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Permanence of Early European Hand-made Papers

To the memory of Georg Thomas Mandl (1923-1997), an experienced papermaker, the Vice-President of the International Association of Paper Historians (IPH), and Friend.

Abstract

An investigation into (and explanation for) the remarkable permanence of early European papers made by hand in accordance with Italian practice is presented. The use of added lime ("addita calce") during the beating process (referred to by F.M. Grapaldo in his description of the Italian technique, c.1494, and in the late sixteenth-century Regensburg Regulations) is shown to be the responsible cause. The early Italian technology is described and comparisons are made with modern machine-production of permanent papers.

Key words: paper permanence, alkaline beating, fibre loading, gelatine and lime, craft technology, machine-made paper.

In his 1996 paper, presented at the 23rd IPH Congress in Leipzig, Timothy Barrett summarised previously-published data by the author and his colleagues [2]. Using a modern and chiefly non-destructive method of analysis, Barrett was able to demonstrate the important role played by the amount and condition of the gelatine in gelatine-sized papers (1400-1799) in relation to their strength and permanence. Barrett also showed that the oldest (fifteenth-century) papers, still in good condition, had levels of magnesium, calcium, manganese and zinc that were higher than those in younger papers. In his view, calcium is particularly significant, and he was able to report a relationship between low calcium content and low (i.e. acidic) pH values; after further research this may one day allow us to predict - using non-destructive methods - a given paper's probable pH from its calcium data [2].

Barrett's results confirm Barrow's earlier work, and his new point of view on the role played by gelatine in the permanence of historical papers is an important contribution. Certainly modern analytical methods are valuable tools enabling us to decode the messages concealed in the make-up of old papers, but Barrett's explanation of the alkalinity of early European papers is inconclusive. He writes: "It is not clear if this resulted from papermaking practice (the addition of chalk to keep the paper colour whiter) or by chance (such as a mill water supply that happened to be naturally high in

calcium or magnesium carbonate)" [2]. Moreover, gelatine, as a proteinaceous substance, is very sensitive to attack by micro-organisms, and we need an answer to the question 'why has not the gelatine degenerated over the centuries?'

The genuinely European technique of making paper by hand was developed in Fabriano, after paper-making was introduced to the town in the second half of the thirteenth century. Later it spread to other parts of Italy, and then to other countries. However, recent publications dealing with the beginnings of paper-making in Fabriano [3], or with the Italian technique of the craft [4], do not provide any basis for discussion of the above questions. Moreover, according to Dard Hunter, the first documented use of filler (china clay) in European paper-making took place in England in 1807 [5], and - curiously - both Barrow's and Barrett's data strongly suggest that early European papers, made by hand according to the Italian method, contain carbonate pigments. These pigments are alkaline, and as such need a neutral or alkaline medium because otherwise the acidity of the paper would break them down yielding carbon dioxide. We may therefore conclude that the early Italian craftsmen 'invented' alkaline papermaking, as well as the unlikely process of filling the paper with carbonate pigments - without, however, adding the pigments to the fibrous slurry before the forming of the paper, i.e. the typical process of paper-filling.

Introduction

The results of a famous investigation conducted by William J. Barrow and published in 1974 leave it in no doubt that acidity is the main reason for the unwellcome changes which occur in paper during its natural ageing process. Acidic paper becomes fragile and brittle during lengthy storage in archives and libraries until it finally disintegrates, destroying written documents and printed publications alike [1].

Probably the first reference to the presence of calcium carbonate in old European hand-made papers was published in 1935 by Włodzimierz Budka in his article on the Balice paper-mill near Cracow [6]. In addition to historical information about the mill (established in 1518-21 by Seweryn Boner) and its watermarks, Budka reported the presence of calcium carbonate at values of 3.0 and 3.7 per cent in two samples of paper made at the Balice mill and dated 1535 and 1553 respectively.

Better known is a publication by Fred S. Hanson of 1939 [7]. Hanson found that a book published in 1576 was made from various papers, some of which had aged badly, while others were in a good state of preservation. He showed that the well-preserved papers contained at least 2 per cent calcium carbonate and had a slightly alkaline pH. Hanson concluded that these characteristics were a recipe for permanent paper. His investigation is of great importance, for the book which he analysed included different papers, and this implies that the composition of each individual paper-stock was decisive for its condition, and not the storage regime. However, in a recent article Hanson's contribution is referred to as an example of "the relative importance of anecdotal, historical, and scientific evidence relating to paper-ageing and paper permanence" [8] - a comment which suggests a not uncommon lack of knowledge about technological aspects of the historical European papermaking craft.

