Western Michigan University

REPORT

INSIGHT INTO PAPERMAKING AND INK CHEMISTRY OF “U.S.THREE-CENT BANK NOTE

by

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INTRODUCTION

This article aims to clarify differences in substrate, printing procedure, and ink quality of Unites States Three-Cent stamp, or bank note. According to the research done by John Barwis [Barwis, 2001], more than 6.6 billion of these stamps were printed during years 1870 - 1883. Very likely, this stamp was printed on different paper stock, using different printing plates, possibly different ink chemistry printed on various printing presses [Barwis, 2001]. The differences in paper stock, and print plate relief combination as reported by Barwis are illustrated in the **Figure 1**.

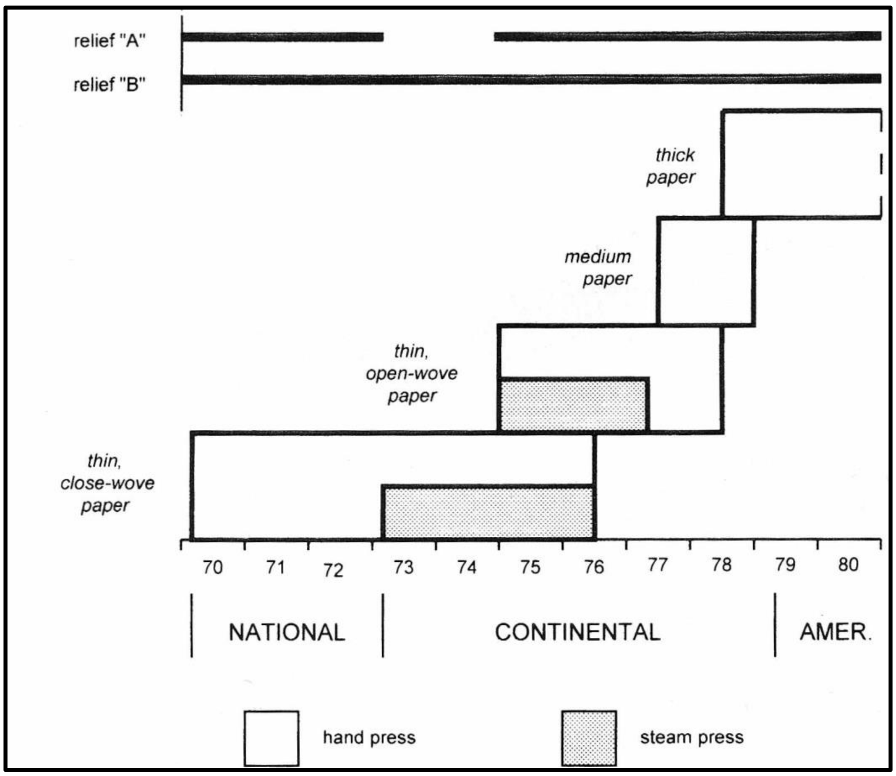

Figure 1: Production of 3- cent stamp on variety of paper substrates [Barwis, 2001]

Today, stamps are printed mostly by gravure process, formerly known as intaglio. The image used to be cut or etched below the surface of the non-image area. Intaglio means to “etch” or to “cut”. Using flat plates, intaglio first appeared in the early 1500s. Intaglio plates were cut into the surface of the image carrier. Easier than hand tool engraving was acid etching, which became next step in modern gravure process development. In this process, the artist draws the art onto the coating, and then acid creates the grooves in the metal plate. Not only does this make it easier on the artist, but the final print has a different, freer look than engraving. This was a major step forward for the gravure process and high quality printing in general as known today and used for printing stamps, security documents and currency, but also products like decorative laminates, furniture, or flooring [Pekarovicova et al, 2009]. Early presses were using high pressure and were using flat bed plate and press design, which later developed into rotary printing presses. The image carrier for Three cent American was made using following steps:

1. A steel die was hand-engraved with the three-cent design.
2. The engraved die was case hardened in a furnace using the carburization technique patented by Perkins in London.
3. A Steel roll was impressed into the hardened die.
4. The roll was then case hardened.
5. The hardened roll was then used to impress 200 images of the design into a steel printing plate.
6. The plate was then case hardened.

Multiple plates of the three-cent design were prepared using the above steps, and used to print the stamps.

Material used for early papers was cotton and cotton rugs. First pulp, manufactured from wood, had been made in Germany by soda process in 1854 [Smook, 2002]. Soda process employed strong alkaline solution of sodium hydroxide for wood or straw delignification. Sulfite pulping process, which was acid process, involving sulfurous acid (H_2SO_3) and calcium bisulfite $Ca(HSO_3)_2$ was patented in USA in 1867, and the patent was first commercially used approximately around 1874. Commercialization of sulfite process was very fast during following decades, making it the most important pulping process worldwide. Kraft pulping process is alkaline, involving cooking the wood chips with solution of sodium hydroxide and sodium sulfide (Na_2S). It was invented in 1884 in Germany [Smook, 2002]. Kraft pulping was commercially first applied in Sweden in 1885-1890 [Smook, 2002; Biermann, 1996]. Process became very popular due to better strength properties of pulp, easy recovery of chemicals, and wider variety of wood species applicable for delignification.

Early inks used for printing stamps in 19th –early 20th century contained elements such as sulfur, lead, iron, potassium, calcium, lead, mercury, sulfur, aluminum, chromium and barium [Oliaiy et al, 2009; Ferrer, 2006]. These elements were components of various inorganic salts like $Cr2O_3$ and $PbCrO_4$, making up green pigments, $Pb(OH)_2$ and Pb_3O_4 inorganic orange pigments, HgS (cinnabar) and hematite, Fe_2O_3,, being components of red pigments. Prussian blue ($Fe_4[Fe(CN)_6]_3$) is likely component of blue ink compositions for stamps printing [Castro et al, 2008]. Combination of Prussian blue, a synthetic iron (III) hexacyanoferrate (II) pigment ($Fe_4[Fe(CN)_6]_3$. 14–16 H_2O) and chrome yellow ($PbCrO_4$) was used for green inks. As an example, this pigments combination was found on 1858–62 early Mauritian 4d green Britannia-type postage stamp [Chaplin, 2004]. When the stamp was printed with premixed Prussian blue and chrome yellow, the ink pigment was called "chrome green", while forged green stamps were sometimes made by coating blue stamp with solution of chrome yellow [Chaplin, 2004]. Baryte ($BaSO_4$) and calcium carbonate ($CaCO_3$) served as white extender for pigments [Oliaiy et al, 2009; Odenweller, 2009], carbon black (C) was found to be pigment used in cancellation inks [Chaplin, 2004].

Ultramarine blue, a sodium aluminosilicate mineral ($Na_8[Al_6Si_6O_{24}]S_n$) was sometimes found in between pulp fibers of the stamps, most likely with the aim to enhance the brightness of the paper of the stamp, as found in forgeries of Mauritius stamps [Chaplin, 2004]. Some inorganic compounds were added to ink formulations for security reasons. Good example is potassium prussiate or potassium hexacyanoferrate ($K_4\{Fe(CN)_6\}\cdot 3H_2O$), which was found during analysis of one-penny stamp printed in Britain in 19th century [Ferrer, 2006]. This chemical used to be added into ink to make it more difficult to erase cancellation marks on stamp with the aim to reuse it. Fraudulent removal of cancellation marks used to be done with alkaline solutions, which as a side effect caused destruction of image by decomposing potassium hexacyanoferrate [West Fitzhugh, 1997], resulting in blueing effect of the postal stamps [Ferrer, 2006].

The aim of this work was to analyze chemistry and morphology of paper the stamps were made of, and figure out how many paper types were involved in production of these stamps. Another question was to find out if the stamps were printed with the same type of ink, or if several different types of inks were involved. Thus, the key questions were:

- How should the papers used by each company be best described and classified?
- Are there actually four distinct types? If not, how many are there?
- Philatelists think National BNC used only one kind of paper, Continental BNC two types, and American BNC one type (or possibly two). This hypothesis needs to be proved or disproved.
- What is the range of variation of key parameters such as composition, fiber morphology and charge, and measurable paper properties *within* each fundamental paper type?
- What causes the surface texture in Continental's "ribbed paper"?

