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Investigation of ancient and new Japanese papers[1]

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Abstract

Two Japanese papers, one from a colour wood-block print (ukiyo-e) by the artist Kunisada amd a similar recent paper, have been investigated comparatively by thermoanalytical methods, infrared spectroscopy and scanning electron microscopy. Two further paper samples, produced from different plant raw materials, have been included in the morphological comparison.

This combination of methods allows to characterization and differentiation of different papers and a qualitative determination of their age.

Keywords: Thermoanalytical investigation; Characterization; Papers; Qualitative age determination.

1. Introduction

Paper is a material which played a major role in the development of cultures all over the world. Depending on the local vegetation, the discovery of papers is tied to different raw materials. The bark of certain trees and plants has been used as a writing and painting material in various periods and localities.

Real paper was invented around 105 A.D. in China where Ts'ai Lung produced the first usable writing material from tree bark and plant fibres, as well as from old rags and fishing nets. Since that time, paper has been in general use all over China.

Later, thanks to the construction of the Silk Road, the use of paper travelled west, first to Turkestan and then to the Arabic countries. The manufacturing methods used

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[1] Dedicated to Takeo Ozawa on the Occasion of his 65th Birthday.

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for the production of paper and silk were jealously guarded secrets which were not revealed to the Arabs until after the battle of Samarkand (in 751 A.D.) by Chinese prisoners of war. In Europe, it is virtually certain that the techniques of paper manufacturing were not used until the time of the crusades, i.e. the 12th and 13th century.

Advancing via Korea, the technology of paper manufacturing also arrived in Japan, where the first paper was produced around 610 A.D. in Kyoto. Over the centuries the technology of paper manufacturing was constantly refined and modified with respect to the raw materials used in its production.

In the 18th century, the Japanese produced paper from the bark of the mulberry tree. A mixture of rice starch and roots was added and served as a binder. This Japanese paper is called "kozo". It is very dense and snow white, and is still produced today. Later on, other suitable raw materials were discovered, such as the plants mitsumata and gampi. While kozo and gampi could be cultivated, mitsumata had to be produced from wild plants.

The purpose of the investigations reported here is to characterize and compare paper used for Japanese colour woodcut prints, "ukiyo-e", products of certain Japanese artist schools from the 17th century on, as well as similar recent Japanese paper, by thermoanalytical and other methods such as infrared spectroscopy and scanning electron microscopy. These methods allow the kind and history of manufacture of different papers [1–4] to be determined and a definitive classification can easily be reached [5].

2. Experimental

2.1. Instruments

The Mettler Thermosystem TA8000 was used for thermogravimetric measurements (TGA850) in air. The samples were heated at a rate of 5 K min^{-1} in a platinum liner. The oxidation behaviour of the different fibres in air was measured by scanning calorimetry (Mettler DSC30) in platinum pans, at a rate of 0.5 K min^{-1}. The various paper fibres were also investigated by scanning electron microscopy in a Philips SEM 515 after gold coating. Infrared spectra were recorded by means of a Fourier transform spectrometer BIO-RAD FTS-45 after imbedding in KBr discs.

2.2. Materials

One of the paper samples was taken from an ukiyo-e print from 1820 by the artist Kunisada, showing an actor on stage (Fig. 1). For comparison, a recent mitsumata paper, produced in 1952 and corresponding to the kind of paper used by Kunisada, was also investigated. Additional measurements were made on other papers, of Japanese manufacture, which were put at our disposal by the company E. Müller, Zürich. They are mulberry tree bark paper (kozo) and a plant paper (ohmi gampi shi), respectively, both dating from the 1950s.

Fig. 1. Ukiyo-e print by Kunisada (1786–1864). Also called Toyokuni III, a pupil of Toyokuni, whose name he adopted in 1844, after another elder pupil, Toyoshige, had called himself Toyokuni II after the death of the master in 1825. The development of Kunisada reflects the tragic decline of ukiyo-e. With his obvious talent and great verve, his early prints are of high quality, like those of the best days of his school, but the majority of his prints appear hastily drawn, much too colourful and poorly printed. His few landscapes, however, are excellent. The present plate shows an actor on stage, circa 1846. (38 × 26 cm) Publisher: Sanoki, Maima and Kinugasa (1847–48), Sign.: Toyokuni ga and toshidama seal.

