

NATIONAL ARCHIVES OF AUSTRALIA

Research Project Report

20th Century Paper Quality

1. Introduction

The National Archives' holdings are largely paper-based. On a very rough estimate we currently hold 35 million paper-based items which approximately equates with one billion sheets of paper. This holding will continue to grow well into the future as agencies transfer their older paper-based records into custody. Even as agencies move towards digital recordkeeping the Archives will continue to be responsible for preserving a very large and deteriorating asset.

Because of the size of this holding it would be useful to break it down into categories of quality. This analysis will help inform decisions about which records to target for storage and other preservation treatments.

There had been anecdotal talk amongst archives staff that during certain periods of the 20th century, paper quality waxed and waned. It was suggested that paper produced at times of economic hardship such as the war periods and depression were poor quality and therefore more prone to degradation.

The aim of this survey was therefore to look at a range of quality issues relating to paper and see how these varied over the period covered by the NAA collection. In this way it is hoped to produce information that will assist in making preservation decisions. It was also hoped to provide a research resource for the National Archives and other cultural institutions with paper-based collections.

As part of the project a level of historical research was carried out using printed and archival sources. This was to assist in better understanding the economic and social climate during the period which may have had some bearing on the properties and quality of paper. The questions of interest were:

- Who were producing commercial papers in Australia during the 20th Century? And in what quantities and qualities? How might this quality have changed over time?
- Where was Australia importing paper and pulp from during the 20th century? And in what quantities and qualities? And how might this have changed over time?

2. Paper deterioration/permanence

The deterioration of paper is caused by the breakdown of the cellulosic substrate and this is related to both internal and external factors (El Saied et al. 1998, p. 155). The benefits of ideal storage, handling and correct conservation treatments to slow the effects of external deterioration due to light, excess humidity and pollution are well known. The complication often lies with the inherent weaknesses of the material, embedded with the fabric of the paper at the time of manufacture. These internal factors include fibre quality (due to length, source, pulping method), sizing, coatings, fillers, and the presence of acidic and metallic compounds. (Browning 1977, cited in Rose & Nitsche 1991 p. 251).

3. A partial history of paper importation and manufacture in Australia during the 20th Century

Introduction

Prior to 1938 when APPM began production of fine paper in Burnie, Tasmania Australia's fine paper supply was imported (Robertson & Trace 1983 p.119). Australia did not have a strong fine writing and stationary paper manufacturing sector for a variety of reasons. A lack of softwood for pulp and early technical difficulties associated with manufacturing pulp from Eucalypt hardwoods were not overcome until the interwar years (Robertson & Trace 1983 p.119). Heavy costs associated with importing raw materials made competing with cheaper imports incredibly difficult despite tariffs in place by state governments. There had been relatively unsatisfactory results from initial testing of eucalypt for pulps and a general opinion that it 'could not be done'. The view was that eucalypt pulp, with its short fibre, would only be able to be used as a filler and would not impart strength to the paper (Jefferys 1947 p65).

Paper Production and Eucalypt Pulp

Early papers made in Australia had utilised rags as raw material. By the latter half of the 19th Century newsprint and toned papers were produced from rags, straw, old sugar bags, rope and waste paper and continued to do so until 1911, after which Australian companies began to import chemical wood pulp (Rawson 1953, p.27).

From 1918 tests were carried out by Boas and L.R Benjamin in laboratories in WA and Victoria and in a semi-commercial scale at an APM mill in Geelong. These experiments demonstrated that soda pulp made from eucalypts could be utilised to manufacture fine printing and writing paper.

In 1928 the semi-commercial mill owned by Tasmanian Paper Pty Ltd at Kermadie, which included a digester for sulphite cooking, carried out over two years of experimentation which covered "sulphite pulping, grinding, bleaching and decolourising, and the conversion of pulps to several grade of paper" (Cohen 1948 p.311). The results found that mechanical and sulphite pulps made using mature Eucalyptus Regnans produced a dark pulp which required decolourizing. Contact with iron in the standard machinery reacted with the tannin, resulting

in a greyish-blue paper (Jeffreys 1947 p.66). This was counteracted by lining the machinery with stainless steel.

In 1935 a joint investigation was carried out by Tasmanian Paper Pty Ltd, Paper Makers Ltd and Australian Paper Manufacturers Ltd confirmed that writing and printing paper could be made with eucalypt pulp but it was not particularly economical as it was “supplying a comparatively small market that demanded innumerable grades of paper for different purposes” (Jeffreys 1947 p.67).

A 1943 Commonwealth Tariff Board report on the manufacture of paper and paper boards examined wrapping paper and board, fine printings and writings and newsprint paper. It also gave an overview of raw materials, mechanical and chemical wood pulp methods.

