Papermaking and Ink Chemistry of "United States Three-Cent Bank Note"

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Keywords: Stamp, fiber length, paper porosity, bending index, color difference

Abstract

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. Stamp paper analyses revealed that each of the companies was using paper with different properties. Moreover, through the bending index measurement and calculation of population distribution of bending indices for each stamp manufacturer it was found that National BNC used two discrete types of paper, one with a bending index 85–115 GU/g reaching 52% of total tested samples, the other stiffer with a bending index 115–159 GU/g. The Continental BNC population (88%) had the bending index in the range 69–142 GU/g, the rest was within 142–192 GU/g bending index. Possibly three different papers were used by the American BNC within the first period (1879), one (20%) with bending index 66–89 GU/g, a second (52%) with bending index 89–113 GU/g, and a third (28%) with bending index in the range of 113–145 GU/g. The re-engraved issue (1881) was printed on two different papers, one (70% of population) with bending indices in the range 59–100 GU/g, and the other with bending indices in the range of 100–128 GU/g. "Green" as recognized by philatelists was found to be different for every manufacturer in terms of CIELAB values.

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Introduction

This article aims to clarify differences in the substrate used to print United States three-cent stamps of the 1870s. More than 6.6 billion of these stamps were printed during years 1870–1883 [Barwis, 2001]. Very likely, this stamp was printed on different paper stock, using different printing plates, possibly different ink chemistry, and printed on various printing presses. The differences in paper stock, and printing-plate relief combinations as reported by Barwis are illustrated in **Figure 1**.

Today, many stamps are printed by the gravure process, a modification of what was 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, using photographic process along with carbon tissue for etching. 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 flat-bed plate and press designs, which later developed into rotary printing presses. Material used for early papers was cotton and cotton rag. The first pulp manufactured from wood was made in Germany by the soda process in 1854 [Smook, 2002].

It was found that research into stamps in 20th century was highly underrepresented. Chemical analysis of stamps was carried out on minimum level, even in countries like UK, France, or Germany [Jones, 2002; Jones 2001]. Spatially resolved x-ray fluorescence (XRF) technique was applied to philately [Sanchez, 2006] to specify elements used in printing inks, which helped in authentication of stamps and revealing fakes. Another spectroscopy method, Fourier transform infrared spectroscopy (FTIR) was applied to the characterization of red inks used to print one-penny stamps in Britain from 19th century [Ferrer, 2006], which helped to analyze the development of red ink formulation over period of years 1841–1880. Elemental analysis of ink in stamps was performed by Odenweller [Odenweller, 2009].

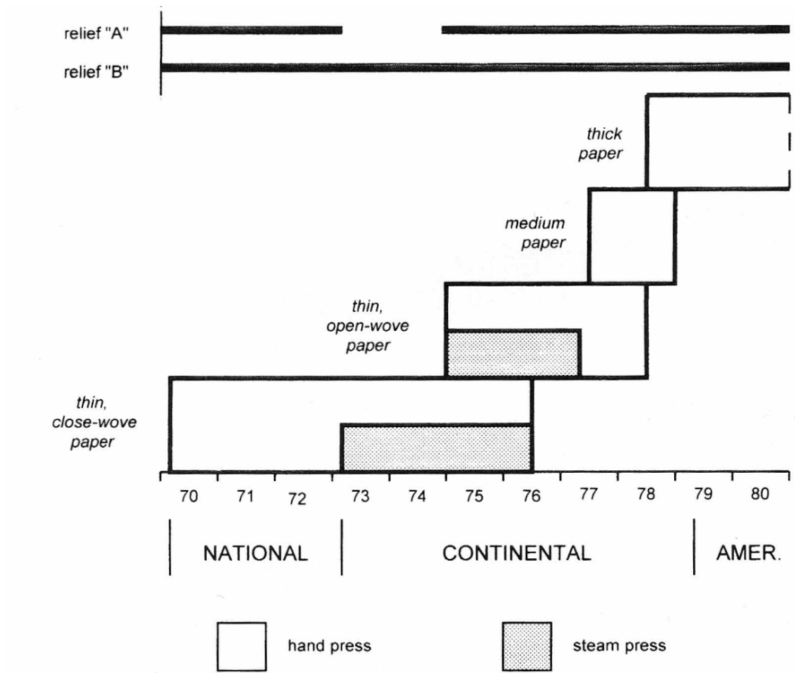

Figure 1. Production of 3-cent stamp on variety of paper substrates [Barwis, 2001].

