Comparing the properties of contemporary Chinese papers manufactured in China with Japanese Kozo Washi paper

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Summary
Since the Han dynasty, the Chinese have been using different plant fibers, like Hemp (Ma zhi), Mulberry (Sangpi zhi), Paper mulberry (Chupi zhi), Rattan (Tang zhi). bamboo (Chu zhi), wheat or rice straw (Cao zhi) to make papers. Since the invention of paper in China two thousand years ago, there have been tremendous amounts of Chinese paper manufactured in China. As quite a number of papers have similar softness, whiteness, textures, laid pattern etc., it is difficult to select a kind of suitable paper among different available options for treatment purpose by simply observing through naked eye and physical sensing. It may be of some help if one knows how the paper was made. However, the quality control of paper making in China is still very loose. As such, performance of scientific analysis is the most reliable way to help one to decide. This paper investigated the permanence of some contemporary Japanese and Chinese papers in related to their composition.

Zusammenfassung
Seit der Han-Dynastie benutzen die Chinesen Pfanzenfasern wie Hanf (*Ma zhi 麻紙*), Maulbeerbaum (*Sang pi zhi 桑皮紙*), Papier-Maulbeerbaum (C*hu pi zhi 楮皮紙*), Rattan (*Tang zhi 藤紙*), Bambus (*Zhu zhi 竹紙*), Weizen- oder Reisstroh (*Cao Zhi 草紙*) und *Xuan* (*Xuan zhi 宣紙*), um Papiere herzustellen. Nach zweitausend Jahren gibt es riesige Mengen Papier, das in China hergestellt wurde. Weil eine groβe Anzahl von Papieren sich ähneln im Hinblick auf Weichheit, Weiβgrad, Struktur, Siebmuster usw., ist es schwierig, eine passende Papiersorte für eine Restaurierungsmaβnahme unter den verschiedenen zur Verfügung stehenden Alternativen auszuwählen, indem man sie nur mit dem bloβen Auge und durch Abtasten untersucht. Es kann hilfreich sein, wenn man weiβ, wo das Papier hergestellt wurde. Allerdings wird die Qualitätskontrolle von Papier in China immer noch sehr locker gehandhabt. Deshalb ist die Durchführung einer wissenschaftlichen Analyse der zuverlässigste Weg für die Auswahl.

In diesem Vortrag wird Hadaura Sippou Mino-Papier ausgewählt als Untersuchungsbeispiel und Referenzobjekt. Seine Eigenschaften wurden analysiert und mit *Xuan*-Papieren vom Festland verglichen. Sämtliche Papiere wurden mit folgenden zerstörenden Methoden untersucht und die Ergebnisse für nachfolgende Analysen dokumentiert. Zunächst wurden EDAX und FTIR benutzt, um die anorganischen und organischen Papierbestandteile sowie die Füllstoffe und die Binde- und Leimmittel offen zu legen. Ein Elektronenmikroskop zum Scannen diente der Untersuchung der Oberflächenstruktur der Papiere. Es war keine Überraschung, dass die meisten der zeitgenössischen chinesischen Papiere heterogen sind, d.h. sie bestehen aus einem Gemisch von verschiedenen Fasern, überwiegend Bast mit Reisstroh oder Bambus, während Mino-Papier homogen ist. Die Veränderung des Säuregrads des Papiers wies auf molekulare Veränderung der Fasern nach dem Altern hin. Die Haltbarkeit sowohl von chinesischen als auch japanischen Papieren konnte anhand der erwähnten Parameter verglichen werden.

Résumé
Dès la dynastie *Han*, les chinois ont utilisé la fibre végétale, comme le chanvre (*Mazhi*), la mûre (*Sang pi zhi*), la mûre (*Chu pi zhi*), le rotin (*Tang zhi*), le bambou (*Zhu zhi*), les arbustes de blé ou de riz (*Cao Zhi*) et le Xuan (*Xuan zhi*) pour la fabrication de papier. Après deux mille ans des quantités énormes de papiers chinois ont été fabriquées en Chine. Comme un nombre

considérable de papiers ont des qualités semblables de douceur, de blancheur, de texture, de dessin vergé etc., il est difficile de distinguer une espèce de papier utile parmi une multitude d'options matériel. Ça peut aider si l'on saît où le papier a été fabriqué, cependant, la surveillance de qualité de papiers fabriqués en Chine est toujours très lâche de telle manière que la performance de l'analyse scientifique reste le moyen le plus fiable à vour guider dans la sélection.

