The General Issues



Forensic Studies of Stamps Issued by the Confederate States of America Part II. The Engraved 2-Cent Andrew Jackson Issue

By Col. Harry G. Brittain



Figure 1. Example of a CSA-8 block, illustrating the pale-red color of the stamp images from the first printing of this issue.

The initial stamps printed by the Confederate States of America were produced using a lithographic process, and these were followed by stamps printed by means of typography. It is known that Confederate postmaster-general, John H. Reagan, sought to print stamps whose quality equaled those printed by the United States Post Office Department, and eventually the Confederacy developed the technology necessary to print stamps by the intaglio process using steel plates.

One of these steel-plate engraved stamps was designed and line engraved by Frederick Halpin, and featured a portrait of Andrew Jackson that is thought to have been modified from either a miniature by John Wood Dodge or a painting by Miner Kilbourne Kellog. The image achieved by Halpin is quite similar to the vignette of the United States 2-cent stamp of 1863 (i.e., Scott No. 73). The earliest recorded date of use is April 21, 1863, and this issue was most often used to pay the two-cent drop letter and printed circular rates¹⁻³.

There were 1,650,000 stamps printed from a single steel plate, which contained two hundred subjects that were further divided into panes of one hundred and separated by a vertical gutter. There was no inscription used on the plate, and at least two printings are known to have been made. The images of the first printing have been characterized as pale-red, while the images of subsequent printings are described as being brown-red of varying shades¹⁻³. Examples of the stamp colors associated with the two printings are found in Figures 1 and 2.

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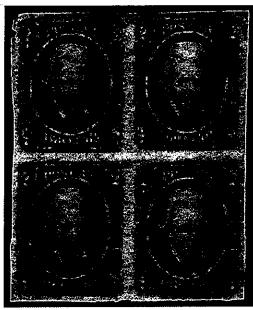


Figure 2. Example of a CSA-8 block, illustrating the darker brown-red color of the stamp images from the second printing of this issue.

In the preceding paper in this series⁴, the forensic analytical method of infrared absorption spectroscopy (coupled with attenuated total reflectance sampling) was shown to be highly suitable for the study of substances absorbed onto surfaces, and this technique was used to identify components contained in the various printing inks. In addition, since X-ray diffraction was appropriate for studies of the crystalline nature of surfaces (and since the X-rays penetrate more deeply into the medium), this technique was used to characterize the paper used in the various printings. The synergistic use of the FTIR and XRD methodologies has been discussed in sufficient detail in the preceding paper⁴, and more detailed discussions of the technology are available^{5,6}. The present work describes the use of this technology to obtain a deeper understanding of the ink and paper used in the printings of the CSA-8 issue⁷.

Also as discussed in the previous work⁴, it has been established that microcrystalline cellulose (MCC) is an excellent model compound for building characterization studies of stamps issued by the Confederacy. In particular, one can prepare synthetic mixtures of MCC with compounds of interest in order to obtain verification that such compounds are present in either the ink or the paper of a stamp.

Study of the Paper Used in Printings of the CSA-8 Issues

Figure 3 contrasts the XRD patterns of microcrystalline cellulose with the corresponding spectra obtained from the non-printed regions of stamps having large margins. Also shown in this figure is the XRD pattern obtained from a physical mixture, prepared to contain microcrystalline cellulose (MCC) and white kaolin clay in an approximate 3:1 ratio. It is immediately evident from an examination of the figure that different types of paper were used in the first and second printings of the CSA-8 stamps.

The XRD analysis demonstrates that the paper used in the first printing did not contain crystalline fillers, and that the cellulose in the paper contained the usual types of crystalline domains known in the literature as lattice types $I\alpha$ and $I\beta^{8,9}$. On the other hand, the paper used in the second printing was definitely found to contain significant amounts of kaolin clay as the filler, as evidenced by the XRD peaks at scattering angles of 12.25 and 25 degrees 2θ .

Although not as revealing as the XRD patterns, FTIR spectroscopy can also be used to distinguish between the paper used in the two printings of the CSA-8 stamps. As shown in Figure 4a, the FTIR spectra of the paper used in the first printing is effectively that of cellulose, while the expanded FTIR spectra of Figure 4b permit one to observe the peak that is associated with absorption by the kaolin component.