Papermaking technology changed over the centuries, but the original Italian method involved technological aspects which are critical to paper permanence. The excellent survival record of early European papers made in accordance with the Italian method is well known, and our study is intended to elucidate this phenomenon alone. Further changes in technology are outside our scope, and our data relating to machine production of permanent papers is included only for purposes of contrast with early craft technology.

Evidence Provided by Historical Sources: Grapaldo and the Regensburg Regulations

An outline of the early Italian technology of papermaking was included in a

book published in Warsaw in 1991 entitled *Rękodzieło Papiernicze* (The Papermaking Craft). This was based on the technological data included in early descriptions. It is clear from these that the genuinely European art of papermaking, as invented in Italy, formed paper under alkaline conditions. Lime (calcium hydroxide) introduced during the stamping process created these conditions, and the calcium hydroxide retained in the paper must have reacted with atmospheric carbon dioxide to produce particles of calcium carbonate even though no pigment as such was used [9]. A detailed discussion of the above technical remarks is presented below.

The specific use of lime in the stamping process of paper manufacture must first have been mentioned in a work (*De partibus aedium*; GW 11331) printed in Parma probably in 1494. Its author, Francesco Maria Grapaldo (1460/2-1515), belonged to a family established in Parma since the fourteenth century¹). Grapaldo's book, the *De partibus aedium*, was often reprinted during the first half of the sixteenth century, this in spite of the fact that the book is more concerned with the theoretical views of classical authors on buildings rather than with the more practical aspects of architecture²). Nonetheless Grapaldo's account of papermaking which he includes in the ninth chapter of the second part of his book ('Bibliotheca') shows a very hands-on acquaintance with details of the craft which he presumably acquired at his local, Parma, paper-mill - established in 1451 and noted for the fineness of its product [10]. The relevant passage runs in English translation (the Latin original is at Appendix A):

"Nowadays we make paper from linen scraps and hempen strips of old and worn material. These are cut into small pieces and water is added to them and they are soaked for eleven days; then, after maceration with metal-shod hammers in water-filled mortars they are transferred to another mortar *after the addition of lime* ["addita calce", our italics]. They are then removed and placed in a vat in which they dip meshed forms and extract single sheets. These they interleave with felts and place in a press; then they dry them in a well-ventilated building. Later they are steeped in glue made from the waste scraps which tanners and parchmenters save for this purpose; they are hot-dipped, dried, and glazed, rendering

them apt to take the pen and not to soak up the ink. In this matter Parma papers are unrivalled, whereas Fabriano papers are distinguished for their whiteness. For the first requirement of a paper is that it be non-absorbent and does not suck in the ink, for if it does, one must dry the writing to prevent blots occurring."

The second early reference to the use of lime occurs in the Regulations of the Regensburg papermill which was established in 1539 [11]. These were located by C.M. Briquet in the Regensburg Archive in 1898, and the original German text (with a French translation) was published in 1900 by Augustin Blanchet [12]. The document is undated but it is probable that it dates from the second half of the sixteenth century. The important technical information about lime is included in the detailed description of the duties of the craftsmen who worked at the Bavarian mill. Incidentally, details of this kind are not included in the older and higher-grade document regulating Polish papermaking, approved by Sigismund the Old, King of Poland, in Cracow in 1546 [13].

The technical details in the Regensburg Regulations show that papermaking at the mill was carried out in accordance with the Italian technique - as described by Grapaldo. At Regensburg the rags were cut into small pieces before the fermentation process. The duration of the process is not specified, but the Regulations require that both the master and the stamper-hand should be careful not to over-extend the process. The fermented rag-scrap were de-fibred in the stamper for twelve hours and the fibres were later beaten in another water stamper for twenty-four hours. The master was also to be responsible for testing the stuff by pouring a sample into a vessel, and the stamper-hand was to beat the fibres until the master's test yielded a positive result.