Dans cet exposé le papier Hadaura Sippou Mino a été choisi comme exemple d'enquête et de référence. Ses qualités avaient fait l'objet d'une analyse et d'une comparaison avec les papiers chinois Xuan fabriqués en Chine centrale. Tous les papiers étaient analysés par destruction selon la méthode suivante et certifiés par analyses consécutives. Dans une première étappe, les deux méthodes EDAX et FTIR étaient utilisées pour révéler et leurs compositions inorganiques et organiques de papier et leurs charges et agents de liant/collage. Un microscope scanneur électron et un microscope polarisé par éclipse Nikon E600 étaient utilisés pour enquêter la morphologie de surface des papiers et leur espèces de fibre. Ce n'était pas une surprise que la plupart des papiers contemporains chinois étaient hétérogènes, c'est à dire qu'ils sont mélangés avec des matériaux différents, principalement le liber avec de la paille de riz ou de la fibre bambou tandis que le papier Mino est homogène. Le changement de l'acidité du papier faisait avertir qu'une transformation moléculaire des fibres avait eu lieu après le vieillissement. La permanence des papiers et chinois et japonais pouvait faire l'objet d'une comparaison à l'aide des paramètres susmentionnés.

Introduction

In this article, several contemporary Japanese handmade papers were chosen as study examples and references for comparing with the quality of Chinese papers in the market. Their properties were analyzed and compared by studying their changes in pH and colour before and after 28-day ageing. Moreover, a scanning electron microscope was used for studying the topographical features of papers, while EDAX was used in revealing the inorganic and organic composition of papers, as well as their fillers and binding/sizing agents. It was found that paper made of a single plant fiber, e.g. Pi zhi (Paper mulberry), bamboo and kozo performed well. Their pH changed less than one unit and CIE values less than two after 28-day ageing.

History of papermaking

It was well documented that Cai Lun made paper from old rags hemp (Ma), tree bark and fish nets for his emperor at about 105 A.D, Eastern Han dynasty (25A.D-280 A.D.). However, some paper-like materials, Baqiao zhi was excavated at Xian at 1950s, which are the earliest paper made in the world. Group of hemp fibers were found inter-mingling with each other under microscopic inspection. This discovery has proven that papermaking began at the Western Han dynasty, one hundred years before the paper invention at Eastern Han dynasty.

People used hemp, grass, rattan, mulberry and paper mulberry fibers, a kind of pi materials (sang pi and Ku, Chu, Kou pi) for making their papers since the beginning of Han dynasty. At Tang dynasty (618A.D.-907A.D), various hemp fibers used, namely: Daima, Jute (Huangma), Flax (Ya- ma), Ramie or China grass (Chuma) as well as bamboo and grass fibers.

Papermaking techniques developed to an apex stage at Song dynasty (A.D.960 – 1279). Paintings and calligraphies from that dynasty could be kept till now in many renowned museums, like: The Palace Museum in Beijing, in Taiwan and the Freer Gallery of Art, The Smithsonian Institute. We found that these paintings had been generally kept over

several hundred years without any signs of degradation or any insect problems as long as they had been stored properly.

By the tremendous demands on different uses of Chinese papers, Gu Xuanzhi () was developed at the late Song dynasties. Gu Xuanzhi was mainly made of the indigenous plant fiber, Pteroceltis tartarinowii Maxim, together with straw. Strictly speaking, it was made by Cao dai-san at the Anhui province. Owing to the existence of straw fiber, the paper showed magnificent effects with the Chinese ink. Many calligraphers or painters liked to draw or paint on Xuan paper from then on.