EXPERIMENTAL

Totally, 402 stamps were used for analysis. The colors are as described in the Scott Specialized Catalogue of United States Postage Stamps, which are generally accepted by collectors and specialists. All stamps were soaked in distilled water to remove gum and hinge remnants. They were then air dried, all in a uniform manner. Issue and amount of stamps from individual categories are listed in the **Table 1**.

Table 1: Description of analyzed stamps

Issue	Printer	Stamps	Analysis	Notes
1870	National B.N. Co.	81	Paper	How many different paper types?
1870	National B.N. Co.	9	Ink	What is the cause of color variation?
1873	Continental B.N. Co.	74	Paper	How many paper types?
1873	Continental B.N. Co.	14	Ink	What is the cause of color variation?
1873	Continental B.N. Co.	14	Paper	Origins of "ribbing" and extraneous fibers?
1878	American B.N. Co.	75	Paper	How many different paper types?
1878	American B.N. Co.	9	Ink	What is the cause of color variation?
1881	American B.N. Co., re-engraved	115	Paper	Same paper as 1878 issue?
1881	American B.N. Co., re-engraved	11	Ink	What is the cause of color variation?

Bending resistance
Stamps bending resistance was measured following T543-om-00 TAPPI Standard. Gurley Bending resistance tester was employed. Bending resistance of paper is done by measuring the force required to bend a specimen under controlled conditions. Customary bending index was calculated by dividing bending resistance with stamp weight.

Porosity
Oil Gurley porosity was measured at least for five times at each stamp using Technidyne Profile Plus instrument (Technidyne Co, New Albany, IN). Oil Gurley porosity measures time in second necessary to pass 100mL of air through certain area of substrate. Thus, the higher the number, the lower is the porosity of the substrate. Because the stamp was smaller than instrument measuring land, two layers of PET sheet (100x80mm) were taped together to create a folder and circular aperture of 9mm was cut through it. Stamp was placed into PET folder and porosity was measured on the perforated area of 63.6 mm^2.

Fiber analysis
Stamps were cut in half and immersed in cuvettes filled with 20mL of 0.05N NaOH and glass beads. Samples were shaken for 12 hours to separate fibers for fiber analysis. Fiber suspensions were then analyzed using FQA Fiber Quality Analyzer (Op Test Equipment, Inc.)

Metals Analysis

Metals in the ink were measured using EAGLE III µProbe – Energy-dispersive X-ray Fluorescence Spectrometer. All the measurements were done in vacuum. Detector was cooled using liquid nitrogen (MCT Cooled). Aperture: 150 um x 150 um, Signal filter: Beer-Norton. Conditions of the measurements are given below.

Anode: Rh (Rhodium)

High voltage: 10-40kV

Current: 20-1000µA

Diameter of X-ray beam: 300-1000 µm (monocapilary)
Time of measurement: 100s
Detector: semiconductor Si (Li) with active area 30 sqmm
System Resolution for 5.9 eV Manganese Ka X-rays (Taken with a radioactive Fe55 source): 132.7 eV F.W.H.M. at 1 KCPS
Amplifier Resolution Time: 17µs

IR Spectra
IR spectra were measured on the paper using Thermo Scientific Nicolet iN10 MX - Fourier Transform Infrared Spectrometer equipped with MCT/A detector, KBr Beam splitter. The conditions of measurements are given below.
Sample spacing: 2.0000. Number of sample scans: 128; Collection length: 24.7 sec; Resolution: 8.000; Levels of zero filling: 0 Number of scan points: 4384; Number of FFT points: 4096; Laser

frequency: 15798.0 cm^{-1} Interferogram peak position: 2048; Apodization: N-B Strong; Phase correction: Mertz ; Number of background scans: 128; Background gain: 1.0

DATA DESCRIPTION- Number of points: 863; X-axis: Wavenumbers (cm-1); Y-axis: Absorbance; First X value: 674.9634; Last X value: 3999.6401; Data spacing: 3.856934; Digitizer bits: 24; Optical velocity: 2.5317; Aperture: Medium resolution; Sample gain: 1.0; High pass filter: 200.0000; Low pass filter: 20000.0000.

Color

X-Rite 530 Spectrodensitometer with 4mm aperture was used to measure CIELAB color values of stamps. D50/2 viewing conditions were used. Color difference was determined by means of ΔE_{ab} color difference calculation.

RESULTS AND DISCUSSION

Paper Properties

Bending Index

Unites States Three-Cent stamp or bank note, has dimensions, which are too small for standard TAPPI Test methods, used in paper industry. Therefore, only tests which could be modified for these stamps were applied. Bending resistance using T543-om-00 TAPPI Standard was done, only using modified dimensions. Bending resistance was divided by weight of stamps and custom "Bending index" was calculated as shown in the **Figures 2-5**. Average bending index for all companies were calculated (Table 2). From the **Table 2** is apparent, that the bending resistance was decreasing from oldest stamps (National) with bending index of 116 g^{-1} to 89 g^{-1} in American BN 1881 edition, and thus most likely every company was using different paper, the oldest being most bend resistant.

Table 2: Bending Index of Unites States Three-Cent stamp

Stamp	Bending Index/±STDV [g^{-1}]
National BN	116±19.9
Continental BN	107±25.1
American BN 1878	103±17.1
American BN 1881	89±16.9

In order to distinguish if there were more different paper types used within each company, population distribution was calculated for each manufacturer (**Figures 6-9**). It is likely that National BN used two discrete types of paper, one with bending index 85-115 GU/g reaching 52% of total tested samples, the other was stiffer with bending index 115-159 GU/g (**Figure 6**).