The important piece of information about the addition of lime to the rag fibres during the beating process (reported by Grapaldo) is also referred to in the Regensburg Regulations: it is in fact mentioned twice (as 'gekalcht' and 'kalchen')³) - in connection with the duties of both the master and the stamper-hand. The Regulations record that after a week, i. e. six working days, nine hundredweight of rags should be processed into

three bales and six reams of paper (thirty-six reams). At another point in the Regulations it is stated that one and a quarter hundredweights of animal glue is used in the production of seven bales (seventy reams) of writing paper. On this basis, consumption of animal glue for paper-sizing stood at a level of seven per cent by mass of the rags used in the papermaking process. Taking into account the loss of mass during the fermentation of the rags, we can estimate that the animal-glue content in writing-paper made at the Regensburg mill stood at about ten per cent. Indeed, the paper probably contained an even higher percentage of animal glue, because the Regulations recommended that the animal glue used for sizing should not be stinted. It should also be noted that the use of alum is not mentioned in the Regulations.

Technological Aspects of the Sources

The technological details in the sources reveal aspects which throw light on the permanence of early European papers manufactured according to the Italian method. The important operation was the fermentation of the rags. This helped their disintegration and accelerated the subsequent beating process thanks to the activities of cellulotic micro-organisms, fungi, and bacteria. In the modern pulp and paper industry, the application of enzymes produced by the micro-organisms is studied instead of the more troublesome fermentation process. The enzyme treatment of pulp results in an improvement in its beatability as well as in a reduction of strength properties as regards both fibres and paper. It is accompanied by a degradation of the cellulose, indicated in the measurement of pulp viscosity [14]. One could therefore conclude that fermentation should have a negative effect only on paper permanence. In the historic papermaking technique, however, immediately after fermentation the rags were de-fibred in a water-powered stamper to form "half-stuff". The wooden hammers of the stamper were shod with spikes and each trough was supplied with clean water. During the disintegration process the rag fibres were thoroughly washed and the water, together with any impurities, was filtered out. The rag fibres were accordingly purified, and the products of the degradation of the cellulose (and also

any other easily degradable substances) were removed from the fibres during a process which lasted for twelve hours (if we are to believe the Regensburg Regulations). Consequently, the fermentation process (which lasted for eleven days if we are to believe Grapaldo) together with the subsequent disintegration of the rags and their thorough washing in the first stamper seem to have led to a significant upgrading of the rag fibres, and should also have had some positive influence on paper permanence.

In the next stage, the fibrous slurry was beaten with wooden hammers working in the trough without a flow of water through it. The addition of the lime (which is rather a strong base) to the slurry reinforced the beating action upon fibres which swelled better in an alkaline medium. During the beating, which according to the Regensburg Regulations lasted for nearly twenty-four hours, the rag fibres underwent thorough disinfection and any cellulolytic micro-organisms were neutralised.

After the beating was completed, the alkaline "whole stuff" was poured into the vat. Its dilution with water produced a fibrous slurry which was slightly alkaline and suitable for moulding paper by hand. "This white linen's pure child" (as Francesco Stelluti (1577-1652), a native of Fabriano, wrote in his *Sonetto sulla carta*) was brought forth in pure conditions [15]. Later on, the newly-formed sheets were couched, pressed and dried. When drying was completed the paper was dipped in a solution of animal

glue. The sheets were then pressed to remove the superfluous gelatine, and then were again dried. Each sheet was burnished by hand using a glazing-stone. The paper was then fit for writing or printing.

In the Italian method the lime retained in the paper produced an alkalinity. Lime or slaked lime is the product of the reaction of water with quicklime, i.e. calcium oxide. The latter is made by burning limestone, i.e. calcium carbonate, in which there may be some admixture of magnesium carbonate. Consequently in the lime retained in old papers some admixture of magnesium hydroxide may occur. The lime easily reacts with atmospheric carbon dioxide to produce calcium carbonate, sometimes with elements of magnesium carbonate. This reaction of carbon dioxide with the lime present in paper was a protracted process which slowly neutralised the alkalinity of the paper.