There are three main types of Xuan paper according to their fiber composition currently supply in the market, namely : Jingpi (60% bast fiber, 40% straw fiber), Techong Jingpi (80% bast fiber, 20% straw fiber), Mianliao (40% bast fiber, 60% straw fiber). Artists usually draw on Jingpi and Mianliao papers. Mounters for Chinese painting usually use Mianliao as a backing paper because of its softness and flexibility. Each type of paper may be sub-divided into three groups - fully sized; half sized or no sized depending on the purpose of usage.

Table I: The development of Chinese papermaking at different dynasties

Dynasty	Period	Type of Fiber Used
Western Han	206 BC – AD 9	Hemp: Baqiao zhi
Eastern Han	AD25 - 280	Hemp paper with tree bark made by Cai Lun Paper mulberry
Eastern Jin	AD 317 - 420	Rattan paper originated at Shanxi
Southern and Northern Dynasties	AD 420 - 588	Grass and rattan fiber
Tang	AD 618 - 907	Classification of Hemp fiber: Hemp (Daima) Jute (Huangma) Flax (Yama) Ramie or China grass (Chuma) Mulberry (sang，*Morus alba*). It is the food for silkworm. Paper mulberry (ku chu or kou 構，*Broussonetia papyrifera*). Paper mulberry was called ku sang or chu sang Rattan, Grass and Bamboo paper became popular in the middle of Tang dynasty First kind of Xuanzhi made at Xuancheng, Anhui.
Northern Song	AD 960 - 1127	Straw discovered Rice is widely grown as a staple at the south of the River Yangtzi. Its stalk can be easily and cheaply processed to form a pulp.

Southern Song (Later Song)	AD 1127 - 1279	Hemp and rattan paper were replaced by bamboo and Paper mulberry fibers. Gu Xuanzhi made by Cao dai-san*:* *Pteroceltis tartarinowii Maxim*, or *Ulmus Cavaleriei Leveille*,
Yuan	AD 1279 - 1368	Gu Xuanzhi
Ming	AD 1368 - 1644	Gu Xuanzhi Be tested with *100% Pteroceltis tartarinowii Maxim*, or *Ulmus Cavaleriei Leveille*, in content
Qing	AD 1644 - 1911	Xuan zhi Mixture of straw fiber with *Pteroceltis tartarinowii Maxim*

Testing samples

We collected twelve Chinese paper samples generously donated by the Zhongshan University. These papers have been used for the book conservation. The samples fall into groups of Pizhi (Paper mulberry fiber), Bamboo paper (bamboo fiber) and cotton paper (bast fiber) with pH ranging from 5.89 to 9.11. They are namely: Jingpi, Cotton paper, bamboo paper, old bamboo paper, Fengpizhi, pizhi, Fengpizhi (light yellow), Ningbo cotton paper, Ningbo cotton paper (dark and light yellow).

For the Japanese papers, we have chosen nine different kinds of paper which had been tested in 1985 with satisfactory results in their permanence (5). They are Uda-Sinfukutora (95% Kozo/ 5% Pulp), Hadaura-Siprou (100% Kozo), Misu- Manyou (100% Kozo), Jin gang Li (100% Kozo), Kitakata (90% Phillipine Gampi / 10% Pulp), Silk Tissue (Gampi and Sulphite pulp), Hosokawa Ohban (100% Kozo) and Kaji (100% Kozo). They are now currently supplied by the Masumi Japanese Washi Paper in Japan and the University Products in the United States. The pH of these papers ranged from 6.9 to 9.2.

Papers' characteristics before and after ageing

Experiment Methods

pH

Twenty-two samples were aged in a 90^{o}C, 50%RH ageing chamber for 28 days. The changes in pH were studied by cold water extraction conforming to ASTM D778-97. The pH values were determined using an Orion 650 Bench top pH meter equipped with an Orion pH Sure Flow electrode. The electrode was calibrated using pH 4 and pH 7 buffers.