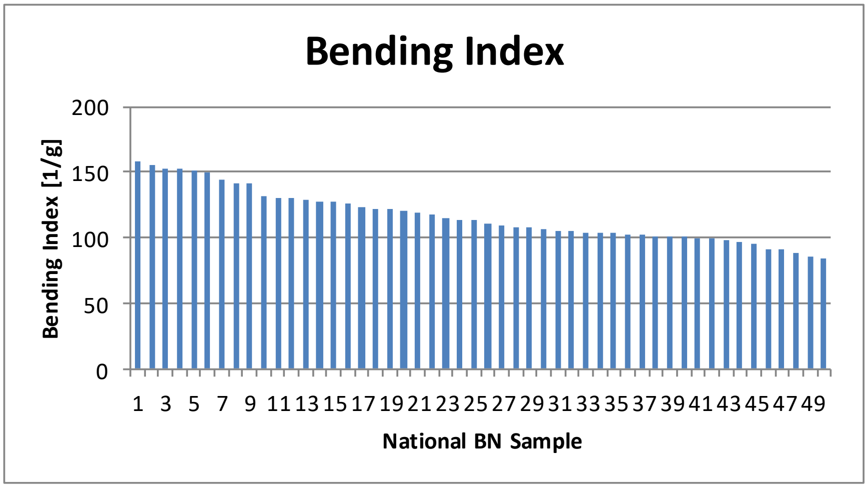

Figure 2: Bending Indices of National BN Stamps

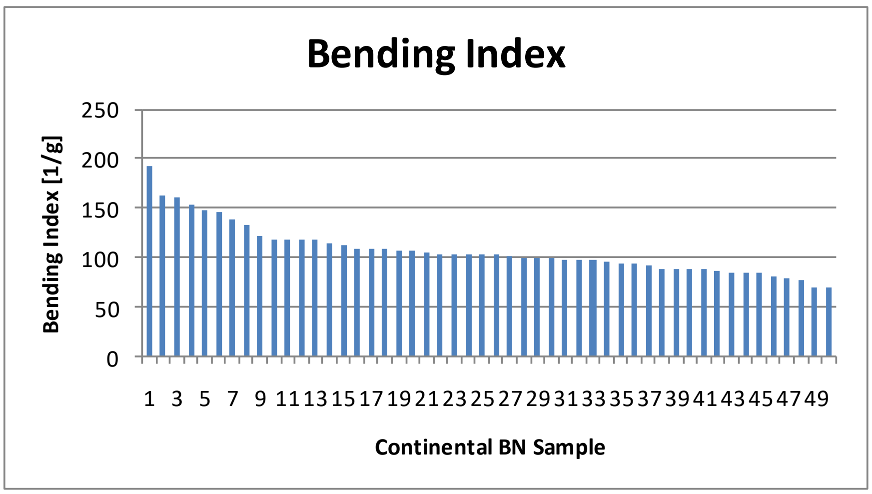

Figure 3: Bending Indices of Continental BN Stamps

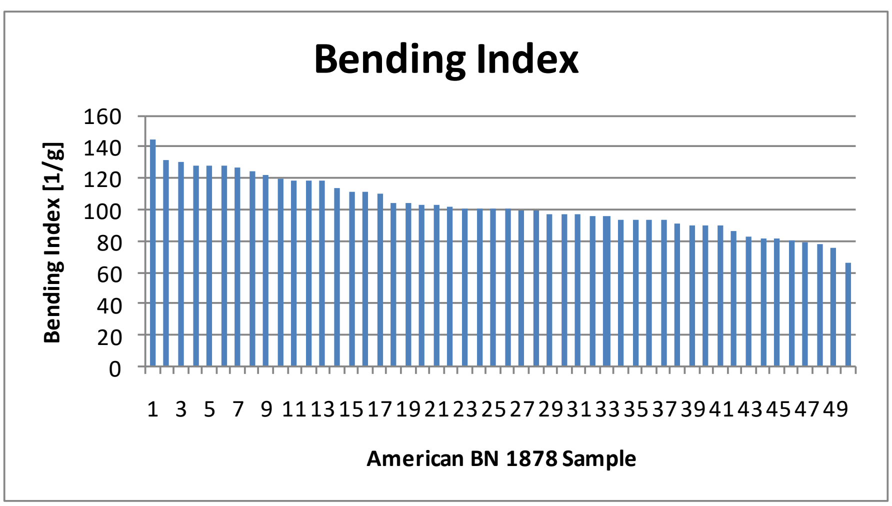

Figure 4: Bending Indices of American BN 1878 Edition

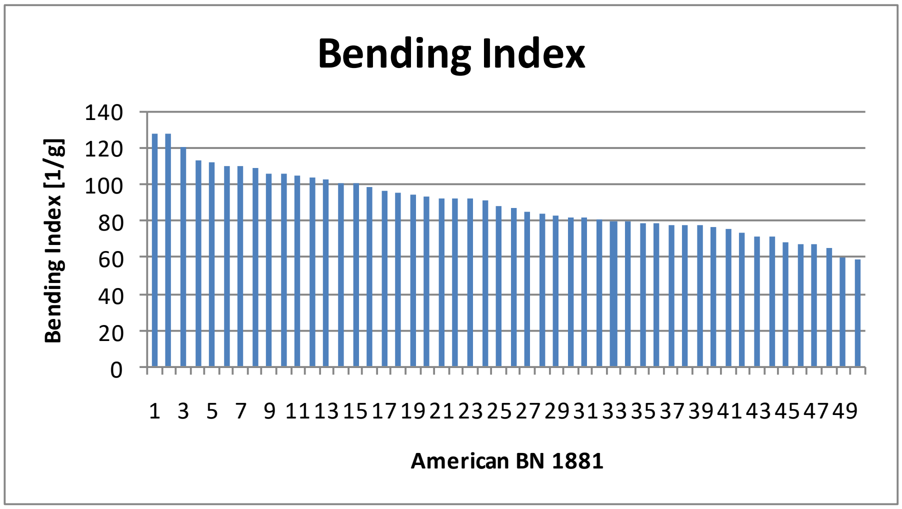

Figure 5: Bending Indices of American BN 1881 Edition

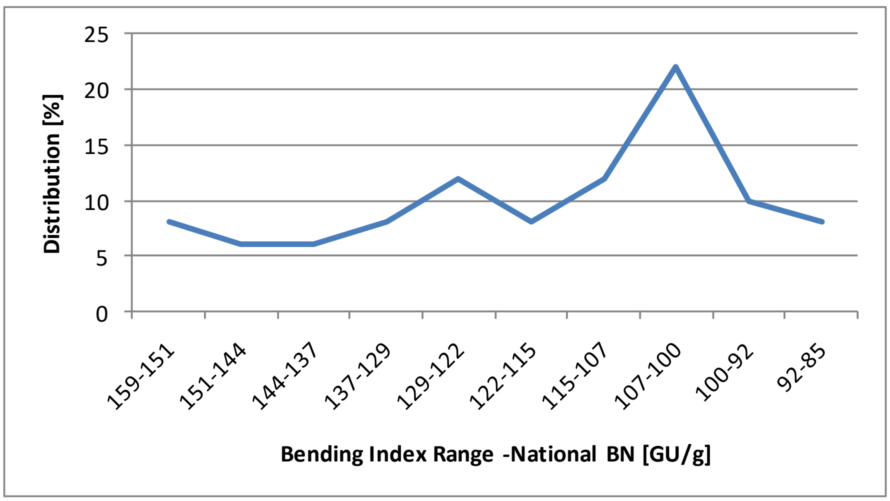

Figure 6: Population Distribution of National BN stamps (GU Gurley Units)