In studies on the technology of hand-made paper for conservation purposes carried out in the Pulp and Paper Research Institute (ICP) at Łódź in Poland, attempts were also made to investigate this reaction. The papers involved were formed from cotton linters beaten in water with added calcium hydroxide [16]. Our Figure 1 shows an X-ray trace of a paper⁴ which before the X-ray diffraction was kept for one week in an atmosphere of pure carbon dioxide. The X-ray trace contains the strongest characteristic peaks of crystalline form of cellulose (at angle 2 theta of about 15 and 23 degrees) as well as of calcite, i.e. calcium carbonate (at angle 2 theta of

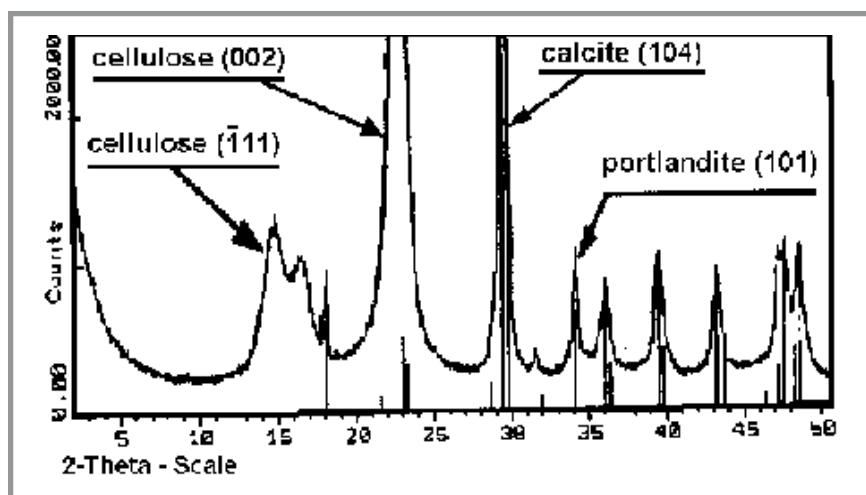


Figure 1. X-ray trace of paper formed in the laboratory from cotton linters beaten in water with a calcium hydroxide blend, which before the X-ray diffraction was kept in an atmosphere of pure carbon dioxide for one week.

about 30 degrees). The latter can only be the result of the reaction between the calcium hydroxide retained in the paper and the carbon dioxide, because no calcium carbonate was present in the fibrous slurry used for making the sample. However, some of the calcium hydroxide was preserved in the paper in the crystalline form of portlandite, whose characteristic peak (at angle 2 theta of about 34 degrees) is visible in the X-ray trace shown in Figure 1.

The ICP experiment seems to provide evidence for the very slow neutralisation by atmospheric carbon dioxide of the lime-residues in old papers, although we should bear in mind the very restricted access of the gas to the internal structures of the papers when in book-form as well as the very low concentration of atmospheric carbon dioxide (about 0.05 per cent by mass). But it **could** work, and centuries later calcium carbonate (sometimes with an admixture of magnesium carbonate) can be detected in old papers made in accordance with the Italian method. The technology involved particles of the carbonate pigments developing in the paper without having been present in the original papermaking process but arising naturally much later.

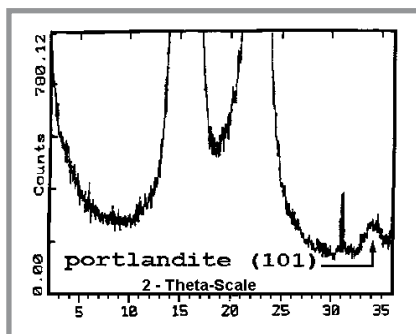


Figure 2. X-ray trace of the historical paper dated 1508.

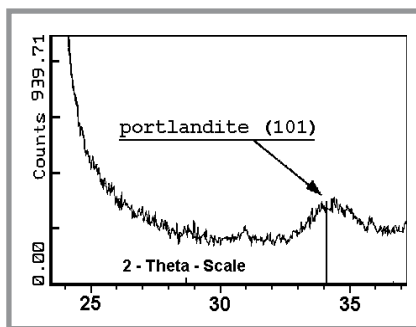


Figure 3. X-ray trace of the historical paper dated 1509/1510.