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printings. It tering angle and that the it was in star The identi filler composcattering pe was due to tl is illustrated Since the j peak at 11.5 It is therefore concluded from this forensic analysis that the presence or absence of the kaolin component in either the X-ray diffraction pattern or in the infrared absorption spectrum of a 2-cent Andrew Jackson stamp can be used to determine whether a given stamp corresponds to the first or second printing of this issue. The presence of kaolin clay is demonstrative that the stamp was from the second printing, and this is most evident in the XRD pattern (i.e., scattering peaks at angles of 12.25 and 25 degrees 2θ).

Studies of the Stamp Surfaces of the CSA-8 Issues

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Since in the previous study⁴, it was established that the XRD patterns obtained from the printed faces of CSA-6 and CSA-7 stamps were superimposable with those obtained for the paper on which these stamps were printed, it was concluded that the XRD patterns did not contain any contribution from the printing ink. This conclusion is reasonable, considering that the layer of ink on the surface of a typographed stamp (or a lithographed stamp) is fairly thin. However, the surfaces of stamps produced by an intaglio process will generally contain a thicker ink layer¹⁰, and therefore the forensic scientist must account for ink contributions in both the XRD patterns and in the FTIR spectra.

Figure 5 contrasts the XRD patterns obtained for representative examples of both printings of CSA-8 surfaces with the XRD patterns obtained for the non-printed margin regions of stamps from the same

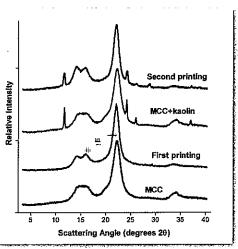


Figure 3. X-ray diffraction patterns of microcrystalline cellulose, the corresponding XRD patterns of the non-printed margins of the reference stamps, and the XRD pattern of MCC to which approximately 30% (by weight) of kaolin clay has been added.

printings. It was found that the XRD patterns of both printings contained an additional peak at a scattering angle of approximately 11.5 degrees 2θ that was not observed in the XRD patterns of the paper, and that the relative intensity of this peak was invariably greater in stamps of the second printing than it was in stamps of the first printing.

The identity of the XRD peak at 11.5 degrees 20 was established by blending various plausible ink filler compounds into microcrystalline cellulose, and determining which of these would yield a XRD scattering peak at the requisite angle. After experimentation, it was determined that the additional peak was due to the presence of the mineral gypsum (i.e., hydrated calcium sulfate) in the ink. This analysis is illustrated in Figure 6.

Since the paper used for the stamps of the first printing did not contain kaolin, only a single weak peak at 11.5 degree 2θ is observed in the XRD patterns of those stamps. However, the presence of both

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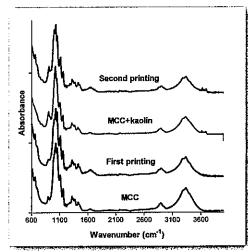


Figure 4a. Full infrared absorption spectra of microcrystalline cellulose, the corresponding FTIR spectra of the non-printed margins of the reference stamps, and the FTIR spectrum of MCC to which approximately 30% (by weight) of kaolin clay has been added.

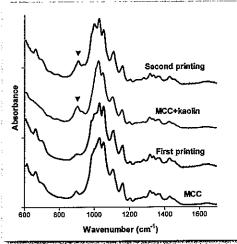


Figure 4b. Fingerprint region FTIR spectra of microcrystalline cellulose, the corresponding FTIR spectra of the non-printed margins of the reference stamps, and the FTIR spectrum of MCC to which approximately 30% (by weight) of kaolin clay has been added. The peak corresponding to the kaolin absorbance has been marked.

kaolin and gypsum in the stamps of the second printing yields a doublet of peaks noted at low angles in the XRD patterns, namely at 11.5 degree 2θ (gypsum) and 12.25 degree 2θ (kaolin). This peak doublet is diagnostic of CSA-8 stamps from the second printing. However, the ratio of relative intensities of the 11.5 degree 2θ gypsum peak and the 12.25 degree 2θ kaolin peak were found to vary considerably among the 39 stamps studied, and this observation suggests that study of the ink in the stamps of the second printing may yield additional information.