CIE L*a*b* colorimetric test

The CIE values of sample papers before and after ageing were measured by Konica Minolta CM-2600d at an observer angle of 10 degree with D65 observation illuminant. The changes of L*a*b* values, i.e. the E values of the samples were compared subsequently.

Scanning Electron Microscopy/ EDAX

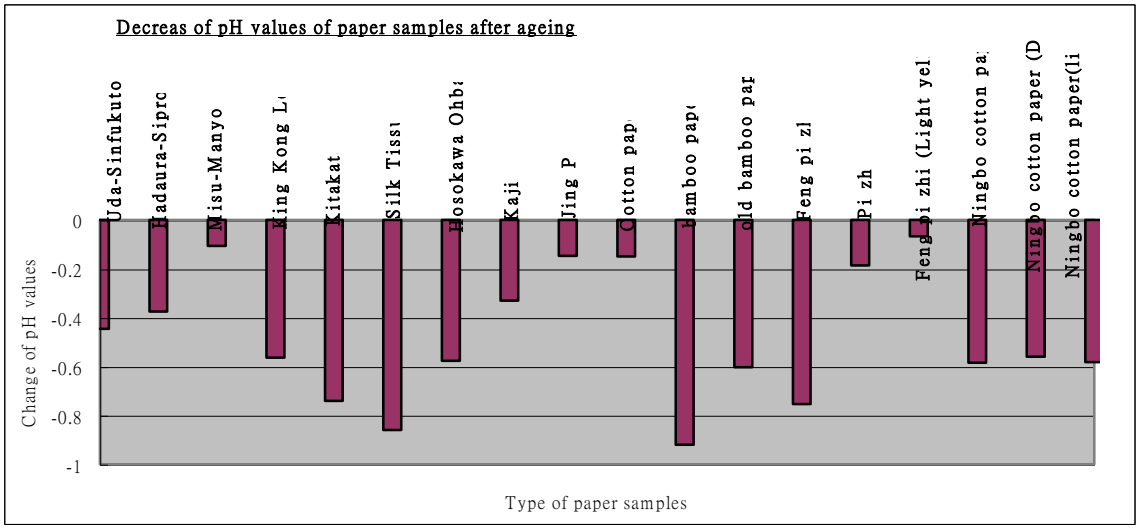
In order to have more detail information of the elemental composition of the samples in related to their performances, a Scanning Electron Microscope equipped with EDAX by FEI Quanta 200 was used for studying the morphology of the paper samples (6, 7). The SEM was operated at an accelerating voltage 12-13.8kV, i.e. the magnification from 200 to 500. It was equipped with a lithium-drifted silicon x-ray detector and a Naron Voyager II x-ray microprocessor. EDAX detect elements from sodium (Na) to uranium (U). Each paper sample was measured five times.

Results

pH

All of the papers did not change much in their acidity. All the pH of the paper samples decreased in the range from 0.05 to 0.9 units individually after 28 days ageing.

Figure I: Decrease in pH values of paper samples after ageing



CIE colorimetric test

We found that most of the Japanese samples changed less than 4 units in their CIE ΔE values. Five of the Chinese samples changed more than 4 units, among two of them changed even more than 5 units. Previous study showed that the ΔE values of paper samples after artificial ageing greater than 5 would pose an observable colour change in respect to their brightness, yellowness/blueness and redness/greenness.

Figure II: Change in ΔE values of paper samples

ΔE value	Paper samples
2	Hadaura- Siprou Misu-Manyou Silk tissue Hosokawa Ohban Kaji Chinese Cotton paper at Zhongshan Old bamboo paper at Zhongshan Sha Zhi Beijing Library Pizhi

> 4	Chinese Jingpi at Zhongshan Bamboo paper at Zhongshan Pizhi at Zhongshan Fengpizhi at Zhongshan Cotton paper at Ningbo

Scanning Electron Microscopy/ EDAX

The photomicrographs revealed that there were jelly-like substances in between the plant fibers of two of our samples. One was Haudura and the other one was Chinese A (Jingpi provided by the University of Zhongshan). There were powders in other samples. For further investigations, EDAX was used. We took five EDAX measurements at the fiber-fiber interception on each of the Chinese and Japanese samples. Resulting photos are shown below.

