Fourier transform infrared spectroscopy (FTIR) investigation focused on Italian postage stamps in the course of time

Imperio E[1], Giancane G[2], Valli L[3]

[1] *Department of Engineering for Innovation, University of Salento, via per Monteroni - 73100, Lecce, Italy*
[2] *Department of Cultural Heritage, University of Salento, via D. Birago, 64 - 73100, Lecce, Italy*
[3] *Department of Biological and Environmental Science and Technology (Di.S.Te.B.A.), University of Salento, via per Monteroni - 73100, Lecce, Italy*

Abstract

From the inscription of the General Post Office in Washington DC: "The stamp is the propagator of news, links between distant families, messenger between friends, solace in solitude, a vehicle for commerce and industry, an element of human progress, promoting brotherhood, peace, goodwill among men and nations". It's hard to imagine how much history can be held in a small piece of paper and how many purposes this little object was destined to have. This is why postage stamps have reached so much importance and interest, which they began to be considered as work of art actually. In order to see beyond the careful eye of the philatelist, FTIR (Fourier Transform Infrared Spectroscopy) in ATR (Attenuated Total Reflection) mode has been successfully employed in material characterization of many stamps. Samples since 1861, year of the unification of the Kingdom of Italy, until to date, across a vast philatelic collection, has been characterized in this study. The immediate response of this type of spectroscopic technique let to achieve significant data information, which led to design history changes in paper making technologies. The first mail stamps published in Italy portrayed King Vittorio Emanuele II and it showed to be made of sheet of cellulose paper. Going forward in years, many differences were detected in paper composition. The mail stamps were also observed by fluorescence microscopy, in order to determine differences in the application of fluorescence. The analyses were performed without any alteration of the samples and no removal of material was needed, which represents the "conditio sine qua non" for investigations on these kinds of Cultural Heritage.

Introduction

Philately can represent an unconventional way to follow the historical, economical, political and custom evolution of a country and society. It is a form of collecting that suffers from the same problems of other kinds of collections, such as conservation, restoration, counterfeiting and understanding of materials and substances employed during the manufacturing procedure. Also stamps constitute a sort of

artwork which could be very rare and precious. In fact, it is reported that one of the surest way of investment is the collection in the field of cultural heritage, since the relative pieces constantly increase their economical and historical value.
The proposed analysis will possibly be employed in determining the period of manufacturing of the samples, which is of fundamental importance in the case of counterfeits.

Materials and methods

Fourier Transform Infrared Spectroscopy (FT-IR) Varian 600-IR series instrument in ATR (Attenuated Total Reflection) mode with an internal reflection element composed of zinc selenide (ZnSe) was used to perform the molecular analysis. The non-destructiveness of the set-up employed allowed to place every stamp directly onto the ATR window in order to achieve an optimal contact between the surface of the sample and the crystal. Thirty-two scans were collected for all the exemplars in the range between 4000 and 600 cm^{-1}. Italian exemplars starting from Unification of Italy in 1861 until today came from a wide philatelic collection. The wide period of time covered a lot of post issues which have been subjected to infrared analysis in order to characterize their constituents. In particular the fibers, fillers, glues and coating, eventually present on the surface, were investigated. Moreover, stamp fluorescence has been observed by means of an inverted system microscope, the Olympus IX50, with the objective of 10x.

Results

Blank regions of the stamp samples were analyzed. The corresponding infrared spectra revealed different information depending on the year of the stamp. Due to the small depth of penetration of the radiation in the ATR mode, the resulting signals in the spectra can be attributed to the surface components.

When the Kingdom of Italy was born in 1861 new postage stamps were needed to standardize mail payment in all the regions. The first issue of the Reign of Italy, which was composed by the same four values formerly used in the Reign of Sardinia, was released in 1862 [1]. It comprehended stamps of 10, 20, 40 and 80 cents that had Vittorio Emanuele II embossed effigy in the central oval and they were painted in yellow, blue and red alongside the rectangle.
The analysis on these first exemplars shows the typical signals of cellulose fibers at 1158, 1106, 1055 and 1030 cm^{-1} [2] attributed to the stretching vibrations of C-O groups in glucose chains (Figure 1, A). This proves that the support chosen for printing the stamps was a cellulose based paper. Going forward in time, it has been possible to individuate in the exemplars from 1896 the use of kaolin as filler into the paper pulp. The presence of just one small peak (Figure 1, B) in the spectrum, at about 3690 cm^{-1}, due to Si-OH stretching mode [3], can be related to the position of the kaolin filler into the fibers. Kaolinite, $Al_2Si_2O_5(OH)_4$, is the principal mineral of kaolin clay used in paper manufacturing as filler [4]. Its powder interposes into cellulose fibers to fill the micro-holes in the paper making the sheet more compact and smooth, thus providing a finer support to be printed. The IR evanescent wave above the ATR crystal detects the first surface cellulose layer and only some kaolin particle emended in the sheet, can be detected.

