm^{-1}, 237(m) cm^{-1}, 143(w) cm^{-1}. Characteristic peaks of linseed oil: 2931(s) cm^{-1}, 1449(m) cm^{-1}, 1291(m) cm^{-1}.

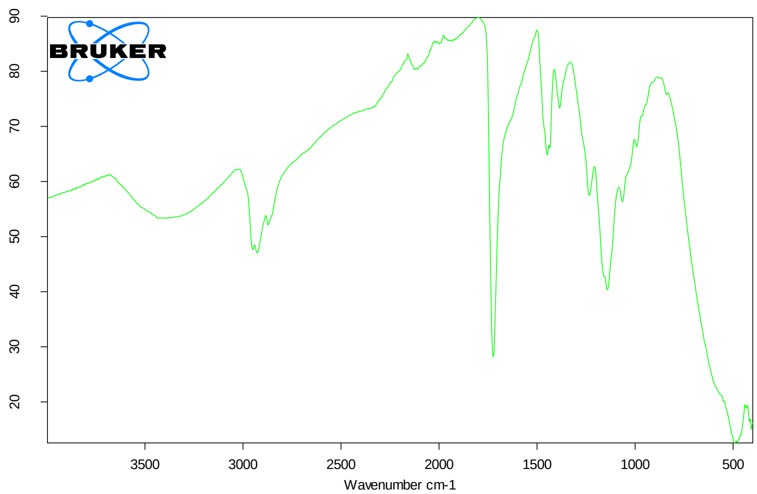


Figure 2: ATR spectrum of the white top finish of Sample #1 – Building 1. Characteristic peaks of oil: 1722cm^{-1}, 1450cm^{-1}, 1234cm^{-1}, 1146cm^{-1}.

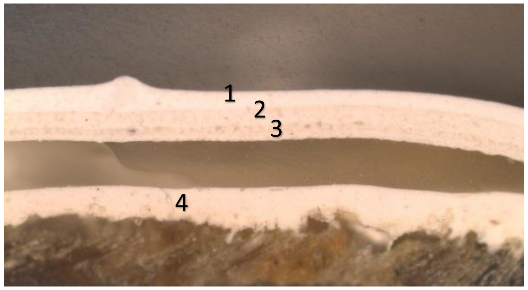
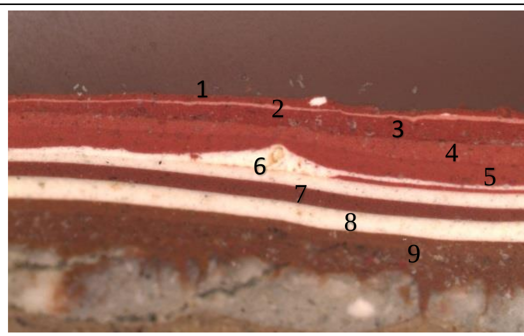
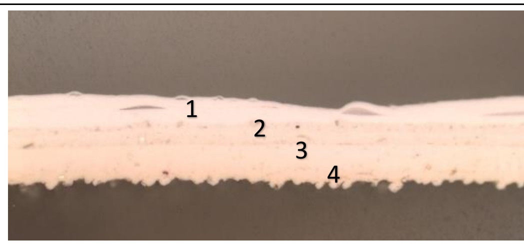
Color matching results