In the report paper is divided into two classes: mechanical and chemical pulp, these are outlined as set out below.

“Mechanical wood pulp is ground on a natural or synthetic grindstone. The resulting pulp consists of all the original constituents of the wood with minimal loss of bulk. This method was used by Australian Newsprint Pty Ltd in Boyer Tasmania utilising Australian Eucalypts to manufacture newsprint, proportioned with 17% Canadian ‘news sulphite’ pulp (Cohen 1948 p.312).

Chemical pulp is produced using a variety of processes (sulphate, soda and sulphite) which use chemicals to dissolve, cook or digest the wood, removing non-cellulose constituents of the wood. This process has results in a lower yield with up to 50-60% of the bulk of wood removed.

The sulphate process (Kraft process) uses a mixture of sodium sulphide and caustic soda (sodium hydroxide) to dissolve the non-cellulosic material from the pulp. Australian Paper Manufacturers Ltd (APM) was operating a Kraft pulp mill at Maryvale Victoria from 1939. The soda process uses caustic soda (sodium hydroxide). Up until the late 1930s hardwood pulps manufactured by the soda process were used as fillers in book and magazine paper to lend bulk and opacity. Treating hardwood in this way led to “low yields of hard to bleach pulp” (Cohen 1948 p.309). Associated Pulp and Paper Mills Ltd mill at Burnie used a modified soda process for Tasmanian hardwood (mixed with 10% imported sulphite pulp) to manufacture fine writing and printing paper. APM also used the soda process at its Botany mill.

The sulphite process employs sodium bisulphate and had been used widely for the processing of long fibred softwoods and at the time of the report in 1943, had not been considered appropriate when manufacturing fine writing paper from short fibred hardwood.”

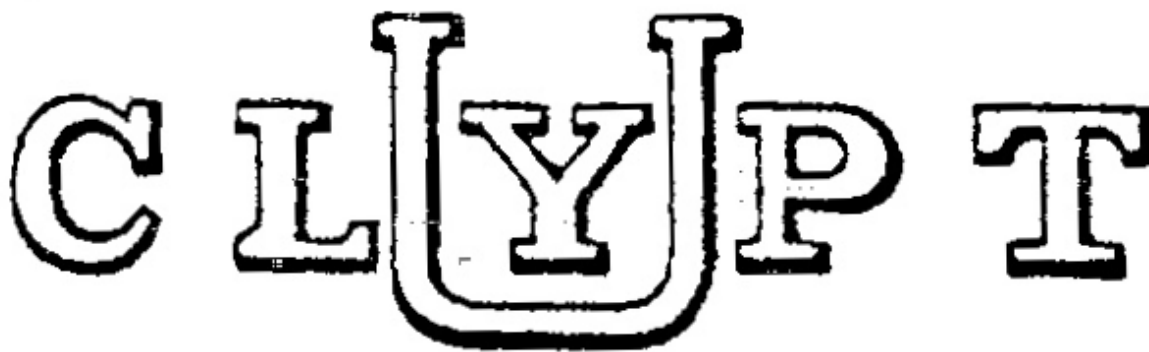
Wartime Supply and Production of Paper

Prior to the First World War 80 per cent of Australia's paper was imported and wood pulp for production of paper in Australia was being imported.

The First World War, which broke out in 1914, created a predicament for an industry reliant on imports. Shipping space required for imported pulp became scarce and chemical and coal prices soared (Sinclair 1990 p.48). Australian paper manufacturers went into overdrive to meet the surge in demand for paperboard, wrapping and fine writing and printing paper. APM's mill at Geelong was supplying Federal and State governments with writings and printings "almost exclusively", at pre-war prices regardless of the 50% increase in market price (Sinclair p.50-53). Shipments of pulp and paper to Australia were heavily impacted by a lack of shipping space and by 1917 there was an acute paper shortage with the demand for paper rising dramatically. Prices doubled between 1914 and 1916 (Rawson p.62) and the government found it necessary to ration the available supplies. In response to this many other alternatives to imported pulp were investigated. In 1916 W.A Hearngraves, head of the South Australian Department of Chemistry carried out investigations into the prospects of establishing a paper making industry in South Australia, believing that using straw mixed with imported pulp would make good writing and printing paper.

By 1936 APPM was producing fine writing and printing paper at their Burnie Mill and in 1938, produced its first paper made from 100% eucalypt pulp "on the largest fine printing paper machine in the British Empire" ('Eucalyptus Pulp' 1938). This paper was given a special watermark U-Clypt.