In order to compare and identify particular inks in forensic material or stamps, a standardized and reproducible protocol is necessary. X-ray diffraction can be modified to be applicable for analysis of small amounts of samples, and thus it can be very useful in pigment detection [Kotrly, 2006]. However, for forensic purposes, there is a need to be able to analyze rest of the printing ink, because many of the inks are using the same pigments—as it is, for example, in the case of carbon black. Because of the fact that most of the black inks use the same carbon black pigment, the analysis of traces of solvents in inkjet ink helped to identify the origin of the digital ink using pyrolysis gas chromatography/mass spectrometry PY/GC/MS [Partouche, 2005]. This complex analysis allows for detection of solvents and semi-volatile compounds in inks and relatively freshly printed samples. In printed stock, some of the solvents evaporate and there is no possibility to detect them any longer.

Standard methodology was elaborated for analyzing inks by high-performance thin layer chromatography (HPTLC) to eliminate variation caused by different timeframe, locality and analytical lab [Neumann, 2009]. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was successfully used for the analysis of red sealing-inks on paper surfaces [Lee, 2008]. The Royal Philatelic Society of London has been publishing results on stamps analyses [Pearson, 2006]. It is clear that this field is highly underdeveloped, and therefore it is appropriate to conduct analytical research in the field of philately. The aim of this work was to analyze chemistry and morphology of the paper the stamps were made of, and to determine how many paper types were involved in their production. 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?

Experimental

A total of 402 stamps were used for analysis. The colors are as described in the Scott Specialized Catalogue of United States Postage Stamps, and are those generally accepted by collectors and specialists in these issues. 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.C.	81	Paper	How many different paper types?
1870	National B.N.C.	9	Ink	What is the cause of color variation?
1873	Continental B.N.C.	74	Paper	How many paper types?
1873	Continental B.N.C.	14	Ink	What is the cause of color variation?
1873	Continental B.N.C.	14	Paper	Origins of “ribbing” and extraneous fibers?
1879	American B.N.C.	75	Paper	How many different paper types?
1879	American B.N.C.	9	Ink	What is the cause of color variation?
1881	American B.N.C., re-engraved	115	Paper	Same paper as the 1879 issue?
1881	American B.N. Co., re-engraved	11	Ink	What is the cause of color variation?

Caliper

The thickness or caliper of the stamps was measured using a Caliper Model 549M Micrometer, made by TMI Testing Machines, Inc., USA (Amityville, NY). One stamp was measured at the time.

Bending Resistance

Stamps' bending resistance was measured following T543-om-00 TAPPI Standard. A Gurley Bending resistance tester was employed. Bending resistance of paper is done by measuring the force required to bend a specimen under controlled conditions.

Porosity

Oil Gurley porosity was measured at least five times for each stamp using a Technidyne Profile Plus instrument (Technidyne Co, New Albany, IN). Oil Gurley porosity measures time in seconds 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 the instrument's measuring land, two layers of PET sheet (100x80mm) were taped together to create a folder and a circular aperture of 9mm was cut through it. A stamp was placed in PET folder and porosity 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 a FQA Fiber Quality Analyzer (Op Test Equipment, Inc.)

Color

An X-Rite Spectrodensitometer 530 with a 4mm aperture was used to measure CIELAB color values of stamps. D50/2 viewing conditions were used. Also, an i1iO X-Rite spectrophotometer was used to measure color. ColorThink 3.0 was used to display colors of different stamps. Color differences were determined by means of ΔE_{ab} calculation.

Results and Discussion

Unites States three-cent bank-note stamps have dimensions which are too small for standard TAPPI Test methods used in the 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 a custom "Bending index" was calculated as shown in the Figure 1. Average bending index for all companies were calculated (Table 2). From Table 2 it is obvious that the bending resistance decreases from the oldest stamps (National) with bending index of 116 g^{-1} to 89 g^{-1} to the American BN 1881 printing, 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 ±STD [g^{-1}]
National BN	116±19.9
Continental BN	107±25.1
American BN 1879	103±17.1
American BN 1881	89±16.9

In order to distinguish if there were more different paper types used within each company, a population distribution was calculated for each manufacturer (Fig. 2–5). It is likely that National used two discrete types of paper, one with bending index 85–115 GU/g comprising 52% of total tested samples. The other was stiffer, with bending index 115–159 GU/g (Figure 2).