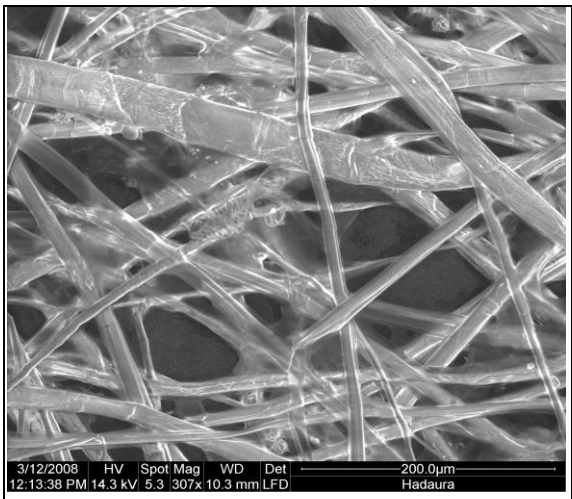


Photo I: SEM micrograph on Japanese paper: Hadaura – Siprou with Jelly like substance; Magnification x 300

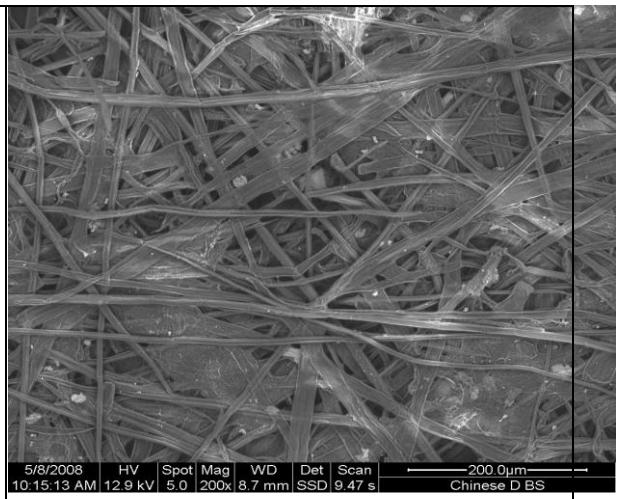


Photo II: SEM micrograph on Chinese paper: Old bamboo paper with powder; Magnification x 200

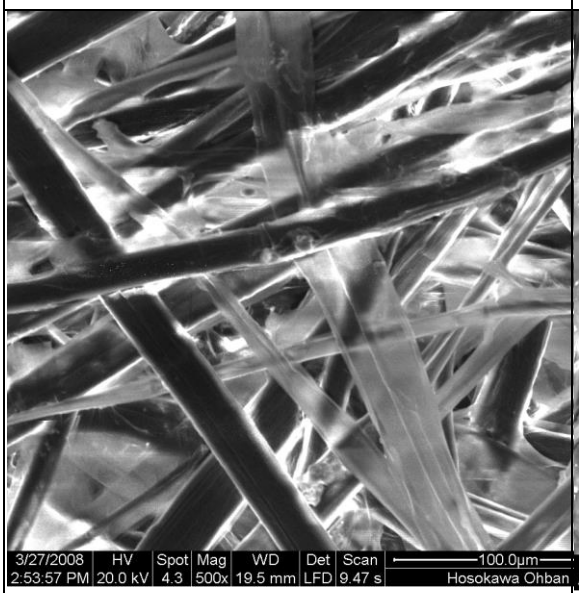


Photo III: SEM micrograph on Japanese paper: Hosokawa Ohban without any substances; Magnification x 500