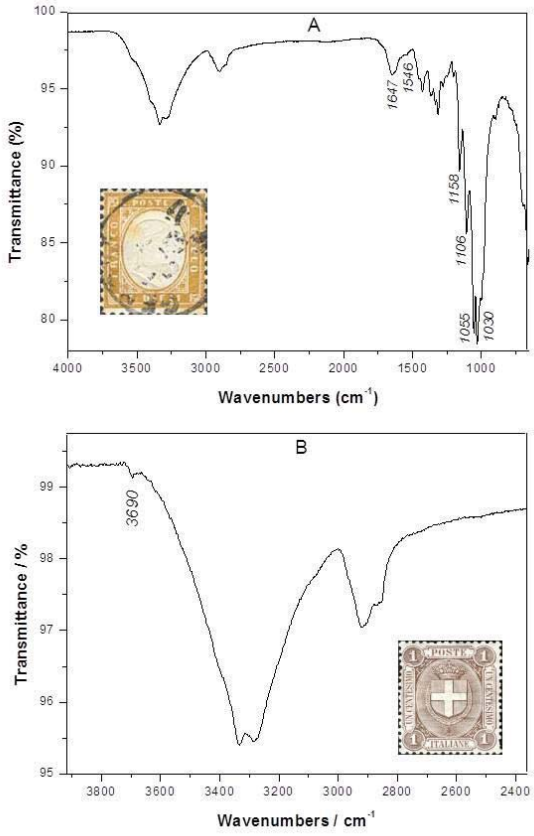

Figure 1. (A) FTIR-ATR spectra of 10 cent yellow stamp of the 1st issue of the Reign of Italy in 1862; (B) O-H stretching region in the FTIR-ATR spectrum of 1 cent brown stamp of the 1896.

The use of kaolin increased in the manufacturing of postage stamps. The analysis attest that the evolution of its employment, completely unknown until now, concerns stamps from 1915 in which kaolin acts as the coating layer above the front of mail stamp since that year. In figure 2, A is displayed the spectrum of the 15 cent value of Red Cross issue, where the kaolin bands become more intense with three distinctive signals in Si-OH stretching region at 3690, 3648 and 3616 cm^{-1} [2]. When kaolin is located as an external coating layer its peaks cover any other evidence of cellulose or glue and two intense signals related to calcium carbonate at 1412 and 870 cm^{-1} appear [5]. This is the case of most of the modern exemplars as visible in the spectrum of a stamp issued in 2004 (Figure 2, B). The improved definition of the pictures has been possible because of the coating process in which the use of calcium carbonate in mixture with kaolin improves ink impermeability and smoothed characteristic to the stamp paper, as any other nowadays exemplar shows.

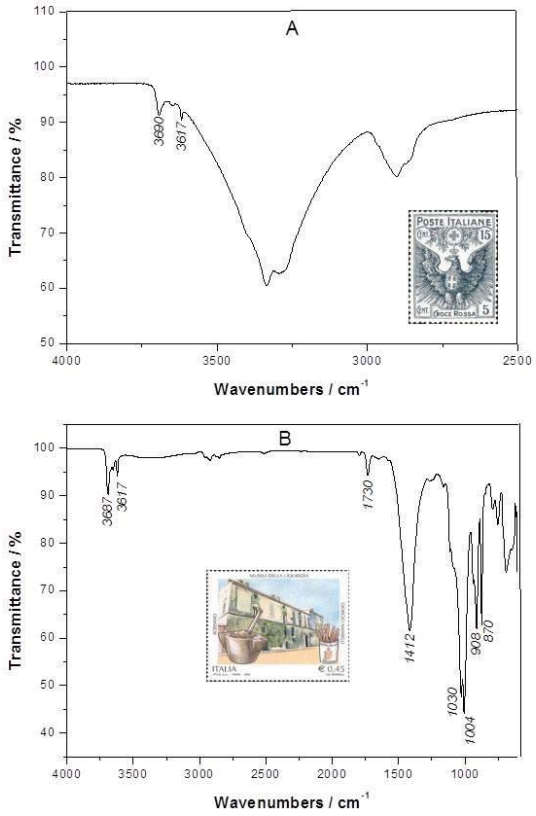

Figure 2. (A) O-H stretching region in the FTIR-ATR spectrum of 15 cent blue red cross stamp of the 1915 displays how Kaolinte was from then more visible due to its position above the cellulose fibers; (B) FTIR-ATR spectrum of 0.451 € stamp of 2004 in which are visible distinctive signals of kaolin coating.

