Synopsis

A Spectroscopic Study of Three Canadian 'Aniline Ink' Stamps

Purpose and Scope: The term 'Aniline Ink' is used broadly to describe a stamp issue that shows prominent bleed of ink through to the gum side. Three Canadian issues are chosen to highlight two possible causes for this effect. Either a separate ink formulation has been used or the original ink formula has been improperly prepared and is defective. Through four different spectrroscopies this question will be addressed.

Importance: The term 'aniline' is closely related to 'fugitive inks'. Williams has given precise definitions of both in his text "Fundamentals of Philately". However, in the cases where a fugitive ink was not required, the question remains as to the cause. If the cause is due to a different dye based pigment or ink formulation, then a separate catalog listing is justified. If the effect results from a poorly prepared ink, then catalogue exclusion is justified.

Treatment: The four spectroscopies used in this study are: X-Ray Fluorescence (XRF), Fourier Transform Infrared (FTIR), reflectance, and wavelength resolved laser induced fluorescence (LIF). The addendum to the synopsis gives a broad overview of each. It is not necessary for the viewer of the exhibit to understand the physics behind the spectrosopies but rather to be watchful for significant differences when comparing spectra of the normal and bleed-through variety. Changes in spectra signal changes in ink chemistry. This is especially true for LIF where only the dyes will exhibit fluorescence. The second derivative of the LIF signal acts as a fingerprint for the dye in use (see the addendum) and gives the strongest conclusions. A summary of the research for each issue follows.

Research:

The Chateau Ramezay Isssue :The Scott catalog does not list an aniline ink variety but the Unitrade Specialized Catalogue of Canadian Stamps does. The exhibit will show through a colour trial die proof, a production colour die proof, a plate proof and an ungummed imperforate pair the intended ink was low fluorescent. Bleed through and much higher fluorescence started to appear early in the production and was most prevalent near the end of the production run. There is no change in the frequency of the LIF peak position during the entire run. This along with narly identical XRF and FTIR spectra show that the aniline ink variety is a 'bad batch'.

The 2¢ Red Admiral Issue of Canada: Neither catalogue lists an 'aniline ink' variety although various authors have documented bleed through problems for stamps from plates 17, 37 and scattered instances between plates 81-94. Through extensive use of plate blocks, the exhibit shows the pre WW1 aniline ink variety of plate 17 has identical LIF spectra, closely related XRF and FTIR spectra when compared to nearby plates of the same printing time. This is indicative of a bad batch. The bleed through for plates 81-94 vary noticeably in their LIF spectra from the other plate blocks. Within this group, the fluorescence clearly partitions into two sub-types, one associated with bleed through. The bleed through plates are devoid of chromium while the normal plates have notable chromium levels *except for one outlier*. It was originally thought that

the lack of chromium signaled a different ink has been used for the bleed-though stamps. However, this is an example where one experiment too many has thrown an hypothesis into question.

The Prince George 1911 Issue of Newfoundland: Catalogues acknowledge two major varieties for this issue, with different shade definitions. All note the very strong bleed though of one variety. The exhibit confirms that different inks were used based on the XRF and LIF spectra. The differences in the elements present are slight with the non bleed-though higher in lead . However, the LIF spectra are shifted by 9 nm, enough to give a shade change discernable by eye. This has confirmed a different ink but it is still a defective ink with inconsistent bleed-through. The exhibit contains a die proof (in light blue) that is possibly the die proof mentioned by Pratt in his BNAPS article (see below). He has reported a large die proof on thin wove paper and in steel blue colour. This copy is stamp sized on cardboard and is light bleu. It has a radically different chemistry than the production issues. The exhibit also contains an archive, defaced copy reportedly from De La Rue & Co.(Eastern Auctions Catalogue, June 2022).

Rare or Unusual Items:
The exhibit contains a rare (only 12 known) gummed imperforate pair (Chateau Ramezay Scott 245a) along with the scarce aforementioned die proofs (Chateau Ramezay). The trial colour die proof from Newfoundland appears genuine but has not been expertized.

Relevant Literature:

FTIR Methods**:** Harry Brittain, " Use of X-Ray Diffraction and Infrared Absorption Spectroscopy for the Study of Paper and Ink in Postage Stamps". Proceedings of the Fourth International Symposium on Analytical Methods in Philately Edited by Thomas Lera and John H. Barwis. 2020 pp 1. (See PowerPoint Presentation on FTIR near the middle) https://drive.google.com/file/d/10TIzB5goE3gZVuWT3tv3n9B4X8YpqTaC/view
XRF and FTIR Methods: Chown, Steve, Thomas Lera and Charles Neyhart "Regulatory ink change and an unrecognized color variety: the 25c Frederick Douglass definitive", The United States Specialist 85 (11) 1017 (2014) pp 501- 512.
Chateau Ramezay: Neyhart, Charles, "'Aniline Violet' and Synthetic Inks", Book Reports: Northwest Philatelic Library, Vol 6, Issue 8, Jan 2010.
2¢ Red Admiral Issue of Canada: Marler, George C. 1982. The Admiral Series of Canada. State College, PA. American Philatelic Society, p292 (For reference to aniline ink).
Young, D. A. 1954. Admiral Addict: Analine (sic) Variety. Canadian Philatelist, 5(1):3
'Newfoundland Aniline Ink': Thompson, Anthony, ""Aniline" Stamps of Newfoundland - Fluorescence and Bleeding", BNA Topics , Vol 77, #1, Whole #562 (Jan/Mar 2020), p. 32(16)
Pratt, Robert, " Additional Data on the Stamps of Newfoundland", BNA Topics, Vol 26(4) Whole #277 (Apr 1969), p.95.
Strange, Arnold "Further Information on the Stamps of Newfoundland 1911-1928", London Philatelist Vol 67, #791 (Oct 1958), p.172.