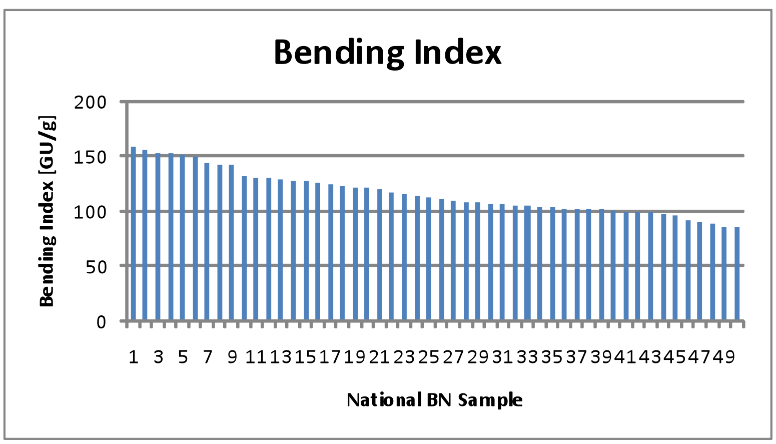

Figure 1. Bending Indices of National BN Stamps.

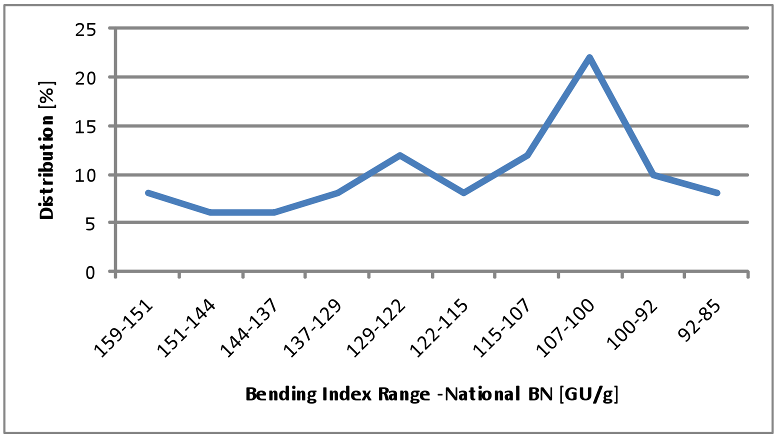

Figure 2. Population Distribution of National BN stamps (GU Gurley Units).

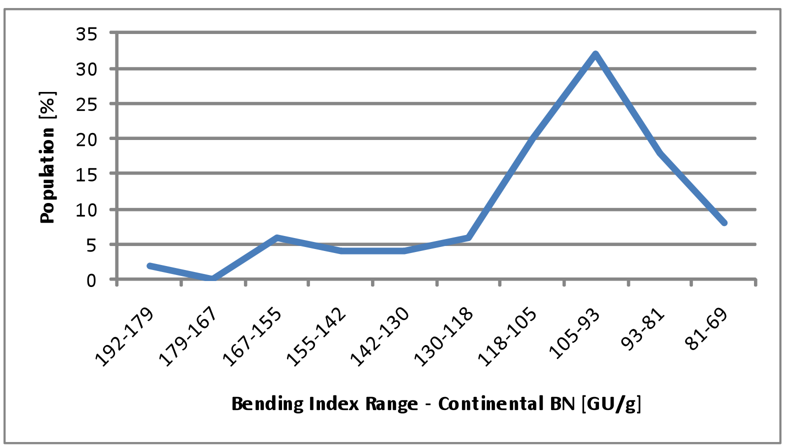

Figure 3. Bending Index Population Distribution of Continental BN Stamps.

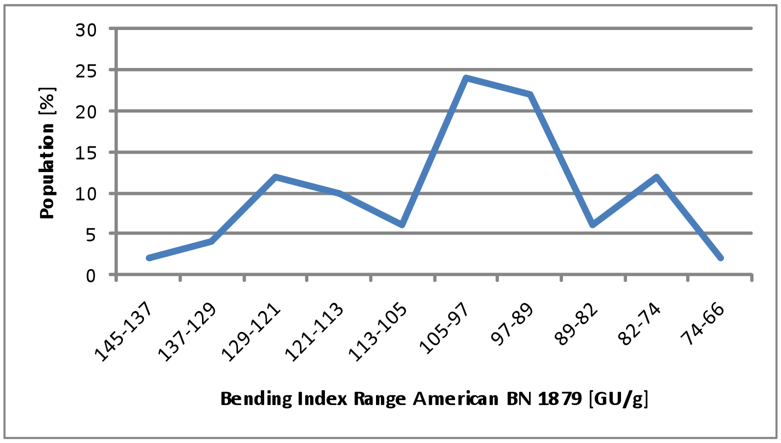

Figure 4. Bending Index Population Distribution of American 1879 Stamps.