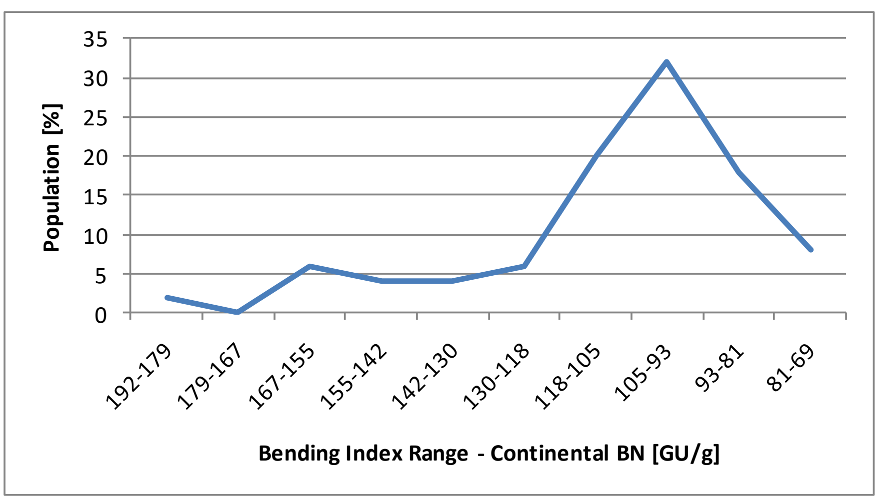

Figure 7: Bending Index Population Distribution of Continental BN

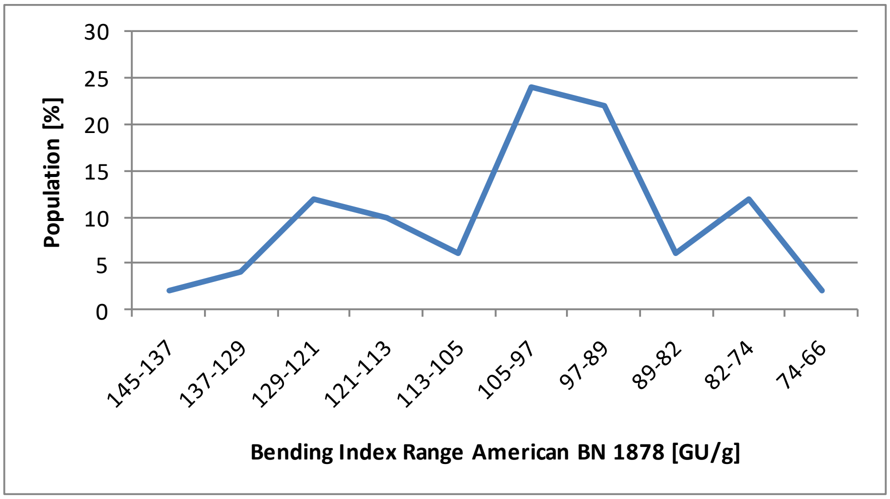

Figure 8: Bending Index Population Distribution of American BN 1878 Edition

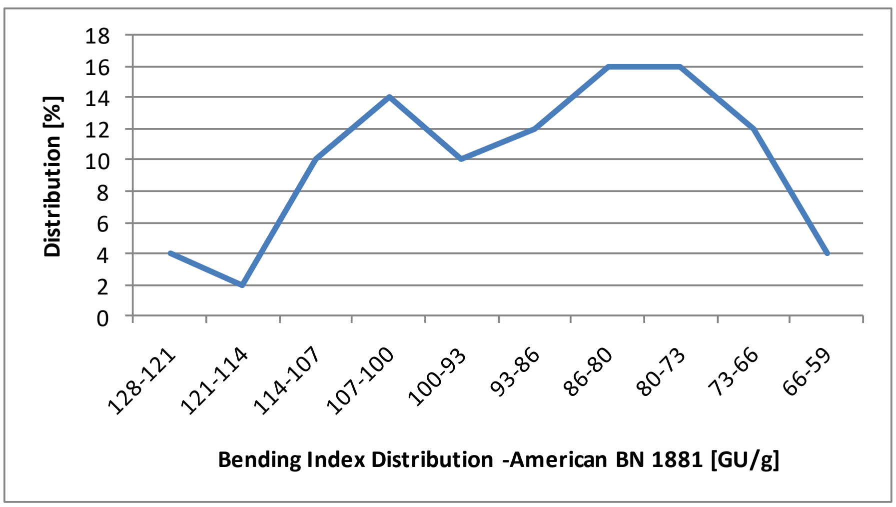

Figure 9: Bending Index Population Distribution of American BN 1881 Edition

Continental BN population (88%) had the bending index in the range 69-142 GU/g, the rest was within 142- 192 GU/g bending index (**Figure 7**). Possibly three different papers were used in American BN Company within first period (1878), first one (20%) with bending index 66-89 GU/g, second (52%) with bending index 89-113 GU/g , and third (28%) had bending index in the range of 113-145GU/g (**Figure 8**). Later, re-engraved edition (1881) was printed on two different papers, one (70% of population) with bending index in the range 59-100GU/g, and the other with bending index in the range of 100-128GU/g (**Figure 9**).

Fiber Analysis

Stamps were further analyzed according to their fiber length. Stamps for fiber length analysis were chosen from maxima of the peaks of bending indices (**Figures 6- 9**). As can be seen from **Figure 6**, maximum stamp population was found to have bending index between 129-122 and 107-100, thus stamps from those two regions were chosen for fiber analysis. Accordingly, at Continental BN, two maxima were found, having bending indices between 155-167, and 93-

105, thus fiber analysis was done for stamps from that region. Stamps from other printers were also selected using this scheme, as seen in the **Table 3**.

Table 3: Selection of Stamps for Fiber Analysis

Type of the Stamp	Range of Bending Index Maximum [1/g]	Stamp Number
National BN	122-129	3
National BN	100-107	24
Continental BN	155-167	42
Continental BN	93-105	4
American BN 1878	121-129	20
American BN 1878	97-105	27
American BN 1878	74-82	26
American BN 1881	100-107	40
American BN 1881	73-80	47

Repulping of the stamps was not equal for all the stamps. Some stamps were repulped easily (Example #1/42, **Figure 10**), and some probably due to internal sizing was difficult to disintegrate (Example 1/24, **Figure 10**). This is also a proof that National used two different paper types, one of which was probably internaly sized (Right, **Figure 10**). Figure 11 shows that stamps could be soaked in colorants after printing. During repulping, bluish coloration was found in some Continental BN stamps repulped slurry, while in American, yellowish bleed was observed (**Figure 11**). Repulping revealed that some of the Continental BN were also internally sized, which resulted in dificulties during repulping procedure (**Figure 11**, Left). This fact confirms again that the Continental BN was probably using two types of paper, one of which was internally sized. Bluish color could originate from potassium prussiate or potassium hexacyanoferrate ($K_4\{Fe(CN)_6\}\cdot 3H_2O$), which used to be added into ink to make it more difficult to erase cancellation marks on stamp with the aim to reuse it [Ferrer, 2006]. Indeed, later during this work was found iron in ink stamps of Continental issue. It is possible that the ink contained hexacyanoferrate besides another iron containing pigments.