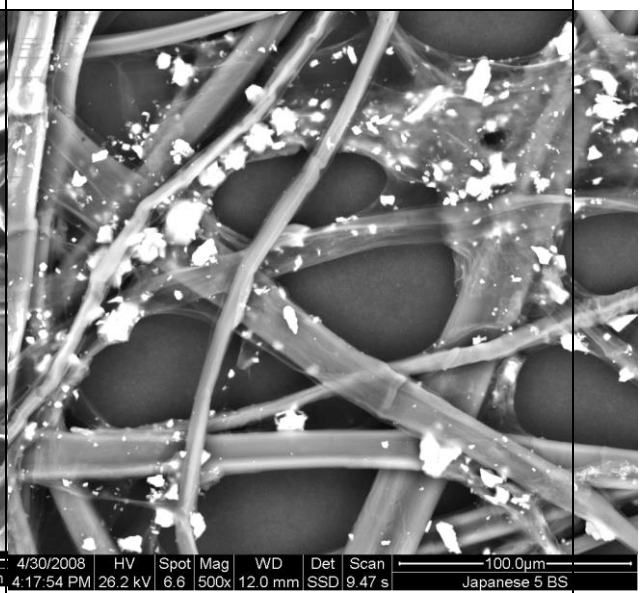


Photo IV: SEM micrograph on Japanese paper: Misu-Manyou with powder; Magnification x 500

Table II: The elemental composition of substances in between the fibers revealed by EDAX

Paper sample with ΔE 2	Elemental composition	Significance
Hadaura-Siprou	C,O,Ca, Al, Mg	Surface sizing agent
Misu-Manyou	C,O, Ca, Cl, S	Filler
Silk tissue	C,O, Al, S	Internal sizing agent
Hosokawa Ohban	C,O,Ca, Al, Mg	Internal sizing agent
Kaji	C,O,Ca, Al, Si, Fe, S	Internal sizing agent, Filler
Cotton	C,O,Ca, Al, Mg, Fe, S, Ni	Internal sizing agent
Old bamboo	C,O,Ca, Al, Si, Fe, Ni	Filler
Shazhi	C,O,Ca, Al, Fe, S, Ni	Internal sizing agent, Filler
Beijing Library Pizhi	C,O,Ca, Al, Fe, Ni	Internal sizing agent

Conclusion

Those jelly-like substances found in Hadaura-siprou paper and Chinese A Jingpi contained carbon and oxygen. It may be the sizing agent which was applied on the surface of the paper after the sheet formation. Most probably they were soluble cellulose derivatives, such as: carboxy methyl cellulose, starch or vegetable gum which constituted a long chain of hydrocarbon polymer. Generally speaking, sizing agent was used to improve the surface physical properties of the paper.

For those papers without any noticeable jelly-like substances or powders around the fibers contained aluminum, sulphur, carbon and oxygen. Aluminum sulphate may be part of the main ingredients added to the pulps during the sheet formation. Aluminum sulphate acted as a kind of internal sizing agent. It was used together with wood resin acids to modify the water absorption properties of fibers by incorporating hydrophobic molecules during the sheet formation (6).

Under the examination of EDAX, the powdery substances contained Aluminum, silicate, calcium and oxide. They were found in some of paper samples, namely: Misu paper, old bamboo paper, Kaji and Shazhi. It may be a kind of filler, i.e. kaolin, $Al_2Si_2O_5(OH)_4$, limestone (Calcium oxide/ calcium hydroxide/ Calcite, $CaCO_3$ or silica. Filler has been greatly used as a whitening agent and smoothening agent for improving the optical properties of paper as well as its surface smoothness (6).

To conclude, the determination of a high quality handmade paper was a difficult and a complex question. It depends on many ubiquitous factors, i.e. I) the quality of plant fiber, the growing environment of the plant, homogeneity of plant fibers used, II) tidiness and completeness of papermaking and converting processes, such as: bleaching, beating, quality of water and the techniques, III) chemical, reagents and additives applied during the papermaking process, i.e. the sizing agents and the fillers.

Notwithstanding, it was found that paper made of homogenous fibers, e.g. Kozo fiber deteriorated less in terms of their change of acidity and colour after the artificial ageing. From the results, it was very difficult to identify a paper performing the best out of the twenty-two samples, but it was interesting to find that paper with the above elemental composition, such as magnesium and calcium salts gave good results on testing performance. The role of elemental salt as well as its concentration used during papermaking would worth further investigation.

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