The lime retained in the paper probably also played a role in stabilising the animal glue in old papers. The content of animal glue in the writing-papers produced in the Regensburg mill was estimated above as being in the area of 10 per cent or more. This figure agrees well with modern determinations (10-12 per cent) of the gelatine content of well-preserved historical papers [17]. It is obvious that such a high animal-glue or gelatine content not only diminished the porosity of the paper - which was important for its sizing - but the animal glue, as a strong adhesive, also strengthened the paper. Having impregnated the fibre wall, the gelatine fortified the fibre itself as well. However, neither Grapaldo nor the Regensburg Regulations (a detailed source) refer to the use of any additive in order to improve the resistance of the gelatine to microbiological attack. We can conclude that the Italian technology added alum to the animal glue only in small quantities (if at all) and that the lime retained in the paper played an important role in stabilising the glue.

In modern papermaking, not so long ago, casein and satin white were used for paper coating, among other binders and pigments. Satin white is the product of the interaction of slaked lime and aluminium sulphate; it is an alkaline pigment, even small amounts of which improve water-resistance in a casein or protein-adhesive coating [18,19]. Probably a residue of the lime or calcium ions in satin white are able to cross-link the proteinaceous chains of the binders, and thus add water-resistance and wet-strength to the coating. Similarly, the lime residue in paper will react with the animal glue which is added to the paper during the sizing process. This interaction should result in the insolubility of the animal glue and in a reduction of its hospitality to micro-organisms.

The interaction of animal glue and lime, however, may be quite complex. Figure 2 shows an X-ray trace of a paper dated 1508 [16]. There are no peaks characteristic of calcite, i.e. calcium carbonate, but in addition to the peaks of cellulose, the peak characteristic of portlandite, i.e. calcium hydroxide, is visible at angle 2 theta of about 34 degrees^{5,6}. The peak characteristic of portlandite, at angle 2 theta of about 34 degrees, is also present in Figure 3 showing an X-ray trace

of a paper dated 1509/1510 which was additionally examined.

Curiously enough, residues of the lime used in making the studied papers can still be detected in the X-ray trace, almost five centuries after they were made. This seems to demonstrate an interaction between lime and animal glue in papers made in accordance with the Italian method - an interaction which deserves closer investigation.

The papers analysed above are still in good condition, and in their structure the watermarks are clearly visible, which depict the double barred cross (1508) and a bull's head surmounted by a shaft with double horizontal bars at the top and an entwined serpent (1509/1510). The watermarks were used in the Prądnik Czerwony mill, established in 1491 and now within the boundaries of Cracow [20,21].

The addition of lime during the beating process may be considered to be the main 'secret' of early European papermaking carried out in accordance with the Italian method [22]. This 'secret' was first revealed c. 1494 in Grapaldo's book and was confirmed by the results of modern analysis of early European papers: it provided an explanation of their permanence. The fact that these papers were made from rag-stock cannot alone account for this, since it was shown some forty years ago that during an accelerated ageing process chemical kraft wood pulps, whether bleached or unbleached, were as stable as rag-pulps provided that their initial degree of cellulose-polymerisation was high (1000-1200 plus) [23]. Rags and animal glue are of course no longer used in large-scale machine-production of paper, and alkaline papermaking is still very important for the machine production of wood-free printing and writing papers.

Machine Production of Permanent Paper

Economics has been the main consideration driving papermakers to make printing and writing papers under neutral/alkaline rather than acidic conditions, although enhanced permanence has also been seen as a valuable selling-point. In Europe, carbonate fillers are both cheaper and less abrasive to screen-wires than kaolin, and research in this field began in the 1950s. This research led to

a shift to neutral/alkaline papermaking. In North America kaolin remained cheaper than carbonate fillers until the 1970s, when precipitated calcium carbonate of an extremely high brightness (and competitive price) was introduced [24]. Research on the manufacture of acid-free printing paper with a carbonate filler started in Poland as early as the 1960s, carried out by Edward Szwarcsztajn (1909-1994) [25], an outstanding Polish scientific papermaker [26]. Pressure from archivists and librarians has resulted in the development of standards such as ANSI/NISO Z 39.48 -1992 and ISO 9706:1994, which lay down the requirements that permanent papers must meet [27]. When these standards were issued the leading papermaking countries were already manufacturing carbonate-loaded printing papers sized in neutral or alkaline media. The only thing that needed to be done was to adjust existing paper properties to meet the requirements of the standards. Modern alkaline papermaking, however, is based on the alkalinity of the carbonate filler-dispersion which is added to a beaten fibrous slurry before the paper is formed. The use of lime as an additive during the beating - the most important process in papermaking - shows that the Italian technology of early European papermaking was fully alkaline. This is the significant distinction between the ancient and modern approaches to the technology of permanent writing and printing papers [28].