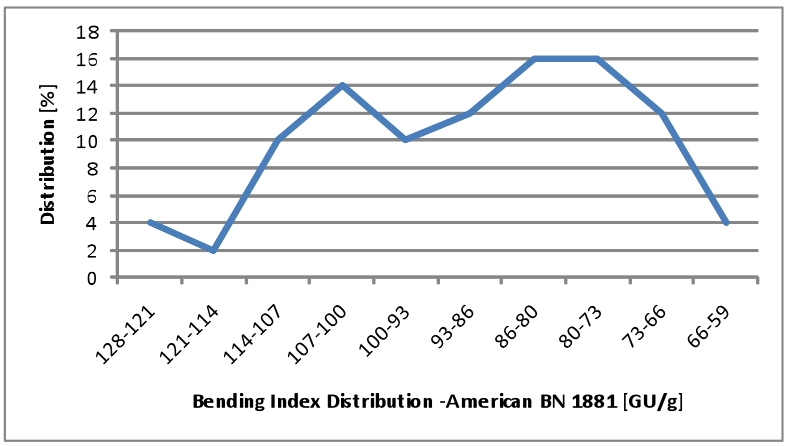

Figure 5. Bending Index Population Distribution of American BN 1881 Stamps.

Most of the Continental population (88%) had a bending index in the range 69–142 GU/g; the rest were within 142–192 GU/g. Possibly three different papers were used by the American BN Company for the 1879 printing, the first (20%) with bending index 66–89 GU/g, a second (52%) with bending index 89–113 GU/g, and a third (28%) had bending index in the range of 113–145 GU/g. American's re-engraved stamps (1881) were printed on two different papers, one (70% of population) with bending indices in the range 59–100 GU/g, and the other in the range of 100–128 GU/g.

Stamps were further analyzed according to their fiber length. Stamps analyzed were chosen from maxima of the peaks of bending indices (Fig. 2–Fig. 5). As can be seen from Fig. 2, the two modes had bending indices between 129–122 and 107–100, thus stamps from those two regions were chosen for fiber analysis.

Accordingly, for Continental stamps 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 the American printings 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 [GU/g]	Stamp Number
National BN	122–129	3
National BN	100–107	25
Continental BN	155–167	43
Continental BN	93–105	4
American BN 1879	121–129	20
American BN 1879	97–105	27
American BN 1879	74–82	26
American BN 1881	100–107	40
American BN 1881	73–80	47

To eliminate very short fibers, mean length, length-weighted data were considered in data analysis, as shown in the Figure 6. The longest fibers were found in National BN stamps, ranging from 0.679 to 0.732 mm. Of course this is not original length of fibers, but only that after fiber disintegration. Shortest fibers were found in Continental BN stamps, ranging from 0.532 to 0.614 mm. The graph also shows that each bending index range is characterized by different fiber lengths (Fig. 6).

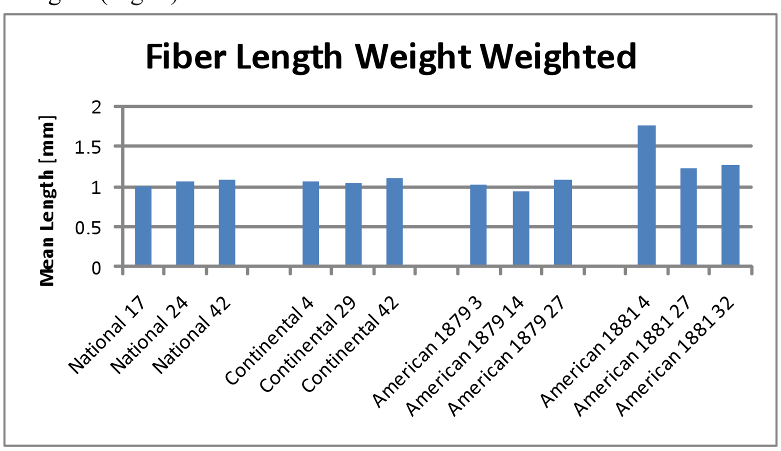

Figure 6. Mean Fiber Length (Length Weighted).