Further insight into the printing inks of the first and second printings was obtained using infrared absorption spectroscopy. Figure 7 shows the FTIR spectrum obtained from the face of a margin block, first printing CSA-8 stamp, which has been contrasted with the FTIR spectrum of the non-printed region of that same block.

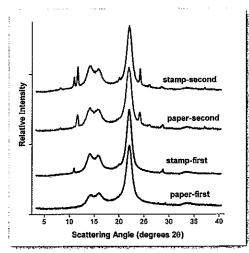


Figure 5. X-ray diffraction patterns obtained of the faces of CSA-8 stamps, and the corresponding XRD patterns of the paper used in the printing of these stamps.

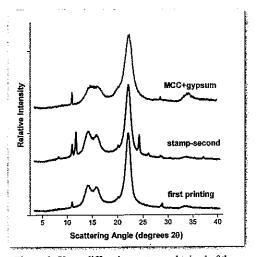


Figure 6. X-ray diffraction patterns obtained of the faces of CSA-8 stamps, and the XRD pattern of microcrystalline cellulose to which approximately 15% (by weight) of gypsum mineral has been added.

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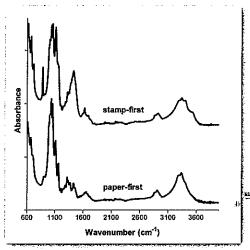
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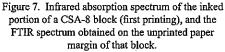
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ned of the ern of miately 15% 1 added. Examination of Figure 7 reveals the existence of a number of additional absorption bands in the FTIR spectrum of the stamp face that are not present in the FTIR spectrum of the paper on which that stamp was printed, and these are especially evident in the fingerprint region of the FTIR spectra.

However, upon further analysis it was determined that the system is not as complicated as first appears, and in fact all of the additional absorption bands can be attributed to the simultaneous presence of both gypsum and chalk (i.e., calcium carbonate) extenders in the printing ink. To demonstrate this, samples of microcrystalline cellulose were separately blended with gypsum (see Figure 8) and chalk (see Figure 9), and the FTIR spectra of these blends were obtained. As evident in the two figures, all of the absorption bands in the FTIR spectrum of the CSA-8 stamp can be attributed to the presence of cellulose, gypsum, and chalk. Interestingly, the amount of chalk and gypsum in the ink are only sufficient so as to barely permit their observation in the XRD pattern of stamps from the first printing.

As discussed above, the stamps of the second printing can be easily distinguished from those of the first printing by the presence of kaolin clay in the paper used for the second printing. A total of 39 examples of the second printing were characterized as to their FTIR spectra, and these were found to fall into two distinguishable classes. One of these types (14 examples) was found to exhibit a gypsum





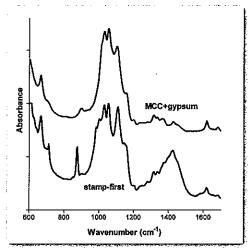


Figure 8. Fingerprint region FTIR spectrum of the inked portion of a CSA-8 block (first printing), and the FTIR spectrum of MCC to which approximately 50% (by weight) of gypsum has been added.

absorption band that was only 20% larger than the cellulose, while the type (25 examples) exhibited a gypsum absorption band that was at least 50% more intense than that of the cellulose band. In fact, the gypsum absorption was often so intense that the underlying cellulose absorption band could barely be distinguished. Representative examples of these FTIR spectra types are found in Figure 10.

It is concluded that one can use a combination of XRD and FTIR analysis to determine whether a given CSA-8 stamp is from the first or from the second printing. In addition, for stamps of the second printing, a careful analysis of the FTIR spectrum enables one to determine the particular ink type that was used in printing of the stamp. These conclusions are summarized as follows:

- First Printing: The XRD pattern contains very little contribution from any crystalline component. The FTIR spectrum contains contributions from gypsum and chalk ink fillers, but the intensity of the gypsum peak at 1110 cm⁻¹ is invariably smaller than the intensity of the cellulose peak at 1055 cm⁻¹.
- Second Printing (type-A): The XRD pattern contains peaks associated with the presence of kaolin in the paper (12.25 and 25 degrees 2θ) and a peak associated the presence of gypsum (11.5 degrees 2θ). The FTIR spectrum contains contributions from gypsum (as indicated by a peak at 1110 cm⁻¹) and

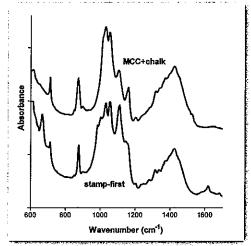


Figure 9. Fingerprint region FTIR spectrum of the inked portion of a CSA-8 block (first printing), and the FTIR spectrum of MCC to which approximately 50% (by weight) of chalk has been added.