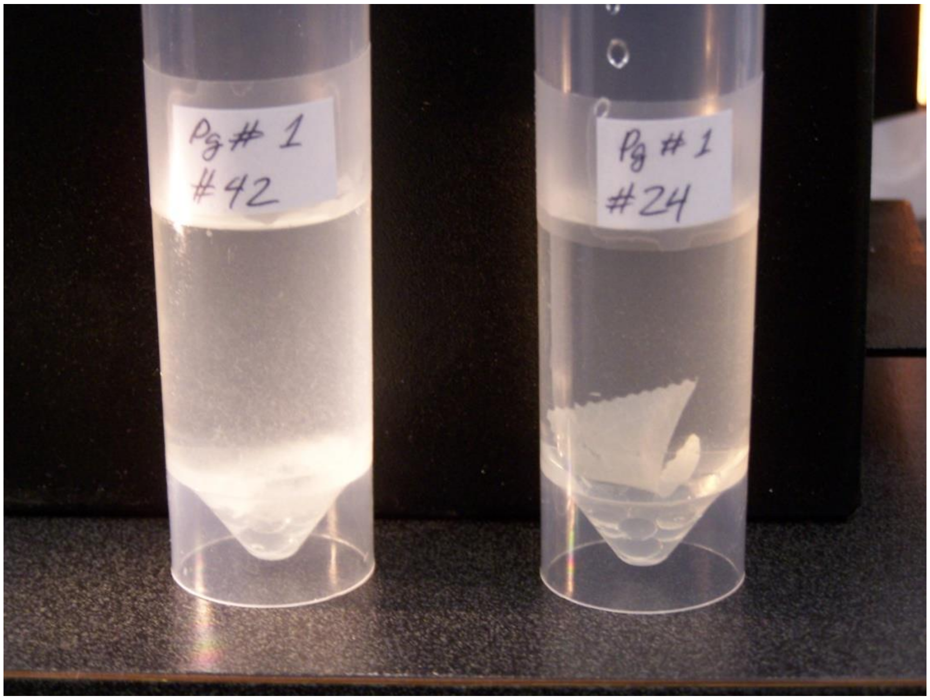

Figure 10: Repulping of National BN stamps prior to fiber analysis

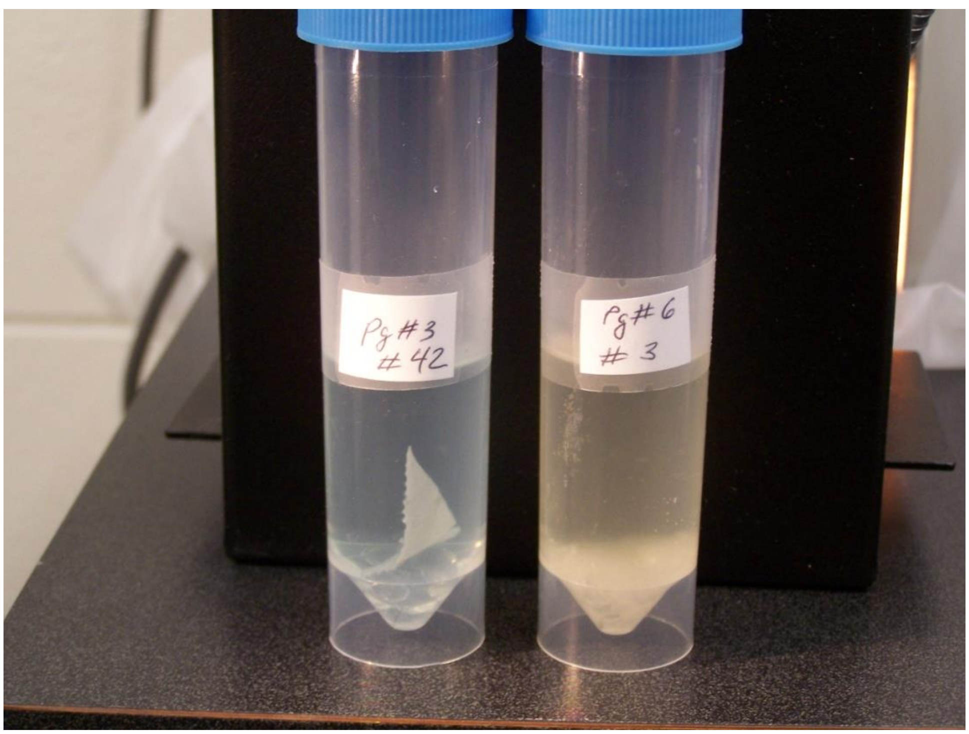

Figure 11: Repulping of Continental BN stamps (Left) and American 1878 (Right) prior to fiber analysis shows bluish coloration (Left) and yellowish color of repulped stamp slurry (Right)

To eliminate very short fibers, mean length, length -weighted data were considered in data analysis, as shown in the **Figure 12**. The longest fibers were found in National BN stamps, ranging from 0.679 to 0.732 mm. Of course, it is not original length of fibers, but only that after fiber disintegration. Shortest fibers were found in Continental BN edition stamps, ranging from 0.532 to 0.614 mm. Graph also shows that each bending index range had different fiber length (**Figure 12**), thus probably produced slightly different paper properties.

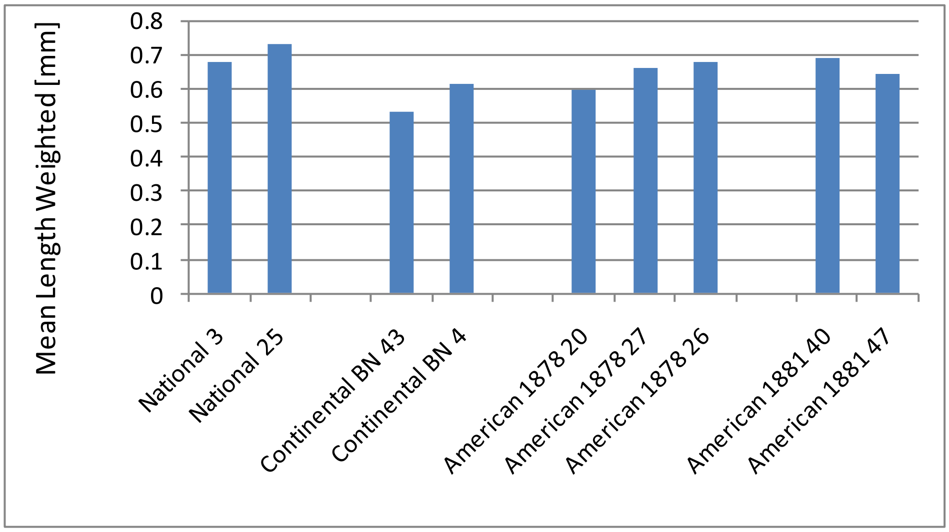

Figure 12: Mean Fiber Length (Length Weighted)

Kink index and fiber width were also analyzed on Fiber Quality Analyzer (**Table 4**). Kinks are defined as abrupt changes in fiber curvature, which may be caused by micro compressions, or misaligned zones in cellulose microfibrils. More kinks occur in fibers, more damage or harsh treatment occurred during processing. Increased number of kinks in fibers may lead to loss of fiber strength [Hakanen, 1995]. Continental BN had highest kink index of 2.76 (mm^{-1}); the lowest was found in National BN (1.63-1.64 mm^{-1}). Fibers from National BN has very similar kink index, thus maybe very similar history of fiber processing (**Table 4**), but fiber width was very different (21.7 and 22.6 µm). Continental BN had quite different kink indices (2.07 and 2.76 mm^{-1}), as well as different fiber width (21.1 and 22.9 µm), thus different fibers could be used, and history of processing was also different. American BN 1878 had fibers with kink indices in the range of 1.95 to 2.22mm^{-1}, and had width of fibers in the range of 19.6-22.6 µm (**Table 4**). The kink indices found in American 1881 edition were in the range of 1.79-1.89mm^{-1} with fiber width 20.7-21.3 µm. Overall, narrowest fibers were found in American BN 1878 edition (19.6-20.6 µm), the widest in National BN series (21.7-22.6 µm). Width of most common wood pulp fibers usually fall within interval 30-45 µm [Kocourek and Stevens, 1993], which most likely indicates that stamp paper was made of annual plant materials.

Table 4: Selected morphological features of stamp fibers compared to different plant material fibers

Plant type	Kink Index [mm^{-1}]	Fiber width [µm]	Source
Sugar cane bagasse	1.89	20.8	[Agnihotri, 2010]
Eucalyptus tereticornis	2.15	14.2	[Panwar, 2001]
Eucalyptus robusta	N/A	19	[Panwar, 2001]
Leuceana leucocephala	N/A	23.3	[Malik, 2004]
Softwood	N/A	38-43	[Sood, 2007]
Mixed hardwood	N/A	18-39	[Sood, 2007]
Bamboo	N/A	15-17	[Sood, 2007]
Straws	N/A	11- 14	[Sood, 2007]
Kenaf	N/A	21.0	[Mossello,2010]
Wheat straw/bagasse	2.83	15.5	[Sood, 2007]
Fiber from "National"BN 3	1.64	21.7	[Pekarovic, 2011]
Fiber from "National " BN 25	1.63	22.6	[Pekarovic, 2011]
Continental BN 43	2.07	21.1	[Pekarovic, 2011]
Continental BN 4	2.76	22.9	[Pekarovic, 2011]
American BN 1878 20	2.22	19.6	[Pekarovic, 2011]
American BN 1878 27	1.95	19.6	[Pekarovic, 2011]
American BN 1878 26	1.99	20.6	[Pekarovic, 2011]
American BN 1881 40	1.89	21.3	[Pekarovic, 2011]
American BN 1881 47	1.79	20.7	[Pekarovic, 2011]

Oil Gurley Porosity

Oil Gurley porosity was measured on stamps (**Figures 13-16**). Measurements were done on printed stamps, which were soaked in water to remove adhesive, and these stamps have unknown history of usage. It is suspected that residual adhesive may be present on some areas or thin spots and damage on others. Therefore, very large non-homogeneity of measurement with very high standard deviations was found during all measurements. Average porosity values are listed in the **Table 5**. Average porosity is highest at National BN (33.45 sec/100mL), followed by American 1881 (40, 02sec/100mL), and lowest at 1878 American stamps (75.18sec/100mL). Porosity of American 1881 series is much higher than 1878 series, but it is also more uniform with lowest standard deviation.