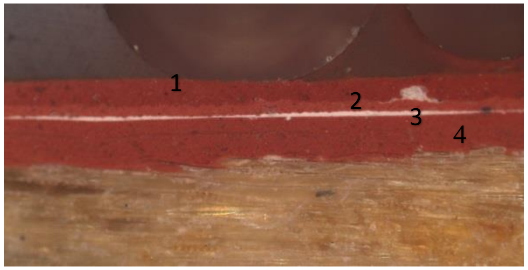
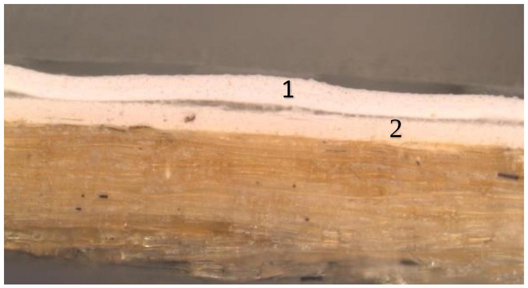
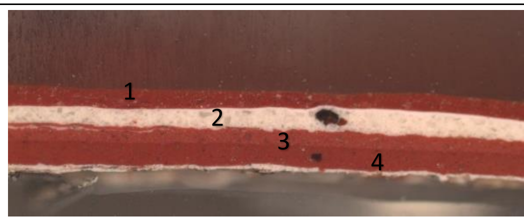
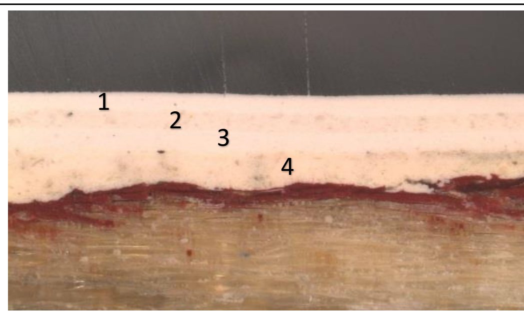
All the top layers of both the white and the red samples were color matched by the Konica Minolta CM-2600d spectrophotometer. The results were displayed in the Munsell code notation. All the inner layers were color matched using the Munsell color chips. Let us not forget though that there will always be a degree of uncertainty and area of tolerance in matching the original paint color to a Munsell color notation under standard conditions of illumination[9]. Furthermore, a certain degree of discoloration (even though and especially for the more susceptible white colours this may be small-see above) is expected to all architectural paints[10]. The color code notation obtained by matching the samples can be used to specify the paint colour desired. The results are summarized in the following table (Table 2):

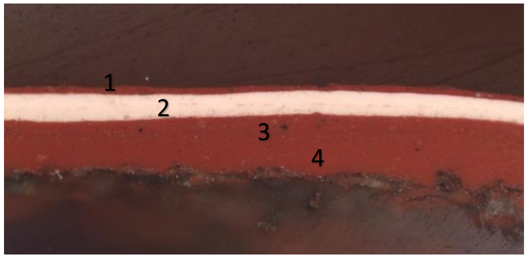
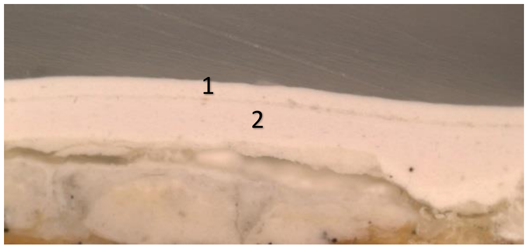
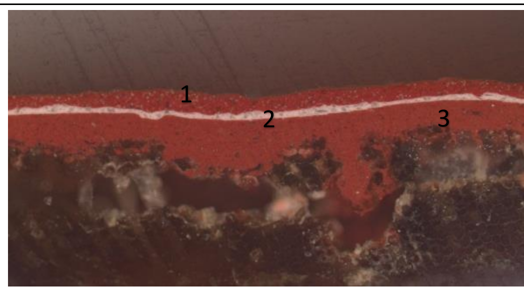
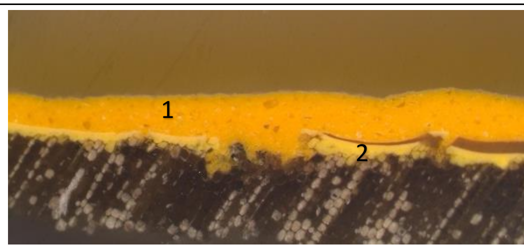
9 https://books.google.ca/books?id=U8a7JhAnLzkC&pg=PA9&lpg=PA9&dq=color+matching+munsell+chips+for+historical+purposes&source=bl&ots=Sf0M04VQCO&sig=gXiyAsRoyaRYJBi0B1xePvwwutI&hl=el&sa=X&ved=0ahUKEwj4lNGtxZPOAhWI6IMKHU09A5kQ6AEIWDAI#v=onepage&q=color%20matching%20munsell%20chips%20for%20historical%20purposes&f=false