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Relevant Research Articles by the Exhibitor:

R.H. Judge “Philatelic Applications of Wavelength Resolved Fluorescence”, Proceedings of the Fourth International Symposium on Analytical Methods in Philately Edited by Thomas Lera and John H. Barwis. 2020 pp 71-78

R.H. Judge “Chemistry of Aniline inks, 2-cent Admiral Issues of Canada”. Proceedings of the Third International Symposium on Analytical Methods in Philately.” Edited by Susan Smith and John H. Barwis, 2017, pp 11-24

R.H. Judge “The Admiral Issue of Canada: A Colorimetric and XRF Study of the Carmine 2¢ Issue.” Proceedings of the Second International Symposium on Analytical Methods in Philately Edited by John Barwis and Thomas Lera 2015, pp 21-30

Portch, Garfield, John M. Walsh and Richard H. Judge. “Does a ‘Prussian Blue’ Shade Variety Exist for the 15c Newfoundland 1919 Trail of the Caribou Issue? ” The Newfoundland Newsletter, 178 (2020) pp 7-10.

R.H. Judge “Two Canadian 'Aniline' Stamps: Two Different Spectroscopic Tales”, BNAPS, Newfoundland Study Group, Study and Regional Group videos (2nd from the bottom). Must be a member of BNAPS to view.

Addendum:

As an aid in interpreting the spectra shown here, additional information about the science behind the exhibit is presented.

The XRF spectra will capture the elements present in the whole stamp: ink, paper and gum plus any impurities within the paper. Also some background from the instrument is present and accounts for weak iron, nickle and copper peaks present in all spectra. This XRF instrument will not be able to observe elements lower than sodium and thus organic compounds like cellulose (paper) will not be seen.

The FTIR will be able to identify molecular and ionic compounds in the ink. Because the sampling area is small and since the infrared beam from this type of FTIR only penetrates microns into the surface of the stamp, potentially only the ink can be studied. However, with engraved stamp, ink free areas are present and thus the paper may also be seen in lightly engraved areas. These extra peaks due to paper are easily identified as microcrystaline cellulose. However, they do obscure the peaks from other compounds. FTIR is often called a fingerprinting technique. Absorption peaks from pure chemical compounds have nearly unique patterns. If this pattern is seen in the FTIR spectrum of a mixture, it is considered proof of its presence. This is the case for Prussian blue with a series of sharp peaks where one is due to the cyanide group (CN) that sits alone at ~2100 cm^{-1}. Other compounds identified in this study are calcium carbonate, barium sulphate and cellulose identified by a match to pure compounds recorded on my instrument. FTIR gives the most convincing proof for Prussian Blue and these other compounds.

Reflectance spectroscopy records the light reflected from the surface of stamp when white light impinges on the surface. The pigments in the ink will absorb (remove) specific bands of colour from the white light. Thus a blue coloured stamp will have pigments that remove the greens and reds from the white light and will show a peak reflectance in the blue end of the reflectance spectrum (400-475) nm. This is the case for the blue stamps studied here. Reflectance spectroscopy is not an excellent diagnostic technique for segregation of shades in stamps. Small variations in ink density, stamp paper whiteness, paper and pigment aging along with environmental factors will alter the reflectance profile and give the impression of shade differences. However, significant peak shifts and profile differences do signal a shade change. A special application here is the reflectance spectrum from the gum side of the stamp. In the case of the Chateau Ramezay issue, red dye has diffused through the paper of the bleed-though stamp and will appear as a dip (darkening) of the normally smooth, curved line of the normal gum/paper at around 600 nm. The depth of the dip is a (very) rough estimate of the degree of bleed-though. An attempt is made to correlate the degree of bleed-though to the LIF intensity (see below).

Wavelength Resolved Laser Induced Fluorescence (LIF) is new to philately. A violet laser (405nm) is used to excite fluorescence from the stamp. Only organic pigments in the ink that still contain some of the original dye, either intentionally or by error, will fluoresce. Unfortunately, the stamp paper will also weakly fluoresce and this fluorescence is always present from engraved stamps. In LIF spectroscopy, the induced fluorescence from the UV laser is directed into a spectrograph to give a spectrum of wavelength (nm) vs intensity. In the case of the stamps studied here, the peak of the ink fluorescence is to longer wavelengths (red shifted) from the paper fluorescent peak. Since the ink may contain more than one dye and this, coupled with the paper fluorescence, results in a convoluted spectrum. As a consequence, no sharp peaks are seen but instead rounded peaks with multiple shoulders is the result. The spectrum can be de-convoluted by performing the second derivative of the spectrum. The negative going peaks of the 2^{nd} derivative spectrum are usually well defined and show the peak and shoulder positions of the paper and dyes well separated from each other. I have found this to be a sensitive method for identifying changes in dye structure or functional group. The experience with the 115 plate blocks of the Admiral stamps showed the method to be reproducible and to act as a fingerprint for changes in the dyes of a stamp.