Table 5: Average oil Gurley porosity of different issue of "US Three Cent" stamps

Issue/Printer	Average Porosity [sec/100mL]	Standard deviation [sec/100mL]
1870/National BN	33.45	14.05
1873/Continental BN	50.89	21.59
1878/American	75.18	33.39
1881/American (Reengraved)	40.02	12.54

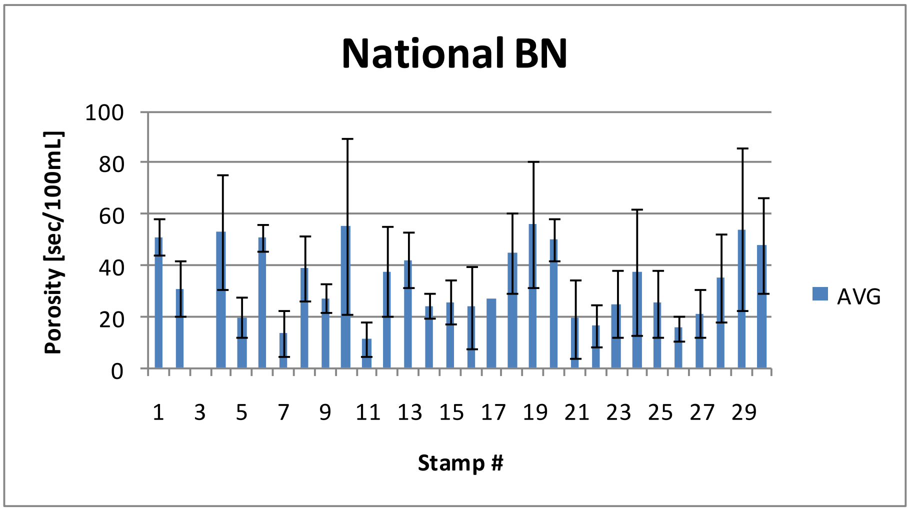

Figure 13: Oil Gurley porosity of National BN Stamps

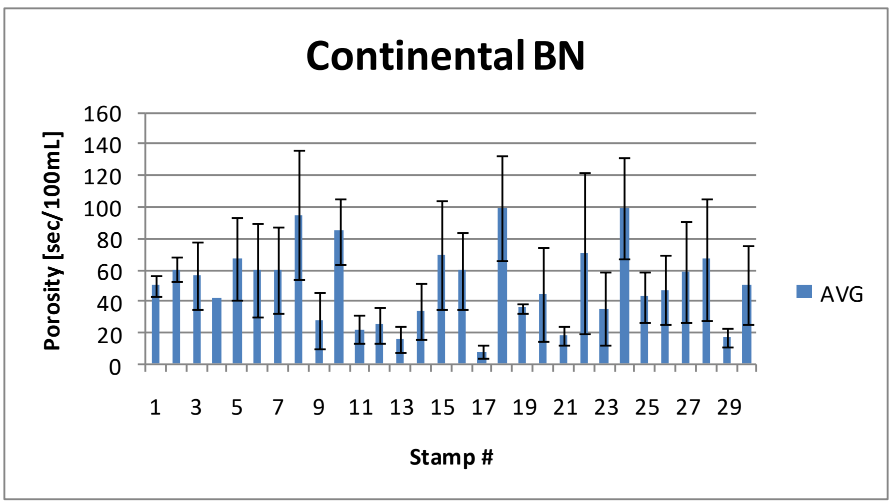

Figure 14: Oil Gurley porosity of Continental BN series

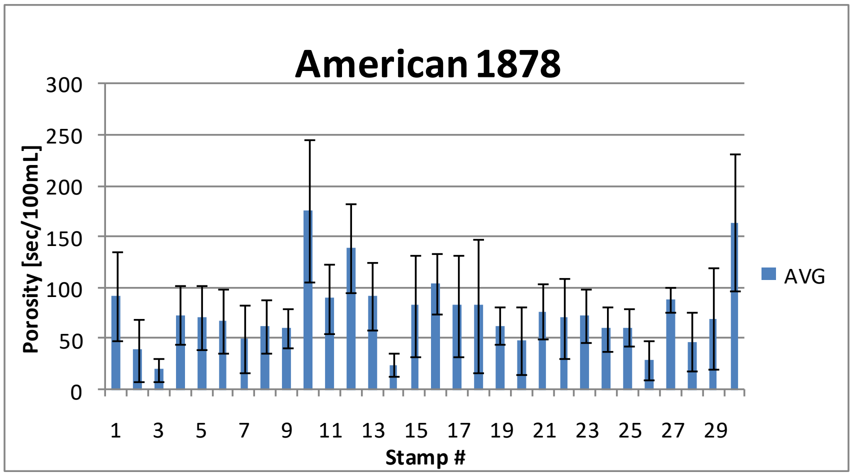

Figure 15: Oil Gurley Porosity of American 1878 series

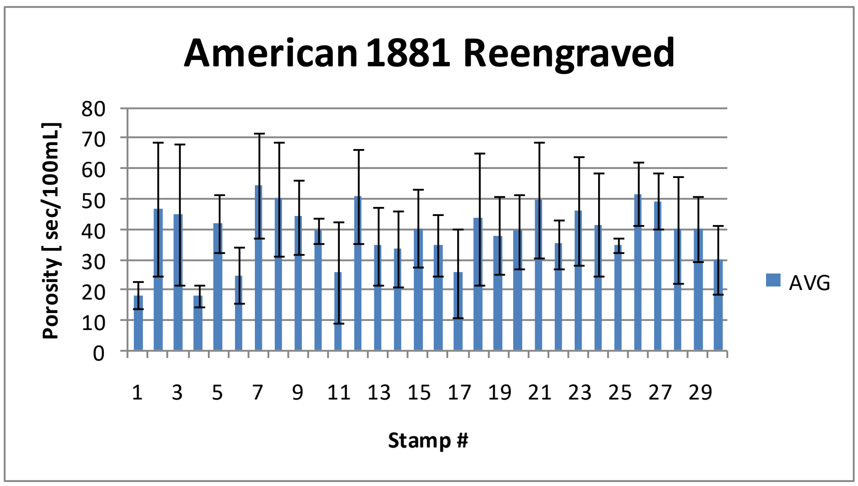

Figure 16: Oil Gurley Porosity of American 1881 Reengraved Stamps

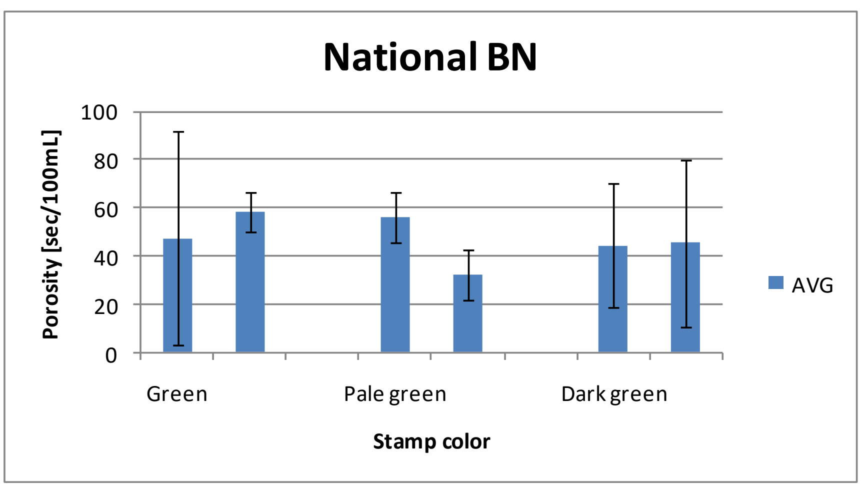

Figure 17: Oil Gurley Porosity of Different Color National Stamps

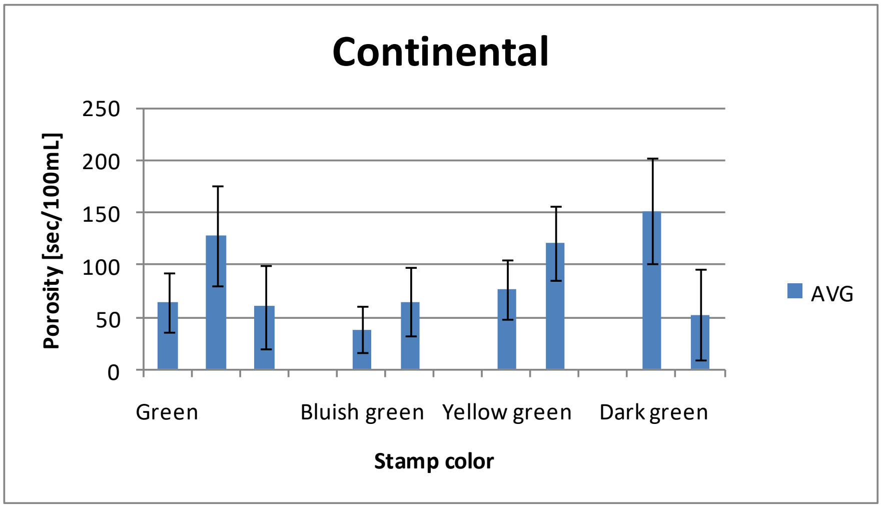

Figure 18: Oil Gurley Porosity of Different Color Continental Stamps

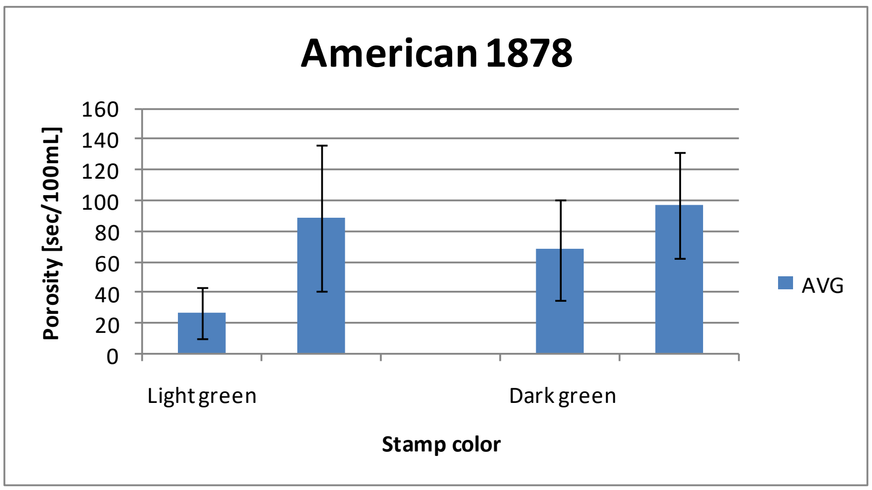

Figure 19: Oil Gurley Porosity of Different Color American 1878 Edition Stamps

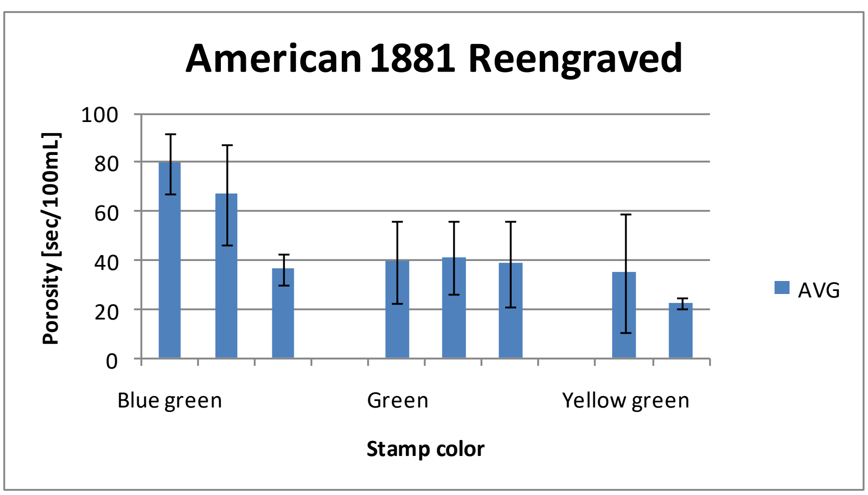

Figure 20: Oil Gurley Porosity of Differently Colored American 1881 Stamps

Normally, paper porosity very much affects optical density of the print. More porous open structure receives ink into pores, depending on pore size and pigment particle size, resulting in lower optical density and color saturation. At the same time, color variation caused by pore size will probably affect CIE L value rather than A and B color coordinates. It is likely that papers with smaller pores, or sized papers with more closed structure will leave ink film on the surface, resulting in higher ink optical density or more saturated color. In the case of these historical stamps, very many factors come into the effect, and it is not known how were these stamps treated, and thus possibly damaged. Overall, they show large standard deviations of porosity measurement. **Figures 17-20** illustrate the porosities of differently colored stamps. In the case of American 1881, “blue green” stamps are less porous than “yellow green” (**Figure 20**), while in Continental series “, it is opposite (**Figure 18**).

<u>Ink Analysis</u>

Metals in the Inks

Metals in the ink were measured using EAGLE III µProbe – Energy-dispersive X-ray Fluorescence Spectrometer. The samples were cooled with liquid nitrogen and measured in vacuum. Qualitative analysis of ink was employed. Results are given in the **Table 6**. From the results is clear that inks, used to print National BN contain the same group of metals (Ba, Pb, Zn, Fe, Cr, Si and Al). Thus, chemistry of inks used by National BN Co was probably identical; color difference may come from non-consistent ink deposition for 1870 issue of stamps, but also from paper differences, which were also found.