10

Table 2: Color matching results

Sample	Image of Cross section under the Optical Microscope	Munsell Colour
Bldg 1 Sample #1		**1 (top finish-white).** Results from the spectrophotometer: 4.5Y 9.1/0.1 Closest Munsell chip: N9.5 (Neutrals) **2 (inner off white layer attached to the top finish).** Munsell chip: 5P 9/1 **3 (coarse off white paint layer)**. Munsell chip: N9 (Neutrals) **4 (innermost off white paint layer).** Munsell chip: N8.75 (Neutrals)
Bldg 1 Sample #2		**1 (top finish-red).** Results from the spectrophotometer: 9.6R 4/5.7 Closest Munsell chip: 10R 4/6 **2 (inner white layer attached to the top finish).** Munsell chip: 5P 9/1 **3 (dark red paint layer)**. Munsell chip: 10R 4/6 **4 (red paint layer).** Munsell chip: 10R 5/6 **5 (red white layer attached to the inner white).** Munsell chip: 10R 4/8 **6 (white coarse paint layer).** Munsell chip: 10PB 9/11 **7 (dark red paint layer).** Munsell chip: 2.5YR 3/6 **8 (white paint layer).** Munsell chip: N9.25 **9 (brown innermost paint layer attached to the white background).** Munsell chip: 2.5YR 4/2
Bldg 2 Sample #3		**1 (top finish-white).** Results from the spectrophotometer: 6.2PB 9.2/0.6 Closest Munsell chip: N9.5 (Neutrals) **2 (inner white layer attached to the top finish).** Munsell chip: 5P 9/1 **3 (off white paint layer)**. Munsell chip: 5PB 9/1 **4 (innermost off white/beige paint layer).** Munsell chip: 5Y 9/1

Bldg 2 Sample #4		**1 (top finish-red).** Results from the spectrophotometer: 9.3R 4/5.7 Closest Munsell chip: 10R 4/6 **2 (inner red layer attached to the top finish).** Munsell chip: 10R 5/6 **3 (white paint layer)**. *Not matched. Very thin layer. Not continuous.* **4 (innermost red paint layer).** Munsell chip: 10R 4/8
Bldg 3 Sample #5		**1 (top finish-white).** Results from the spectrophotometer: 2.8PB 9.2/0.2 Closest Munsell chip: N9.5 (Neutrals) **2 (inner white layer attached to the wood).** Munsell chip: N9.25 (Neutrals)
Bldg 3 Sample #6		**1 (top finish-red).** Results from the spectrophotometer: 9.7R 4/5.9 Closest Munsell chip: 10R 4/6 **2 (inner white layer attached to the top finish).** Munsell chip: 5P 9/1 **3 (red paint layer)**. Munsell chip: 10R 4/6 **4 (innermost red paint layer).** Munsell chip: 7.5R 4/6
Bldg 4 Sample #7		**1 (top finish-white).** Results from the spectrophotometer: 8.5B 9/0.3 Closest Munsell chip: N9 (Neutrals) **2 (inner off white layer attached to the top finish).** Munsell chip: 10PB 9/1 **3 (white paint layer)**. Munsell chip: 5PB 9/1 **4 (innermost off white/beige paint layer).** Munsell chip: 5Y 9/1

Bldg 4 Sample #8		**1 (top finish-red).** Results from the spectrophotometer: 8.5R 4.1/5.5 Closest Munsell chip: 10R 4/6 **2 (inner white layer attached to the top finish).** Munsell chip: 10PB 9/1 **3 (coarse red paint layer)**. Munsell chip: 10R 4/6 **4 (innermost red paint layer).** Munsell chip: 10R 4/4
Bldg 5 Sample #9		**1 (top finish-white).** Results from the spectrophotometer: 4.7B 9.2/0.2 Closest Munsell chip: 5PB 9/1 **2 (inner white layer attached to the top finish).** Munsell chip: N9.25 (Neutrals)
Bldg 5 Sample #10		**1 (top finish-red).** Results from the spectrophotometer: 9.9R 3.9/5.6 Closest Munsell chip: 10R 4/6 **2 (inner white layer attached to the top finish).** Munsell chip: N9.25 (Neutrals) **3 (innermost red paint layer-attached to the wood)**. Munsell chip: 10R 5/6
Bldg 5 Sample #11		**1 (top finish-dark yellow).** Munsell chip: 1.25Y 8/12 **2 (inner yellow layer attached to the top finish and the wood).** Munsell chip: 5Y 8.5/12

References

1. Levison, Henry W. "Yellowing and bleaching of paint films." *Journal of the American Institute for Conservation* 24.2 (1985): 69-76.

2. Garvin, James L. *A building history of northern New England*. UPNE, 2002.

3. Dorge, Valerie, and F. Carey Howlett, eds. *Painted wood: History and conservation*. Getty Publications, 1998.