Oil Gurley porosity was measured for all four printings. All stamps were soaked in water to remove any remaining adhesive. Average porosity values are listed in the Table 5. Note that very large non-homogeneity of measurement with very high standard deviations was found, which may be partly due to residual adhesive in some areas or thin spots and damage in others. Average porosity is highest in National BN stamps (33.45 sec/100mL), and lowest in 1879 American stamps (75.18sec/100mL). Figure 8 shows Gurley porosity of the National BN printing.

Table 5. Average oil Gurley porosity of different issue of "U.S. Three-Cent" stamps.

Issue/Printer	Average Porosity [sec/100mL]	Standard Deviation
1870/National BN	33.45	14.05
1873/Continental BN	50.89	21.59
1879/American	75.18	33.39
1881/American (Reengraved)	40.02	12.54

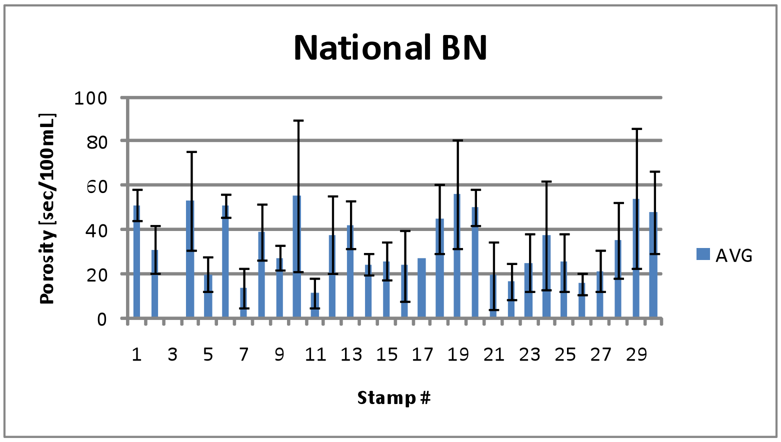

Figure 8. Oil Gurley porosity of National BN Stamps.

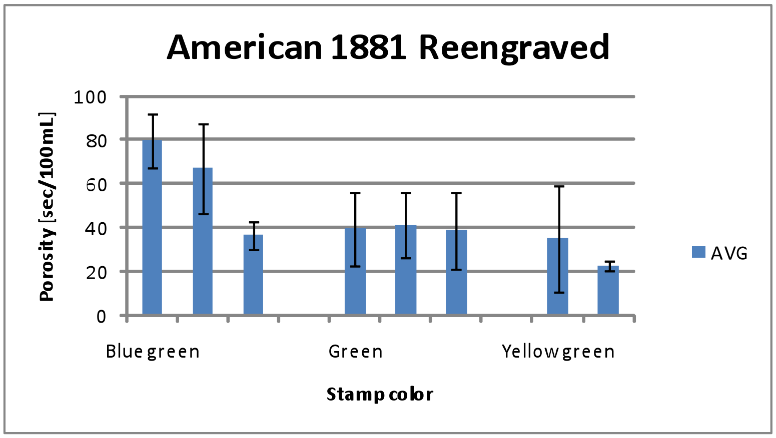

Figure 9. Oil Gurley Porosity of differently colored American 1881 Stamps.

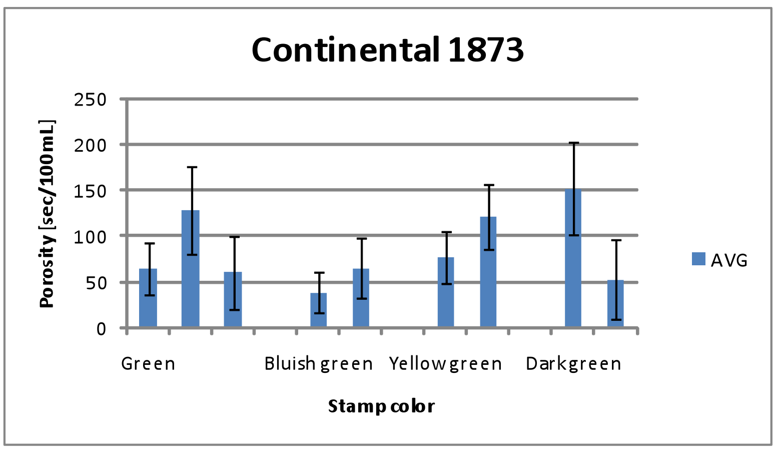

Figure 10. Oil Gurley Porosity of Continental 1873 different color stamps.