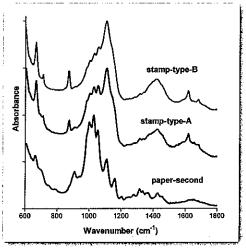


Figure 10. Infrared absorption spectrum in the fingerprint region of the inked portions of CSA-8 blocks (second printing) illustrating the two ink types, and the FTIR spectrum obtained on an unprinted paper margin.

chalk (as indicated by a broad band at 1400 cm⁻¹) ink fillers, but the intensity of the gypsum peak is at most 20-25% larger than the intensity of the cellulose peak at 1055 cm⁻¹.

• Second Printing (type-B): The XRD pattern contains peaks associated with the presence of kaolin in the paper (12.25 and 25 degrees 2θ) and a peak associated the presence of gypsum (11.5 degrees 2θ). The FTIR spectrum contains contributions from gypsum (as indicated by a peak at 1110 cm⁻¹) and chalk (as indicated by a broad band at 1400 cm⁻¹) ink fillers, but the intensity of the gypsum peak is at least 50% larger than the intensity of the cellulose peak at 1055 cm⁻¹.

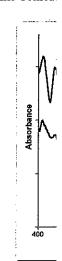
Identification of the Brown Pigment in the Ink of the CSA-8 Issues

So far, XRD analysis has been used to distinguish between the types of paper used in the first and second printings, and FTIR spectroscopy has been used to classify the ink types used in these same printings. Conspicuously absent from the discussion has been the identification of the brown pigment used in the ink that gave the stamps their distinctive color. This situation has arisen since the ink pigment did not contribute to the XRD pattern and was not observed within the spectral range (i.e., 600-4000 cm⁻¹) that was accessible to the attenuated total reflectance (ATR) accessory of the FTIR spectrometer.

However, given the practices of the time, it is most likely that the brown color was due to the presence of red iron oxides, most likely in the form of ochre or sienna pigments. It has been noted that ochre of fair quality has been mined in Georgia and Virginia.¹¹ The most typical source of red iron oxide is the mineral hematite, and that this compound exhibits very little infrared absorbance at energies higher than 600 cm⁻¹.¹²

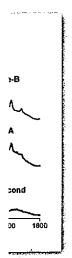
In order to obtain the necessary characterization information the ATR accessory was removed from the spectrometer, and spectra were obtained as dispersions in potassium bromide (KBr) pellets. In this manner, the analyzed range could be extended as low as 400 cm⁻¹, and so Figure 11 contains the spectrum of finely ground hematite dispersed in microcrystalline cellulose. In order to obtain the FTIR, spectrum of a CSA-8 stamp that is also shown in Figure 11, a small scraping of the surface of a second printing (type-B) stamp was made, and that scraping dispersed in a KBr pellet.

Examination of Figure 11 reveals that the same pattern of FTIR absorption bands over the spectral range of 400-600 in the spectrum of the scraping taken from the CSA-8 stamp is present in the spectrum obtained by the blending of hematite in microcrystalline cellulose. Therefore, it is concluded that the red pigment in the CSA-8 issues is due to the presence of red iron oxides, most likely in the form of the mineral hematite, although the iron oxides could be contained in a ochre pigment.



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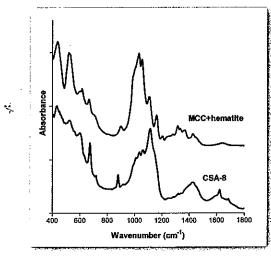


Figure 11. Infrared absorption spectra in the fingerprint region of the scraping from the surface of a second printing (type-B) CSA-8 stamp, and the FTIR spectrum of MCC to which approximately 20% (by weight) of hematite has been added. Both spectra were obtained in potassium bromide pellets.