3. Results

The results of the thermogravimetric experiments (TG) on the two mitsumata samples (Mitsumata 1952 and Kunisada 1847) are presented in Fig. 2, as DTG curves only without the simultaneously recorded TG curves, as the individual components of the papers can best be differentiated in this way. The velocity of the mass changes shows the differences more clearly, i.e. the curves can more easily be compared. For a quantitative evaluation, it is necessary to represent both curves (TG and DTG) by projecting the distance between two minima onto the TG curve, which then corresponds to the respective mass change (see Table 1).

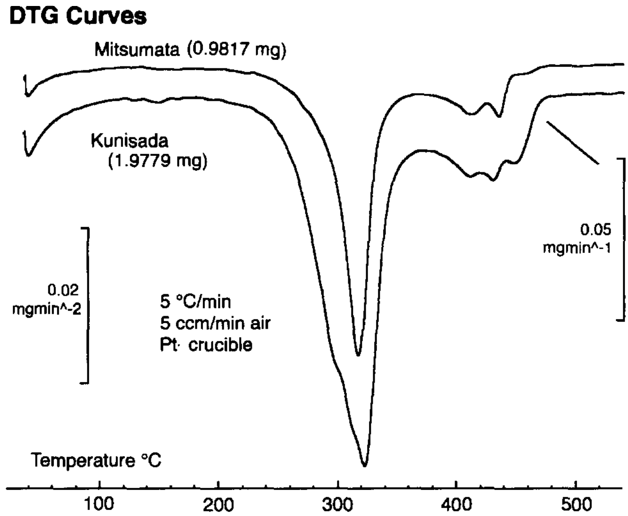

Fig. 2. DTG curves of the mitsumata papers 1952 and 1847 (Kunisada).

Table 1
TG analysis of mitsumata papers 1952 and 1847 (Kunisada)

Composition of paper	Mitsumata 1952	Kunisada 1820
Water	4.94%	6.67%
Monohydrate H_2O	0%	0.50%
Hemicellulose	0%	25.66%
Cellulose	70.45%	42.71%
Lignin 1	9.64%	10.74%
Lignin 2	8.50%	5.06%
Lignin 3	1.28%	4.51%
Ash	4.08%	5.04%

The first deflection of the curves indicates the loss of water (30–100°C). The following small peaks at 140–160°C indicates whether the paper has been beaten during its production, which is the case for the Kunisada sample only. The plant cells have been crushed and the oxalic acid set free has reacted with calcium to form calcium oxalate monohydrate. The slight mass loss corresponds to its dehydration.

The most important mass loss is due to the burning of the cellulose. Both curves also show a group of three peaks assignable to lignin. The values denoted lignin 1–3 in Table 1 refer to mass changes due to the thermal decompositions of the different lignins. They reflect the different degrees of polycondensation of the substituted coniferyl alcohols [5] which consequently exhibit different thermal stabilities. With progressing time and temperature, the polycondensation proceeds under evolution of hydrogen. The decompositions of different lignins occur in dicrete steps, from which the age of the papers can be estimated qualitatively. The mitsumata paper used by Kunisada, which is more than 150 years old, shows different peak heights, which suggests that this print has been exposed to sunlight for extended periods. The relative values of the components of these two papers are listed in Table 1.

The DSC curves of different papers used in Japan both in earlier times and still today (in addition, the usual Western papers are also used) are compiled in Fig. 3. The shapes of these curves are so significant that it can rapidly be decided which fibres are present in the papers.