Following the shift to the acid-free technology of writing and printing papers, scientific papermakers have quite recently re-discovered the stock preparation for papermaking with a calcium hydroxide blend. On a laboratory scale, lime was added directly to chemical kraft wood pulp stirred with water [29]. In semi-commercial trials the pulp, water, and calcium hydroxide blend passed through a disc refiner using its refining plates to mix and refine simultaneously [30]. Carbon dioxide was injected to the stirred or beaten fibrous slurry to speed up the precipitation of calcium carbonate. According to the authors of the reports, calcium carbonate is precipitated mainly within the fibres, so what was involved was a loading of the fibres with calcium carbonate particles [29,30]. This means that calcium hydroxide, in view of its low solubility in water, is able to penetrate the fibre cell walls. It is proba-

ble that while the rag fibres were beaten in water with an admixture of lime in the second stamper for twenty-four hours, a thorough penetration of the fibre wall by lime also took place. A further reaction with atmospheric carbon dioxide outside the mill led to the precipitation of minute particles of calcium carbonate at the points where the lime had been located, i.e. mainly within the fibres. It is highly probable that the fibres of early European papers made in accordance with the Italian method were loaded with minute particles of calcium carbonate. Detailed studies of this aspect of the old technology are required.

In the modern trials, however, the fibre loading is accomplished in fibrous slurry **before** the forming of the paper, and therefore, the lower bonding ability of the cell wall loaded fibres results in a paper with lower strength [29,30]. This differs by comparison with the ancient Italian practice, in which the fibre loading process began **after** consolidation of the paper structure, without damage to its strength. This kind of alkaline papermaking - invented in medieval Italy - has laid a solid foundation for the successful development of the European papermaking craft. From the evidence of Grapaldo (and the Regensburg Regulations) it is clear that it was regular papermaking practice to beat the fibres in water with a lime blend.

What goes on in the fibre-wall is decisive for paper permanence during its natural ageing, but the pH measurements do not precisely evaluate the situation. The pH value indicates the concentration of hydrogen ions in solution; however, the pH value of the water extract of paper always turns on the evenness of the distribution of hydrogen ions between the external liquor and the fibre-wall, which may be altered by the use of the neutral salt-solution, such as potassium or sodium chlorides, instead of water. Thus the results of the pH measurement alter also, and lower values are reported (in the glass electrode spot-test about 0.4 pH units lower [31]), and there is an even greater difference in the pH measurement of paper dispersed in the salt solution [32], by comparison with the pH values measured using distilled or de-ionised water. Bearing in mind the relativity of pH measurements in paper testing, it is somewhat uncertain whether the pH measurement could

clearly differentiate papers carrying identical carbonate pigment contents introduced by fibre-loading or paper-filling. Nevertheless it seems clear that the particles of calcium carbonate (the so-called alkaline-reserve) present in the fibre-wall protect the fibre against acidification during storage more effectively than the particles located between the fibres during a typical filling process. The latter case is characteristic of modern production of machine-made permanent paper, and the former seems to be peculiar to the ancient craft technology.

Conclusions

The genuinely European art of papermaking, invented in medieval Italy, formed paper under alkaline conditions. Lime or calcium hydroxide added to the beating of fibres created those conditions. The use of lime by Italian papermakers is first reported by Francesco Maria Grapaldo, probably in 1494. This Italian technique provided a sound basis for the further development of European papermaking since it was later adopted in other countries; for example, the use of lime in the beating process is referred to in the second half of the sixteenth century in the Regensburg Regulations.

Lime created alkaline conditions during paper moulding, and its residue in the paper would react with the animal glue used for sizing, making its proteinaceous substance much less accessible to micro-organisms. The lime also reacted with atmospheric carbon dioxide to produce particles of calcium carbonate, even though no pigment was used: most probably it was due to a loading of the fibres with the particles.

We neglect the technological data present in historical sources at our peril. Interpreted through the mirror of paper technology, such brief remarks may cast light on the results of modern analysis of early European papers and also broaden our knowledge about paper permanence in general. The permanence of papers manufactured in accordance with old European craft-methods is not accidental: the contents of archives and libraries provide overwhelming evidence for this.