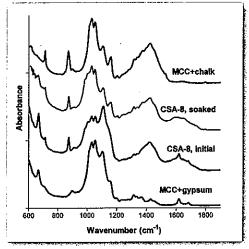


Figure 12. Infrared absorption spectra in the fingerprint region of a second printing, type-A, CSA-8 stamp as initially characterized, and after the exact same stamp was soaked in water. Also shown are the FTIR spectra obtained for MCC blended with gypsum, and MCC blended with chalk.

The Unexpected Effect of Soaking a CSA-8 Stamp in Water

During the investigational phase of the study, a number of stamps were encountered that did not exhibit the XRD and FTIR profiles characteristic of the stamps described above. While the XRD of several stamps identified them as being from the first printing, their FTIR spectra lacked any contribution from gypsum. The XRD of stamps from the second printing exhibited strong peaks due to the kaolin filler in the paper, but the characteristic gypsum peak at 11.5 degrees 20 was missing. In addition, the FTIR spectra of these stamp showed a strong peaks associated with chalk extender, but not any contribution from gypsum.

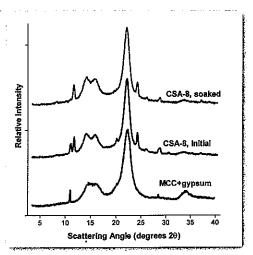


Figure 13. X-ray powder diffraction pattern of a second printing, type-A, CSA-8 stamp as initially characterized, and after the exact same stamp was soaked in water. Also shown is XRD pattern of microcrystalline cellulose to which approximately 15% (by weight) of ground gypsum mineral has been added.

³P. A. Ka

A clue to the origin of these stamps was that every one had no gum. This presumably arose from the used stamps having been soaked off their cover, and from the unused stamps having been soaked to remove the gum.

Unlike the effectively water-insoluble components in the ink and paper of the CSA-8 issues described thus far (cellulose, hematite, and chalk), gypsum is readily soluble in water (approximately 0.7 grams of hydrated gypsum will dissolve in 100 milliliters of water¹³). Given this solubility value, the small amount of gypsum that could be present in the ink layer of a stamp, and the relatively large amount of water that collectors normally use in stamp soaking, it would seem highly likely that the stamps lacking a gypsum component have lost that component due to a soaking process.

To investigate this process, one of the CSA-8 second printing (type-A) stamps that had been fully characterized was soaked in excess water for five minutes and allowed to dry. Figure 12 contains the initial FTIR spectrum of the stamp, as well as the FTIR spectrum of the same stamp after water soaking and subsequent drying. Also included in the figure are the FTIR spectra of mixtures of microcrystalline cellulose with gypsum and with chalk.

It is clear from this study that soaking a CSA-8 stamp fundamentally changes the ink composition of that stamp by removing the gypsum extender from the ink. The loss of the gypsum component upon soaking a CSA-8 stamp in water is highly evident in the XRD patterns, as shown in Figure 13.

Conclusions

It has been determined that the first and second printings of the 2-cent Andrew Jackson stamp were made on different types of paper. The first printing was made on paper that was essentially cellulose in composition, and that any paper filter was non-crystalline. The paper used in the second printing contained significant amounts of kaolin clay as the filler, and hence one can use XRD analysis to determine whether a given CSA-8 stamp was from the first or from the second printing. Because water has no effect on the paper components, this differentiation is possible even for stamps that have been soaked in water

The printing inks used for the first and second printings of the CSA-8 issues contained the same components, namely chalk, gypsum and hematite. However, the amounts of these components differed throughout the printing history, and the ratio of the gypsum to cellulose absorbance in the FTIR spectra is diagnostic. Stamps of the first printing are distinguished by a lower overall amount of pigment, and the height of the gypsum absorbance never exceeds that of the cellulose absorbance.

Two distinct sub-types of the second printing can be identified on the basis of the ratio of cellulose to gypsum absorbance in their FTIR spectra. In general, the larger amount of ink components characteristic of the second printing type-B stamps is associated with their darker color relative to the second printing type-A stamps. Given the accepted historical record that only two printings were made of the CSA-8 stamps, it is possible that two ink formulators were working when the second printings were made, and that each formulator prepared ink according to his particular preference.

To summarize, one can use forensic science to distinguish between the various categories of CSA-8 stamps through the use of the table on the following page.