Indicated by



It was reported that the paper had been pronounced equal in quality to esparto grass pulp paper "usually regarded as being much superior in quality to those which are made from wood pulp alone".

Jeffreys, in the paper he presented at the APPITA Conference of 1947, owned that the paper shortage that occurred during the war "did make customers a little less particular about strength and other properties than they otherwise might have been" (p.65).

During World War II this mill was the sole manufacturer for writing and printing paper in Australia (Cohen 1948 p 312). Perhaps they were not quite so forgiving. According to Rawson (p.86) the company applied to the Tariff board in 1939 for a protective duty on printing and writing paper. The printers and stationers associations protested complaining that members had been less than impressed with the inconsistent quality of the first eucalypt pulp papers supplied by APPM.

The U-Clypt watermarked paper was found in the sample set twice, dated 1942 and 1947. It tested positive for alum and clay and had a pH of 4 for both samples. During World War II this mill was the sole manufacturer for writing and printing paper in Australia (Cohen 1948 p 312).

Copying papers and printing papers were mostly imported from the UK in 1936/37 which was drastically reduced during the war. Prior to the war a substantial quantity also came from Canada. Smaller quantities came from Japan, Norway, Sweden and the US. Imports from Austria, Czechoslovakia, Finland and Germany all ceased in 1940-41. Canada was Australia's main source for newsprint 1936- 1941 whilst Sweden supplied Kraft paper. By 1942 the shortage of paper during the war prompted the NSW government to launch waste paper collections which was then recycled to make up the shortfall in raw material (Rawson 1953 p.113).

Time was not available to carry this research further. Future research will be aimed at fleshing out this story and bringing it up to date.

4. Survey

The aim of the survey was to methodically examine a series of permanence-related factors across the 20th Century. The factors chosen were good indicators of permanence and could easily be determined using observation, spot tests, FTIR analysis or XRF analysis. The following were recorded: Acidity (as pH) as well as the presence of Alum, Lignin, Calcium Carbonate, Clay and Gelatine. The dimensions of the sheet and the presence and wording of any watermark were also recorded.

Methodology

Choice of samples

The sample set included 1130 samples. Ten samples of paper from each year from 1900 up to and including 2013. Every attempt was made to ensure randomness although it was not possible to be perfectly random as papers from some eras were scarce and thus had to be actively sought out.

Samples were collected in a variety of ways:

- a) As files were prepared and treated in the lab in readiness to go to the reading room loose fragments from the file were placed into zip lock bags with the year and details of which file they originated from. These fragments did not hold any information on them.
- b) Pages taken from Archive files marked for destruction.
- c) Personal paper from colleagues collections that could be accurately dated
- d) Collection items with the file barcode, series or container barcode recorded

The paper samples were limited to a particular set of characteristics in order to keep results from becoming skewed by too many variants in paper types. The samples were all plain coloured, fine writing, typing and copying papers. No coloured papers, card or file folder paper etc. were included in the sample set.

Sampling Limitations

The following limitations of the sampling methodology have been recognised and should be considered when interpreting the results of this study.

Sample size

The sample size is relatively small considering the large period of time it covers, and the population of papers in the archive. Ten samples per year is a mere snapshot. To be statistically valid and derive any specific information regarding a particular period of time in the century, a larger sample set, targeting that period will need to be taken. At the end of this project we hoped to have a result that will lead to a further more in-depth focussed investigation of papers produced at certain times based on the conclusion these maybe more vulnerable to degradation.

Sampling Method

The testing involved the use of reagents which stain/colour the paper. It was hoped that a negligible amount applied via a micropipette would allow for a test that did not damage the appearance of the paper or damage them. The unpredictability of levels of absorbance of the reagents into different papers and the process of applying several indicators to arrive at a pH reading proved to be potentially damaging to samples. Initial practice testing on scrap paper showed that irreversible staining occurs on test samples and therefore could pose a risk to any whole document that was part of the collection. A refining of the sampling method as we proceeded allowed for the use of collection items in an inconspicuous area. A small spot of the testing reagents, applied with a writing nib, examined under magnification was enough to give a result. According to Batterham the small remaining spots on the paper do not impair the information contained in the documents it was considered to be worth the information that could be derived from it and therefore justifiable. No paper or document valued for its artistic/visual merit was utilised in the research.

Testing staff

The testing was carried out by Caroline Milne and Ian Batterham with consultation from the Conservation Chemist Rajani Rai. Imaging and recording of watermarks was done by Travis Taylor.

Testing venue

The testing was carried out in the National Archives of Australia's preservation laboratory.