The scanning electron micrographs shown in Fig. 4 illustrate that the fibres of both mitsumata and the other two papers investigated have similar diameters of about 10–20 μm. Artifacts may possibly have been caused by beating or pressing the papers. So, for example, the mitsumata paper shows parallel grooves along most of the fibres. The paper used by Kunisada, furthermore, contains many dust particles in the voids between the fibres, ascribed to its age, in contrast to the recent mitsumata paper. Gampi shi is characterized by strongly curved fibres and relatively large adherence islands with

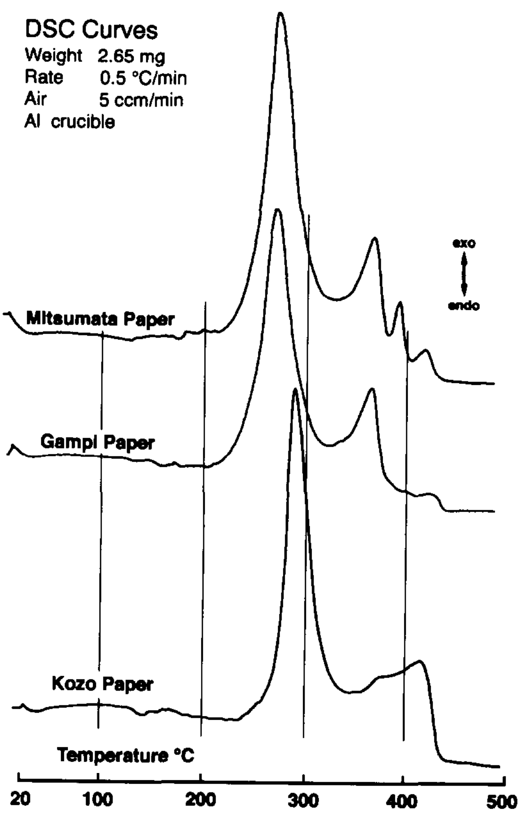

Fig. 3. DSC curves for mitsumata, gampi and kozo papers.

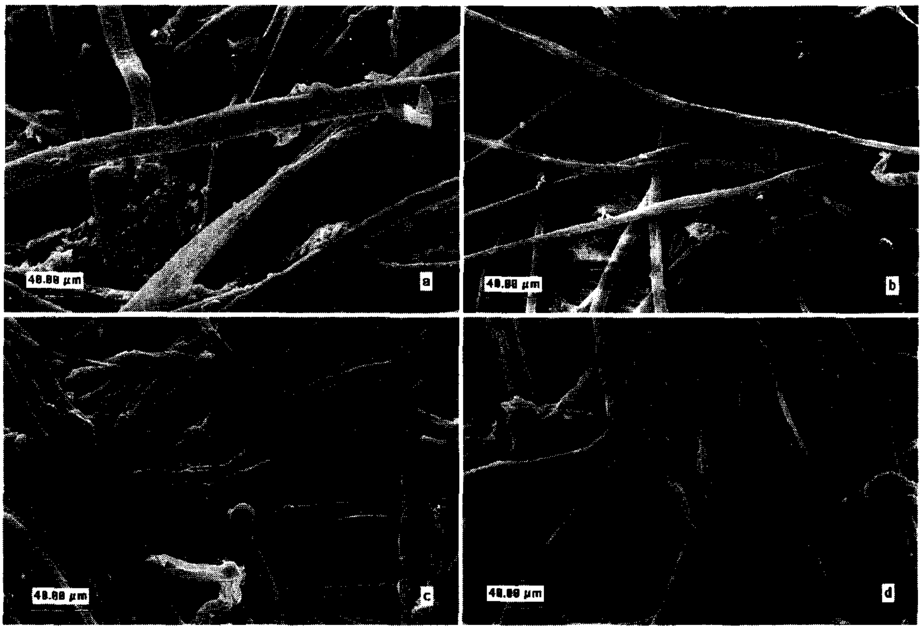

Fig. 4. Scanning electron micrographs of 4 paper samples: a, Kunisada 1847; b, Mitsumata 1952; c, Ohmi gampi shi; d, Kozo.

other fibres. The morphological peculiarity of the kozo sample is the presence of fibres twisted by 180°, indicating their high elasticity. An unequivocal morphological distinction of the various types of fibres is possible, but requires statistical evaluation of many micrographs at various magnifications.

The infrared spectra of different papers do not show any large differences. Only in the range of bound water does the Kunisada paper show higher intensities (wavenumbers 4000–3000). The same is true for the lignins.

4. Summary

The combination of the methods employed makes it possible to distinguish the different kinds of paper, and from the lignin values in the TG experiments, the age of the papers can be estimated qualitatively. Mechanical influences like the beating of paper can be recognized by the loss of the crystal water of the calcium oxalate.

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