Some of Continental stamps have ink with the same metals as National BN (Ba, Pb, Zn, Fe, Cr, Si and Al), resulting in “yellow green” color (**Table 6**). “Bluish green” ink did not contain Zn, and ink used for printing “Green”, ”Dark green”, and “Olive green” contained another group of metals, containing Ba, Pb, Zn, Fe, Cr. Overall, three different variations of metal groups were found in of Continental stamps inks, which could lead to color variation between stamps.

American BN 1878 stamps were printed with ink containing the same group of metals as found in “Bluish green” ink from Continental, and they were Ba, Pb, Fe, Cr, Si, Al. Color differences could come from inconsistency in ink concentration, ink deposition, and paper variation.

American 1881 issue had quite different metals in the ink, than previous stamp issues, and they were Ca, Ba and Pb (**Table 6**).

Table 6: Metals found in the inks

Issue	Stamp color	Metals							
		Ca	**Ba**	**Pb**	**Zn**	**Fe**	**Cr**	**Si**	**Al**
1870	Green		x	x	X	x	X	x	X
1870	Pale green		x	x	X	x	X	x	X
1870	Dark green		x	x	X	x	X	x	X
1873	Green		x	x	X	x	X		
1873	Bluish green		x	x		x	X	x	X
1873	Yellow green		x	x	X	x	X	x	X
1873	Dark green		x	x	X	x	X		
1873	Olive green		x	x	X	x	X		
1878	Green		x	x		x	X	x	X
1878	Light green		x	x		x	X	x	X
1878	Dark green		x	x		x	X	x	x
1881	Green	x	x	x					
1881	Yellow green	x	x	x					
1881	Blue green	x	x	x					

CIELAB Color Analysis of Inks

Color of stamps was measured always in lower left corner of the stamp at areas, not contaminated with cancellation mark. Philatelists described and named the colors in the Scott Specialized Catalogue of United States Postage Stamps, and they are given in **Tables 7-10**. It is obvious that L* value affects the "darkness" of the stamp. Yellowness also varies greatly, causing "bluish" or "yellowish" tint or perceived "darkness". Also, color "Green" as recognized by philatelists is different for every manufacturer in terms of CIELAB values (See **Tables 7-10**). From **Table 7** is obvious that average CIELAB value of stamp is closest to color "Green", having ΔEab = 3.4 color difference from "Green", ΔEab 7.5 color difference from "Pale green", and ΔEab = 4.6 from "Dark green".

Table 7: Average CIELAB Color values for National Bank Note stamps

Color	**L***	**a***	**B***
Green	45.3	-26.2	6.8
Pale Green	53.1	-23.7	12.5
Dark Green	45.1	-25.0	3.8
Average stamp	47.5	-23.8	7.5

Similarly, Continental Bank note Co average stamp has CIELAB value 47.5, -23.8, 7.5 and its color difference from "Green" ΔEab is lowest (3.0), ΔEab from "Dark Green" is 6.8, ΔEab from "Bluish Green" is 8.1, ΔEab from "Yellow Green" is 8.4, and ΔEab from "Olive Green" is 9.5. Thus, average available stamps are closest to "Green" in color.