Test equipment

- Bruker Optik Alpha-P Fourier Transform Infra-Red Spectrophotometer with DGTS detector, operating at 24 scans per sample
- Innov-x Delta XRF gun
- UV source emitting light at wavelength 366 nm
- Glass and metal pen nibs for administering the spot tests

Database

As each page was tested it was individually listed on an Excel spread sheet. The following details were entered:

- Date
- Description (e.g. typing paper, cablegram etc.)
- Watermark (whether present and description of wording)
- Provenance (e.g. Commonwealth Department, Commercial Business, private individual etc.)
- Image (e.g. typed, letterhead, electrostatic, colour etc.)
- Size (e.g. foolscap, A4, 174x208mm etc.)
- Condition based on a scale of 1 – 3 (1 being very good to 3 being bad condition)
- Alum (by spot test)
- Lignin (by spot test and FTIR)
- pH (by spot test)
- Carbonate (by FTIR)
- Optical Brightener (by fluorescence test)
- Clay (by FTIR)
- Gelatine (by FTIR)

Spot tests were applied with a fine writing nib (glass for alum and phloroglucinol) to an inconspicuous place (verso top right corner near file pin hole). It was found that such nibs allowed the placement of a tiny spot of solution. Testing in the same area and an area rarely handled, lessened uncertainty/error.

Testing

Lignin

Background

Lignin, an organic polymer, is the binding component of wood that keeps cellulose fibres together. High yield pulps, such as newspaper, are prepared by mechanical, semi-chemical and chemical processes which have a minimum of the lignin component removed. It is left to bulk up the paper, increasing the yield from a certain amount of wood (McCrary 1991, para 9). It is highly unstable and quickly yellows due to limited photostability, causing the paper to become brittle (Trafela et al 2007 p.6321). The National Archives of Australia have

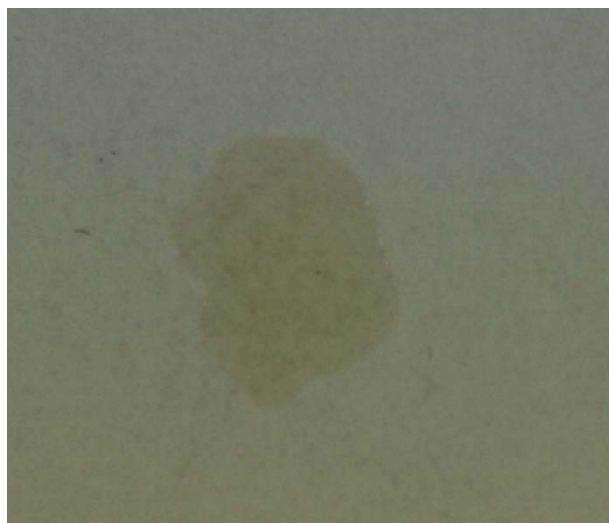
stringent standards which require paper to have nil lignin content in order to be described as permanent/archival quality paper. It has long been considered that mechanical wood pulps which contain concentrated amounts of lignin, produce papers with poor permanence (Barrow, McCrady 1991). Lignin does release acids as it rapidly oxidises and deteriorates yet Bégin et al (1998) demonstrated that if the paper is buffered with sufficient amounts of calcium carbonate it does not have any negative affect on the mechanical or chemical properties of the paper. The slight confusion regarding the effects lignin has on paper may be due to ground wood pulp, chemical wood pulp and alum-rosin sizing all being introduced at around the same time (during 1850-70) McKenzie (1990 p.30).

Problems with lignin detection

Testing for lignin can be problematic (McCrady 1991, Trafela et.al 2007) due to the complexity of its structure. Each end group or radical of the lignin polymer reacts in a characteristic way with chemicals. According to McCrady using the phloroglucinol test for lignin will only give a positive reaction (purple/magenta staining, the depth of colour being an indication of the amount present) when the lignin present in the sample contains the conifer aldehyde end groups. Nevertheless the method is a commonly used one and is included in TAPPI standard T401 om-3 fiber analysis of paper and paperboard. FTIR detection was also used to measure lignin presence.

Methodology

The presence of lignin was determined by both FTIR analysis and the phloroglucinol spot test. The phloroglucinol solution was prepared and applied as per Browning (p. 73). A positive was recorded if any purple colour or purple fibres were present under magnification.