Footnotes:

1. "Grapaldo" seems to be the correct form of the family name though some sources prefer "Grapaldi" [see I. Affo, *Memorie degli scrittori e letterati parmigiani*, 3 (Parma 1791), p. 125; and 6 (1827), p. 389].
2. Grapaldo's book was known to C.M. Briquet at least as early as 1907 ["*Les Filigranes*", 1 (Geneva 1907), p. 18], and the passage relating to papermaking was published in Latin and Polish translation by Janina Pleziowa in *Przegląd Papierniczy*, 1949, Vol. 5, p. 133. The first Western-language account of Grapaldo and of his importance for library history is due to the late Vladimir Lublinsky of Leningrad, and was published in *Bibliothèque d'humanisme et Renaissance*, 1967, Vol. 29, p. 633. None of the three authors drew attention to the critical importance of the role of lime in the papermaking process.
3. The precise significance of "gekalcht" and "kalchen" here (and of "addita calce" in Grapaldo) is all-important - one might say lime, chalk, and even quicklime (!) have been suggested as possible candidates. We are grateful to Prof. Carlo Federici (of the Istituto Centrale per la Patologia del Libro in Rome) for his authoritative confirmation that in a fifteenth or sixteenth century context it is lime, i.e. calcium hydroxide, that is at issue.
4. X-ray traces of the papers were prepared by Prof. Andrzej Korczyński of the Institute of General and Ecological Chemistry (IChOiE) of the Technical University of Łódź. The papers were exposed to a monochromatic X-ray beam, Cu-K alpha radiation, produced in a Siemens Powder Diffractometer D 5000 unit.
5. The peak visible in Figure 2 at angle 2 theta of about 31 degrees is characteristic of mercury amine chloride $\text{Hg}(\text{NH})_2\text{Cl}_2$.
A presence of the mercury compound in paper is a result of the conservator's activity for protecting the paper against deterioration by micro-organisms.

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References

1. "Permanence/Durability of the Book - VII, Physical and Chemical Properties of Book Papers 1507-1949", W.J. Barrow. Research Laboratory Inc., Richmond VA 1974.
2. Barrett T., "Coded Messages in Historical Handmade Papers", IPH Congress Book, 1996, Vol.11, p. 86.
3. Gasparinetti A.F., "Paper, Papermakers and Paper-mills of Fabriano", in "Zonghi's Watermarks (Aurelio & Augusto Zonghi - A.F. Gasparinetti)", E.J. Labarre, ed., The Paper Publications Society, Hilversum 1953, pp. 63-80.
4. Hills R.L., "Early Italian Papermaking, a Crucial Technical Revolution", in: "Produzione e Commercio della Carta e del Libro secc. XIII - XVIII", S. Cavaciocchi, ed., Istituto Internazionale di Storia Economica "F.Datini" -Prato, Firenze 1992, pp. 73-97.
5. Hunter D., "Papermaking, the History and Technique of an Ancient Craft", New York 1974, p. 490.
6. Budka W., *Archeion*, 1935, Vol.13, p. 30.
7. Hanson F.S., *Paper Industry and the Paper World*, 1939, Vol. 20, p. 1157.
8. Gurnagul N., Howard R.C., Zou X., Uesaka T., Page D.H., *Journal of Pulp and Paper Science*, 1993, Vol. 19, No. 4, p. J160.
9. Dąbrowski J., Siniarska-Czaplicka J., "The Papermaking Craft" (in Polish with extended English summaries), Warsaw 1991, pp. 117, 134, 218.
10. Briquet C.M., "Les Filigranes", 1, Geneva 1907, p. 18.
11. Briquet C.M., op. cit. 10, pp. 93-95.
12. Blanchet A., "Essai sur l'histoire du papier et de sa fabrication", Paris 1900, pp. 76, 78-101; and Arvay W., *Przegląd Papierniczy*, 1955, Vol. 11, pp. 12, 21.
13. Dąbrowski J., Simmons J.S.G., "Ad perpetuum rei memoriam.... The Royal Regulation of Polish Papermaking in 1546", IPH Congress Book, 1994, Vol. 10, p. 44 [published September 1996]; and Dąbrowski J., Simmons J.S.G., (both English and Polish versions), *Przegląd Papierniczy*, 1996, Vol. 52, pp. 267, 329.
14. Pere J., Siika-Aho M., Buchert J., Viikari L., *Tappi Journal*, 1995, Vol. 78, No.6, p. 71; Oksanen T., Pere J., Buchert J., Viikari L., *Cellulose*, 1997, Vol. 4, p. 329.
15. Voorn H., *IPH Information*, 1988, Vol. 22, No.1, p. 33.
16. "An Elaboration of the Technology of the Alkaline Hand-made Paper for Conservation Purposes" (in Polish) - studies sponsored by the State Committee for Scientific Research (KBN) and carried out in the Pulp & Paper Research Institute (ICP) under the direction of J. Dąbrowski (unpublished, Łódź 1998, pp. 27-34).
17. Waterhouse J.F., Barrett T.D., *Tappi Journal*, 1991, Vol. 74, No. 10, p. 207.