Normally, paper porosity very much affects optical density of the print. A more porous open structure receives ink into pores, depending on pore size and pigment particle size, resulting in lower optical density. Also, 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 therefore, it is assumed that more likely ink composition affects the color of the print rather than paper porosity. On Figure 9 and 10 are illustrated the porosities of differently colored stamps. In the case of American 1881, “blue green” stamps are less porous than “yellow green,” while in Continental issue, just the opposite is observed.

Stamp color was measured always in the lower left corner of the stamp at areas uncontaminated by cancellation ink. Philatelists described and named the colors after those listed in the Scott Specialized Catalogue of United States Postage Stamps; these are given in Tables 6–9. 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, the color "Green" as recognized by philatelists is different for every manufacturer in terms of CIELAB values (See Tables x-m). From Table x is obvious that the average CIELAB value of stamps is closest to the 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 6. 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, the Continental Bank note Co average stamp has a 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's 1879 printing has average CIELAB values of 44.9, –20.1, 4.9, and 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 the image, American's 1881 printing appeared, with an average CIELAB color of 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 7. 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 8. Average CIELAB Color values for American Bank Note Co 1879 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 9. 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

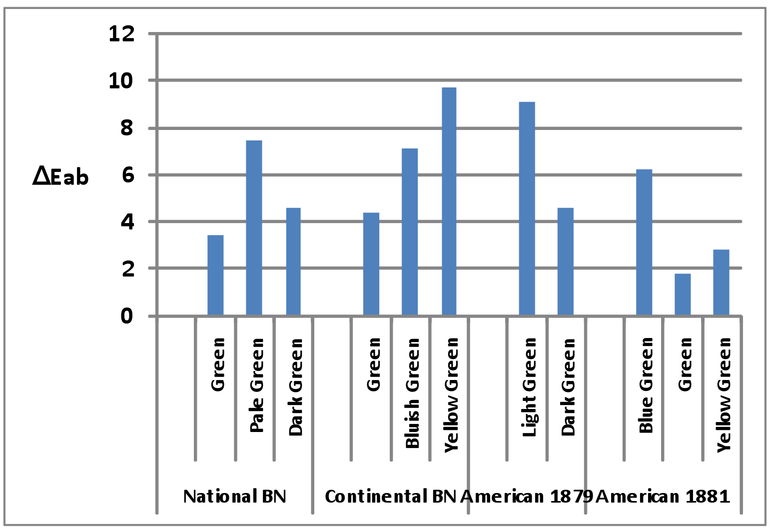

Figure 12. ΔEab Color Difference of Average CIELAB Value of Stamps from Designated Color for Individual Manufacturers.

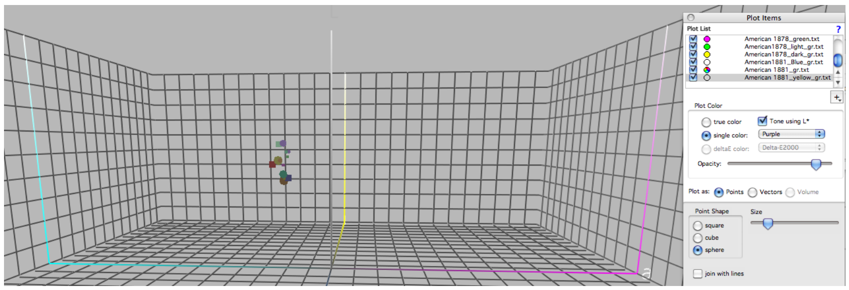

Figure 13. CIELAB Color of National, Continental, American 1879 and 1881 stamps illustrated in Chromix ColorThink 3.0 software.

Conclusion

Bending index analysis, fiber-length analysis, and porosity analysis showed that all three companies used different types of paper. Within a company, National and Continental used two discrete types of papers, as was revealed by bending indices characteristics, and fiber length analysis. Three different papers were used by American in the 1879 contract. Their re-engraved stamps were printed on two different paper substrates, as confirmed by bending-index and fiber analyses. The color "Green" as described by the Scott catalogue is different for every manufacturer. The Average CIELAB value of National stamps shows a ΔEab = 3.4 color difference from National's "Green." Continental's average stamp has a CIELAB value of 47.5, –23.8, 7.5 and its color difference from Continental "Green" is ΔEab =3.0. American's 1879 printing has a ΔEab 4.6 from American's 1879 "Dark green," and American's 1881 printing has a ΔEab=1.8 from the Scott-listed American 1881 "Green."

Acknowledgment

This work was supported by a grant from The Institute of Analytical Philately.

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