Negative for Lignin

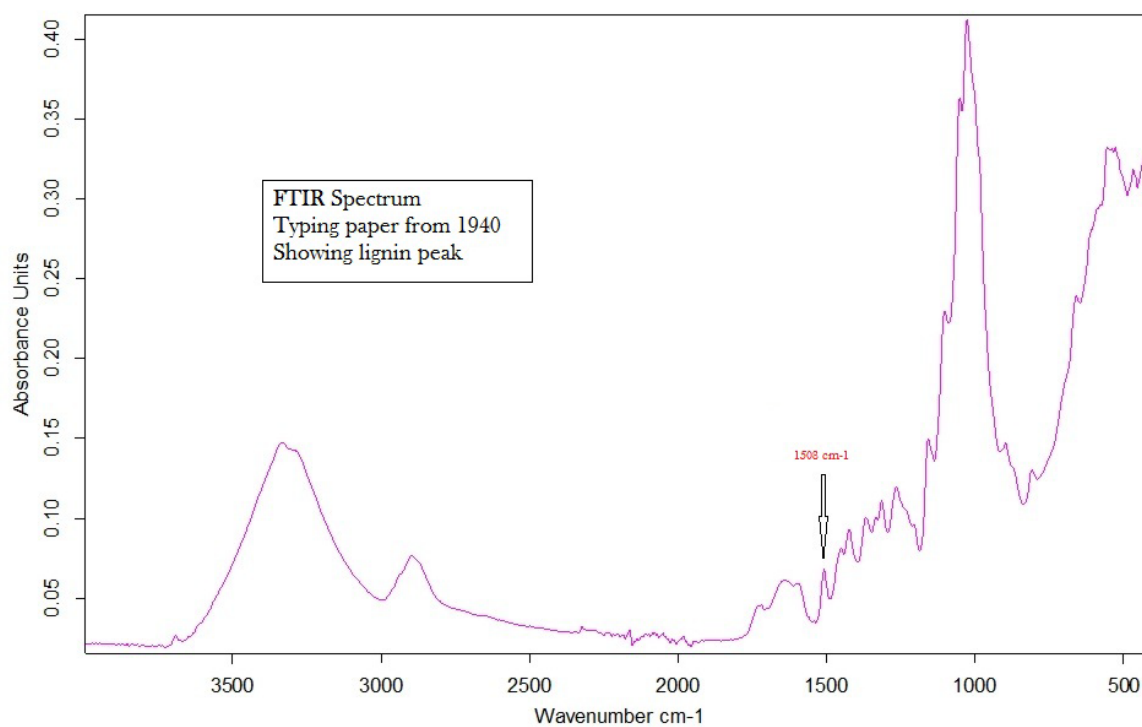


Positive for Lignin

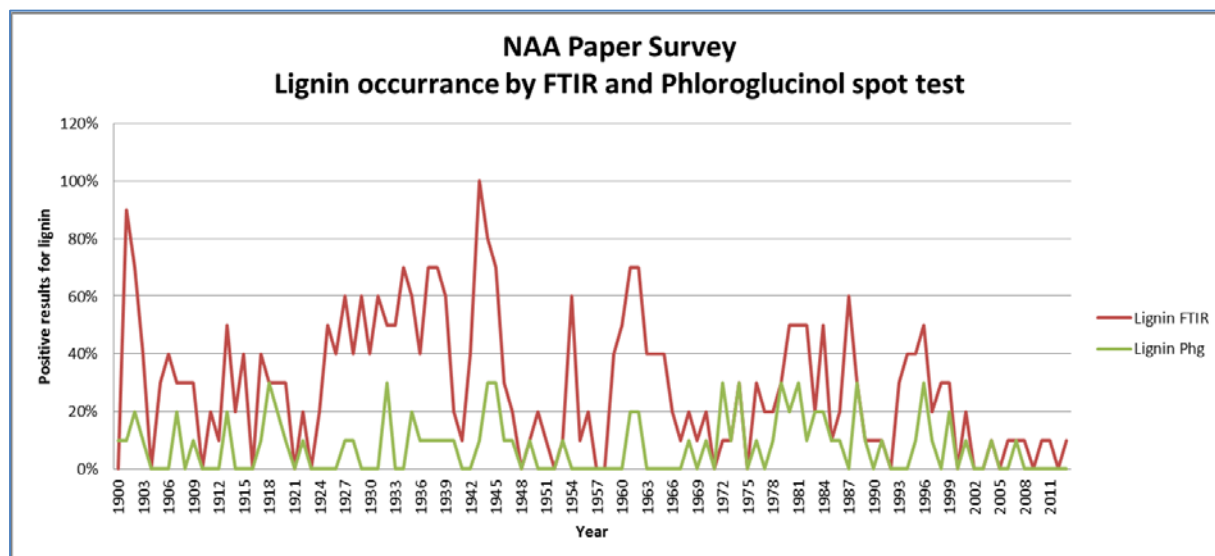


Lignin fibres

The FTIR analysis involved carrying out an integration of the paper spectrum in the 'fingerprint' area for lignin around 1508 cm^{-1} . Any integration result above 0.000 was recorded as a positive. A typical positive lignin spectrum is shown below.