18. Willets W.R., "Titanium Dioxide and other Pigments", in: "Handbook of Pulp and Paper Technology", K.W.Britt ed., New York 1970, pp. 605-615.
19. Dąbrowski J., Głębowski A., *Przegląd Papierniczy*, 1985, Vol. 41, p. 254.
20. Piekarski K., "Memo on the Origin and the later History of the Prądnik p-m" (in Polish), Cracow 1926, pp. 27-30.
21. Dąbrowski J., *IPH Congressbook*, 1992, Vol. 9, p. 63.
22. Dąbrowski J., *Notes Konserwatorski*, 1998, Vol. 1, p. 103.
23. Faulhaber M., Pietrzyk K., *Wochenblatt für Papierfabrikation*, 1956, Vol. 84, pp. 147, 183.
24. Gess J.M., *Tappi Journal*, 1992, Vol. 75, No. 4, p. 79.
25. Szwarcztajn E., Maj J., *ATIP Bulletin*, 1965, Vol. 19, No. 2, p. 75.
26. Dąbrowski J., Libiszowski S., *Przegląd Papierniczy*, 1994, Vol. 50, p. 364.
27. "European Directory of Acid-free and Permanent Book Paper", M. Walckiers, ed., Brussels 1994, pp. 7-15.
28. Dąbrowski J., *The Restorers Bulletin*, 1997, Vol. 8, No.3-4, pp. 20, 89.
29. Siven S., Silenius P., Lindstrom M., "Precipitation of calcium carbonate within pulp fibre walls by means of carbon dioxide process at low pulp consistency", *Lappeenranta University of Technology, Department of Chemical Technology, Publication 64*, Lappeenranta 1996, pp. 11-24.
30. Klunness J.H., Sykes M.S., Tan F., Abubakr S., Eisenwasser J.D., *Tappi Journal*, 1996, Vol. 70, No. 3, p. 297.
31. Flynn J.H., Smith L.E., *Tappi*, 1961, Vol. 44, No. 3, p. 223.
32. Middleton S.R., Scallan A.M., Zou X., Page D., *Tappi Journal*, 1996, Vol. 79, No.11, p. 187.

APPENDIX A

Extract from F.M.Grapaldo, *De partibus aedium* (Parma, 1516), f.115v:

Apud nos hodie charta e lineis canabini-
sque pannis veteribus & attritis producitur.
Secti in frustula aqua inspersa per dies . XI
. macerantur: & in pila aquaria pilis ferratis
minutim contusi addita calce in alteram
transferuntur: exemptos deinde in aquaria
tinia cum posuerint formis aquam transmi-
tentibus in singula extrahunt folia: quae la-
neis pannis alternatim ingestis proelo cal-
cantur: aedificioque ad id patulo prius sic-
cata: mox glutino facto ex pellium quisquiliis
sive ramentis: quae coriarii & membranarii
reponunt ad hunc usum: fervefactis in-
tincta: rursus siccata et vitro levigata aptis-
sima redduntur ad tolerandos calamos: &
atramentum non transmittendum. In hoc Par-
mensis chartae sibi principatum vendica-
runt: cum in candore prae caeteris Fabri-
nae commendarentur. Prima enim chartae
datur adorea: si non est bibula & atramen-
tum non sorbet: quod si fuerit siccandae
scripturae: ne fiant liturae erit utilis.

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