American bank note 1878 edition has average CIELAB values 44.9, -20.1, 4.9, and it is closest to "Dark Green" differing from it by ΔEab 4.6, and its CIELAB differs from "Light Green" by ΔEab 9.1. After re-engraving image, American bank note 1881 edition appeared, and it has average CIELAB color 52.8, -19.1, 6.2. Its color in terms of ΔEab is closest to "Green" (ΔEab =1.8), then "Yellow green" (ΔEab =2.8), and least similar to "Blue Green" with ΔEab= 6.2.

Table 8: Average CIELAB Color values for Continental Bank Note Co

Color	**L***	**a***	**B***
Green	45.7	-22.4	9.6
Bluish green	41.1	-21.3	3.3
Yellow Green	54.0	-24.2	12.9
Dark Green	42.5	-19.2	8.1
Olive Green	49.9	-15.5	11.6
Average Stamp	47.5	-23.8	7.5

Table 9: Average CIELAB Color values for American Bank Note Co 1878 edition

Color	**L***	**a***	**B***
Light Green	53.4	-19.0	8.0
Dark Green	40.6	-19.7	3.3
Average Stamp	44.9	-20.1	4.9

Table 10: Average CIELAB Color values for American Bank Note Co 1881 edition

Color	**L***	**a***	**B***
Blue Green	47.6	-21.4	3.8
Green	51.5	-20.2	5.9
Average Stamp	52.8	-19.1	6.2

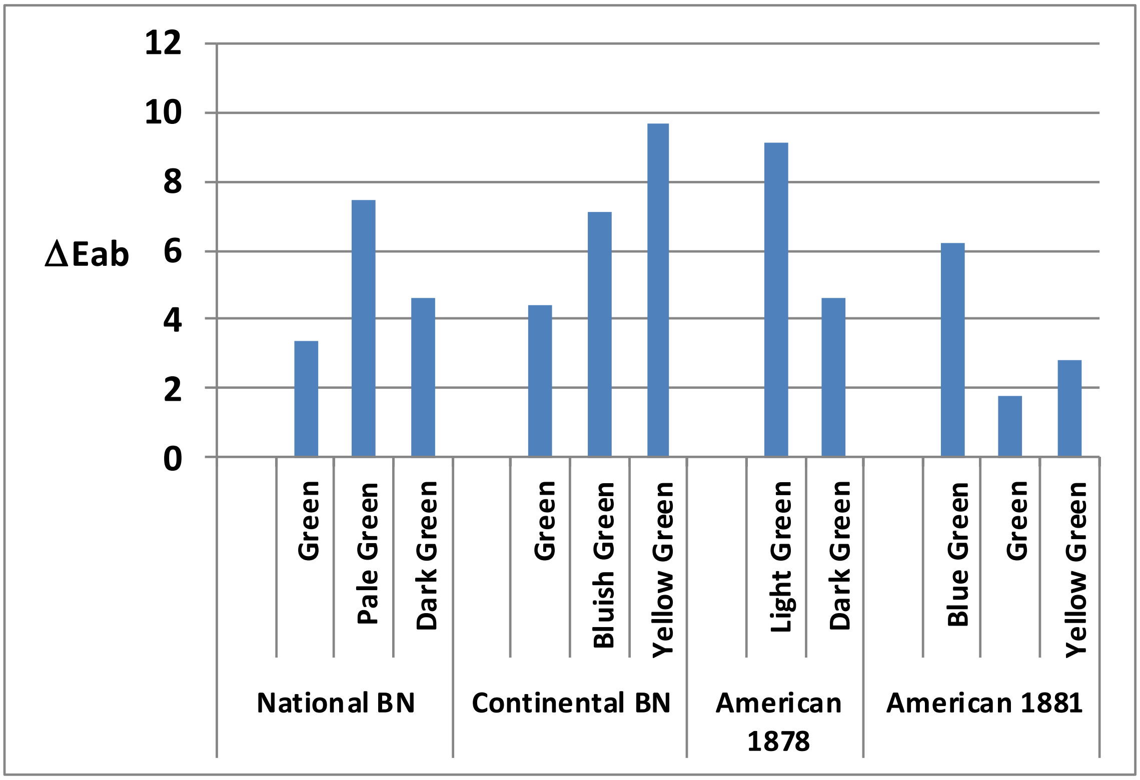

Figure 21: ΔEab Color Difference of Average CIELAB Value of Stamps from Designated Color for Individual Manufacturers (BN- Bank Note)

CONCLUSION

U.S. Three-cent green postage stamps manufactured under governmental contracts with three different private bank note companies were studied concerning paper properties and ink composition. According to paper analyses, it can be concluded that each of the companies was using paper with different properties, and differences were found also within individual issues.

National BN was using the stiffest paper with highest bending index ($116 \pm 19.9 g^{-1}$), and that was also the most porous paper stock with oil Gurley porosity 33.45 ±14.04 sec/100mL. Continental BN had lightly lower bending index range ($107 \pm 25.1 g^{-1}$) and less porous stock with oil Gurley porosity in the range of 50.89±21.59 sec/100mL. American was using different paper for 1878 and 1881 edition, which is concluded from differences in bending indices, and porosities. Average bending index $103 \pm 17.1\ g^{-1}$ was found at 1878 series, and much less stiff paper was used for 1881 series, having bending index of $89 \pm 16.9\ g^{-1}$. 1878 series had much less porous paper with 75.18±33.39 sec/mL oil Gurley porosity values, than 1881 series with 40.02±12.54 sec/mL oil Gurley porosity.

Through the calculation of population distribution of bending indices for each manufacturer it was found that National BN used two discrete types of paper, one with bending index 85-115 GU/g reaching 52% of total tested samples, the other was stiffer with bending index 115-159 GU/g. Two different types of paper were confirmed through repulping, one of which was internally sized. Continental BN population (88%) had the bending index in the range 69-142 GU/g, the rest was within 142- 192 GU/g bending index, thus, they were using two different types of paper. In this group, also one type was internally sized. Possibly three different papers were used in American BN Company within first period (1878), first one (20%) with bending index 66-89 GU/g, second (52%) with bending index 89-113 GU/g , and third (28%) had bending index in the range of 113-145GU/g . Later, re-engraved edition (1881) was printed on two different papers, one (70% of population) with bending index in the range 59-100GU/g, and the other with bending index in the range of 100-128GU/g.

Inks, used for printing National BN contain the same group of metals (Ba, Pb, Zn, Fe, Cr, Si and Al), which shows that the chemistry of inks used by National BN Co was identical for all stamps, color difference may come from non-consistent ink deposition for 1870 issue of stamps, but also from paper differences, which were also confirmed. Some of Continental stamps have ink with the same metals as National BN (Ba, Pb, Zn, Fe, Cr, Si and Al), resulting in “yellow green” color. “Bluish green” ink did not contain Zn, and ink used for printing “Green”, ”Dark green”. “Olive green” contained another group of metals (Ba, Pb, Zn, Fe, Cr). Overall, three different variations of metal groups were found in of Continental stamps inks, which could lead to color variation between stamps. American BN 1878 stamps were printed with ink containing the same group of metals as found in “Bluish green” ink from Continental, and they were Ba, Pb, Fe, Cr, Si, Al. Color differences could come from inconsistency in ink concentration, ink deposition, and paper variation. American 1881 issue had quite different metals in the ink, than previous stamp issues, and they were Ca, Ba and Pb.

Ribbed pattern on stamp paper can come from papermaking process. It can be mirror relief from felts or wires used for forming of the paper sheet. The reason why it is once perpendicular and once parallel to print is probably because the printer did not look on the paper directionality when setting the printing process.

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