Results and discussion



Both the results of the phloroglucinol and the FTIR result (peak area ratio number) were recorded. The two methods did not always give corresponding or predictable results. A positive with FTIR did not always produce a positive colour change when phloroglucinol was applied. Conversely, a colour change with phloroglucinol did not always show a positive reading with FTIR, although this conflict was rare. As referred to earlier, due to lignin's complexity phloroglucinol does not give a positive for all types of lignin and in total only of the 5.2% of the total sample set showed a positive with this method. Also, FTIR was clearly able to detect the presence of minute amounts of lignin whereas phloroglucinol would only detect significant amounts.

Some tentative observations can be made from the graph, for example the continued higher levels of lignin during the great depression years and an apparent leap in lignin content late in WWII, the latter possibly a result of a high use of poor quality recycled pulp for papermaking due to the unavailability of imported pulp. The other large peaks, around 1902, 1961 and 1987 are harder to explain.

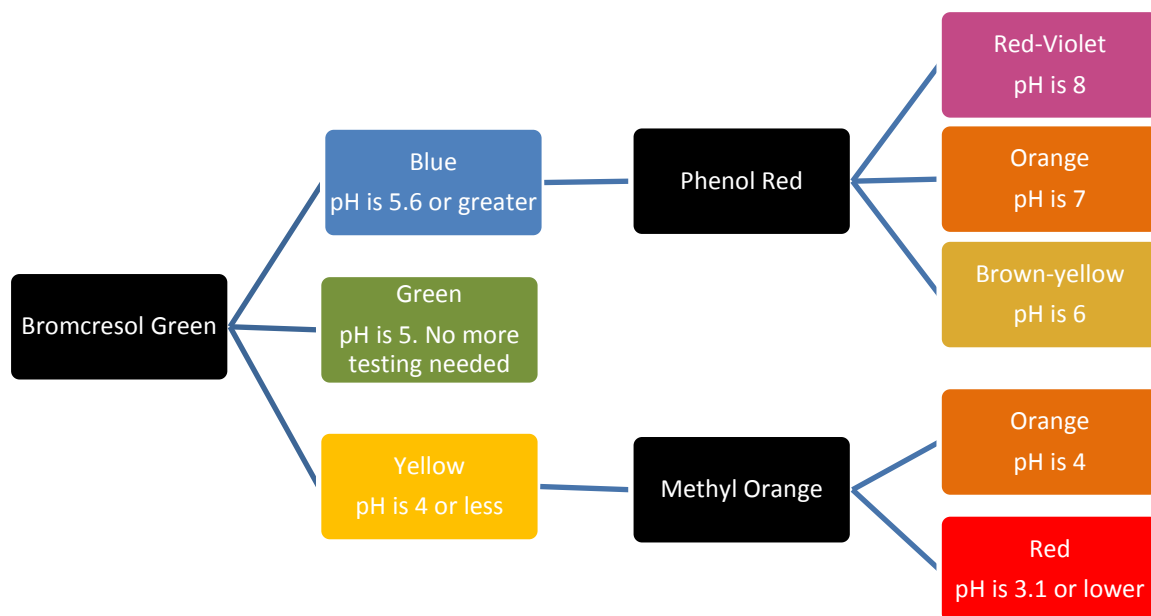
pH

Background

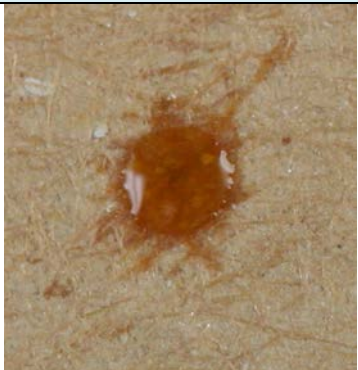


The principal agent affecting paper permanence and durability is acidity (Trafela et al 2007 p.6321). During the mid-20th century there was great alarm amongst archivists and librarians regarding the rapid deterioration and embrittlement of documents and books consisting of machine made paper (Williams 1981, p.203). Due to alum-rosin size, introduced around 1850, papers produced up until around 1990 frequently have a pH below 6. In addition to this, research carried out by the Library of Congress demonstrates that cellulose, considered one of the most stable components of paper, also generates acids (formic, acetic, lactic and oxalic) as it ages.