Acknowledgements

Special thanks are due to Trish Kaufmann for the generous loan of her entire stock of 2-cent Andrew Jackson stamps for the purposes of this study. Acknowledgement is also made to my manuscript review committee, which consisted of Leonard Hartmann, Thomas Lera, Trish Kaufmann, Frank Crown, Jerry Palazolo, and Richard Murphy, who each provided valuable comments on the paper.

References

¹A. Dietz (1929) The Postal Service of the Confederate States of America. Dietz Printing Company, Richmond, VA, pp. 246-249.

²J. L. Kimbrough and C. L. Bush (2011) *Collectors Guide to Confederate Philately*, 2nd edition. Printed by the authors, pp. 137-139.

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³P. A. Kaufmann, F. J. Crown, Jr., and J. S. Palazolo (2012) Confederate States of America: Catalog and Handbook of Stamps and Postal History. Confederate Stamp Alliance, pp. 339-341.

⁴H. G. Brittain (2013) "Forensic Studies of Stamps Issued by the Confederate States of America. I. The Typographed 5-cent Blue Jefferson Davis Issues." *The Confederate Philatelist*, volume 58, issue No. 2, pp. 5-15.

⁵H. G. Brittain (1995) *Physical Characterization of Pharmaceutical Solids*. Marcel Dekker, New *York, NY, chapter 7.

⁶H. G. Brittain (2006) Spectroscopy of Pharmaceutical Solids. Taylor & Francis, New York, NY, chapters 7 and 8.

⁷The analysis database for the first printing CSA-8 stamps consisted of 19 stamps, from blocks of four, pairs, and singles. The database for the second printing of CSA-8 stamps consisted of 56 stamps from blocks of four, strips, pairs, and singles. The majority of these stamps were provided on loan by P.A. Kaufmann.

⁸H. A. Foner and N. Adan (1983) "The characterization of papers by X-Ray diffraction: Measurement of cellulose crystallinity and determination of mineral composition." *Journal of the Forensic Science Society*, volume 23, pp. 313-321.

⁹Y. Maréchal and H. Chanzy (2000) "The hydrogen bond network in Iβ cellulose as observed by infrared spectrometry." *Journal of Molecular Structure*, volume 523, pp. 183-196.

¹⁰C. Ellis (1940) *Printing Inks: Their Chemistry and Technology*. Reinhold, New York, chapter 10. ¹¹H. J. Wolfe (1967) Printing and Litho Inks. MacNair-Dorland, New York, pp 96-97.

¹²S. Vahur, U. Knuutinen, and I. Leito (2009) "ATR-FTIR spectroscopy in the region of 500-230 cm-1 for identification of inorganic red pigments." *Spectrochimica Acta*, Part A, volume 73, pp. 764-771

¹³W. F. Linke (1958) *Solubilities of Inorganic Compounds*, Volume 1, American Chemical Society, Washington DC, pp. 660-661.

• The Various Categories of CSA-8 Postage Stamps •

First Printing	 XRD pattern is effectively that of cellulose. FTIR spectrum contains contributions from gypsum and chalk. The intensity of the gypsum peak at 1110 cm⁻¹ is lower in intensity relative to the intensity of the cellulose peak at 1055 cm⁻¹.
First Printing (water soaked)	 XRD pattern is effectively that of cellulose. FTIR spectrum contains a contribution only from chalk at approximately 1400 cm⁻¹.
Second Printing (type-A)	 XRD pattern contains peaks due to kaolin (12.25 and 25 degrees 2θ) and gypsum (11.5 degrees 2θ) in the paper. FTIR spectrum contains contributions from gypsum and chalk. The intensity of the gypsum peak at 1110 cm⁻¹ is at most 20-25% larger than the intensity of the cellulose peak at 1055 cm⁻¹.
Second Printing (type-B)	 XRD pattern contains peaks due to kaolin (12.25 and 25 degrees 2θ) and gypsum (11.5 degrees 2θ) in the paper. FTIR spectrum contains contributions from gypsum and chalk. The intensity of the gypsum peak at 1110 cm⁻¹ is peak at least 50% larger than the intensity of the cellulose peak at 1055 cm⁻¹.
Second Printing (water soaked)	 XRD pattern contains peaks due to kaolin only (12.25 and 25 degrees 2θ). FTIR spectrum contains a contribution only from chalk at approximately 1400 cm⁻¹.