Other changes in postage stamps production have affected the paper. They have been related to the introduction of the fluorescence. To allow the automatic marking of the mail and to stop the spreading of the fakes, fluorescence was applied to a large number of stamps. Hence, study on stamps fluorescence throughout time has been conducted by fluorescence microscope. It was known that in 1968 *Siracusana* issue was the first fluorescent issue. The fluorescent additives were introduced during the paper production, mixed in the pulp. Observing

Siracusana stamps, during excitation, only the paper support, not the printing ink, gave fluorescence response (Figure 3, A). In the 1980s in order to obtain a better resolution of the stamp subjects, fluorescent additives were no more included in the pulp, but they were introduced in the inks solutions [6]. Examination of modern stamps belonging to this class has been easily recognizable the distinction in the technique of production. In figure 3, A the particles are visibly spread on the paper surface, while in figure 3, B the luminescence is enclosed to the painted area, making visible only certain ink colors. In fact, in the pictures below, the first fluorescent stamps have luminescent centers within the fibres, while in today' stamp sample, rays of a drawn sun in the image can be seen.

The usefulness of the proposed studies consists in easily determine if an exemplar is compatible or not with the correspondence standard postage stamp.

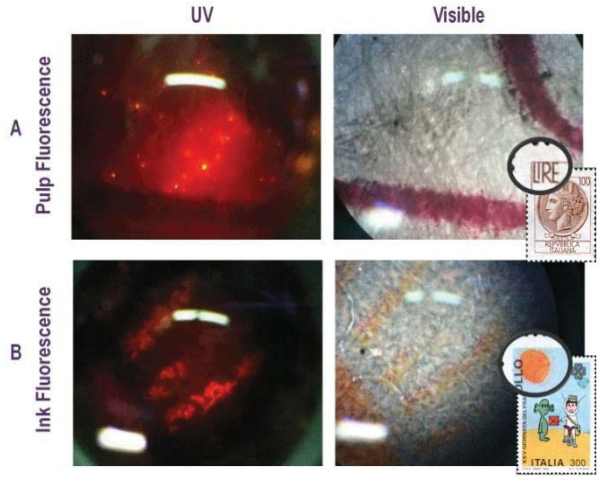

Figure 3. (A) Pulp fluorescence images of the 100 Lire Siracusana stamp exemplar of the 1968, under the UV and visible light; (B) Ink fluorescence images of the 300 Lire stamp exemplar of the 1983, under UV and visible light.

Conclusions

Chronologically analyzed stamps, throughout Italian history, let to know the materials employed in 150 years of postage stamps paper production. Paper was characterized by means of FTIR spectroscopy without causing any alteration to the specimens. This work allows a good knowledge about each change made in the manufacture of stamps paper. This study constitutes an additional demonstration of the importance of performing new scientific approaches to the world of Cultural Heritage and of merging technological data with historical and classical information. In this particular case the analyses proved that FTIR spectroscopy in ATR mode is a powerful and not-destructive tool, ready to be employed against stamps forgery.

References

[1] F. Zeri, I francobolli Italiani, Il Melangolo, Genova, 1993**,** pp.14-18 .

[2] K. K. Pandey, *J. Appl. Polym. Sci* 1999, 71, 1969-1975.

[3] . M. R. Derrick, D. Stulik, J. M. Landry in *Infrared Spectroscopy in Conservation Science*, Chapter 5, Getty Conservation Institute, Los Angeles, 1999, pp. 114-119.

[4] B. J. Saikia, G. Parthasarathy, J. Mod. Phys. 2010, 1, 206-210.

[5] H. Espinosa-Andrews, O. Sandoval-Castilla, H. Vázquez-Torres, E. Jaime Vernon-Carterb, C. Lobato-Calleros, *Carbohyd. Polym*. 2010, 79, 541-546.

[6] G. Riggi Di Numana, La fluorescenza nei francobolli d'Italia (1944-1994), Vaccari, 1995.