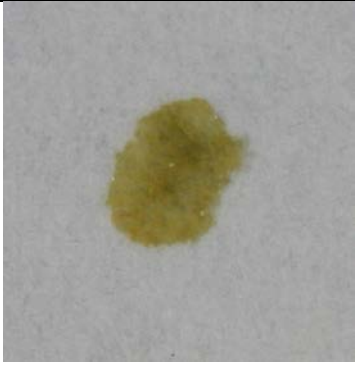
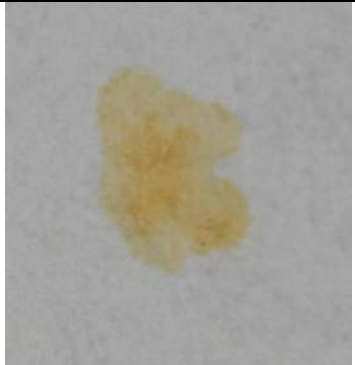
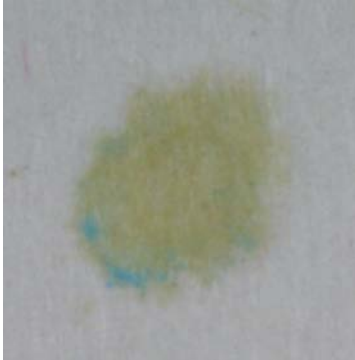
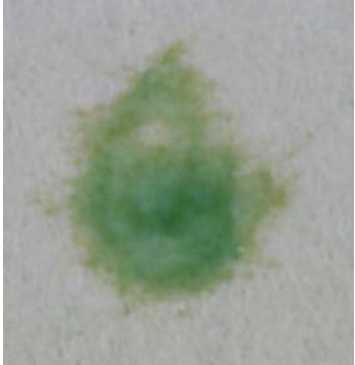
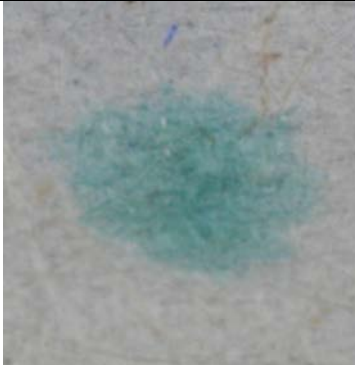
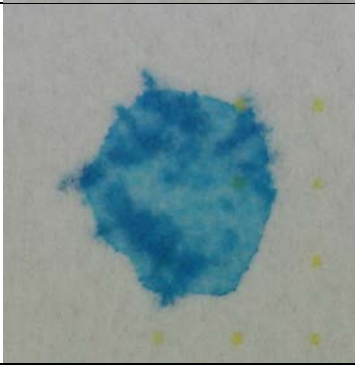

Methodology


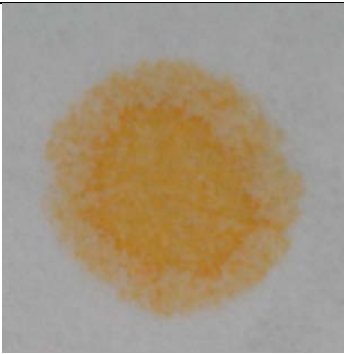
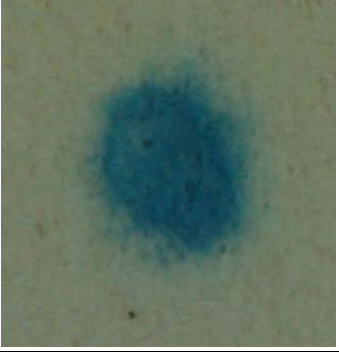
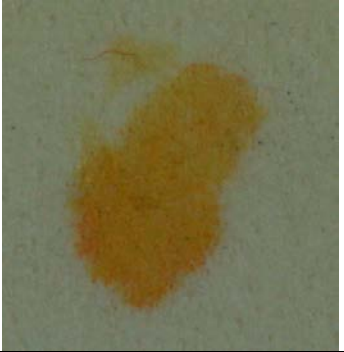


The pH was measured with three indicator solutions: Bromcresol Green, Phenol Red and Methyl Orange. This allowed us to determine the pH of a paper within 0.5 of a pH unit. Microscopic dots of the solutions were applied using glass writing pens. The colour of the spot was checked using a handheld microscope. The protocol followed was as follows:



Examples of papers at different pH values

pH	Bromcresol Green	Phenol Red	Methyl Orange
3.1			

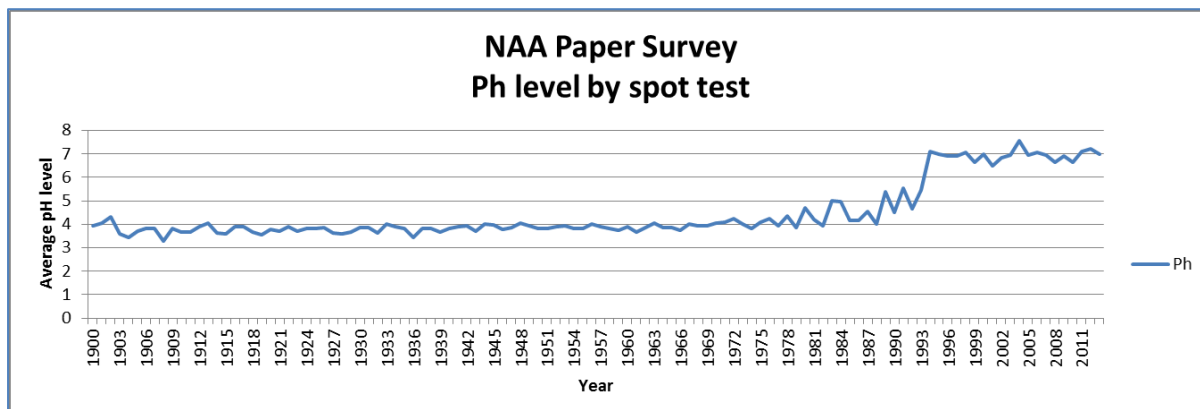
4.0			
4.5			
5.0			
5.5			
6.0			

6.5			
7.0			
7.5			

Limitations of the method

Measuring pH with indicators is not as accurate as measuring via the cold extraction method. Unfortunately the cold extraction method is destructive which ruled it out for this survey, which involved original items. Also, considering the large amount of samples to be tested; this method was judged too lengthy and time consuming to be suitable.

Results and discussion



The pH results are very easy to read and interpret. There is a gentle rise in paper pH up until the early 1970s where there is a series of small hiccups until around 1994 the pH jumps to the alkaline. The early gentle rise could be a result of the lowering of alum content whilst the major jump to alkaline would almost certainly be a result of the introduction of alkaline papermaking methods, specifically the introduction of carbonate as a paper filler.

Calcium Carbonate

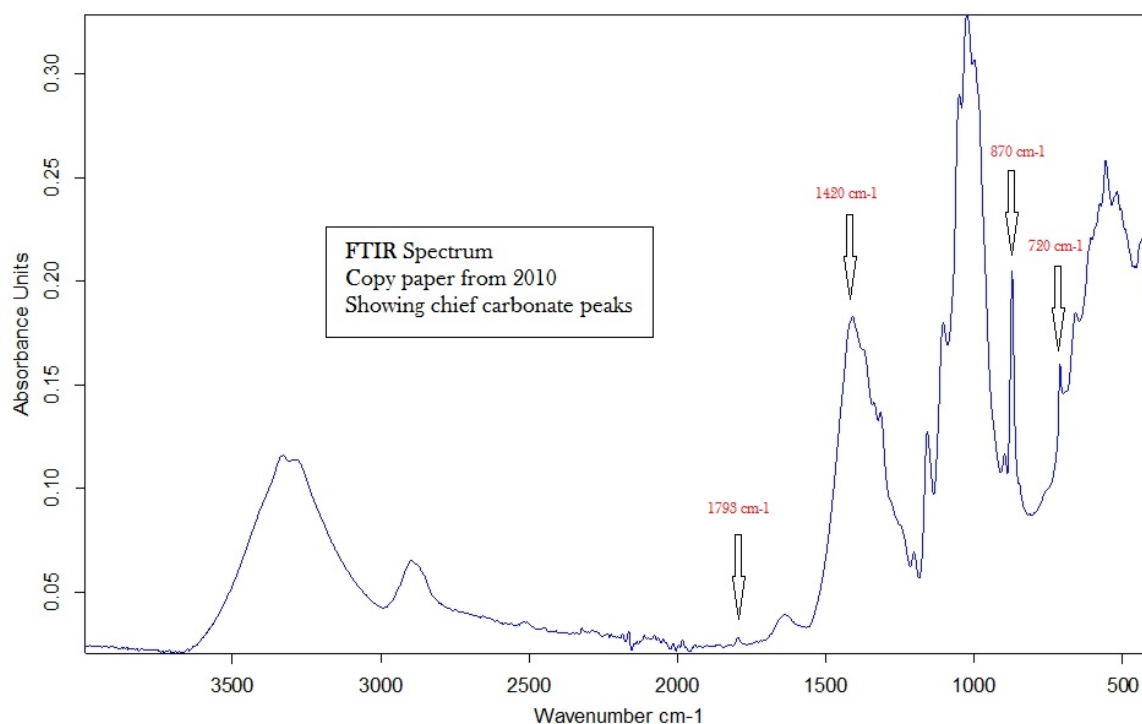
Background

Josef et al (cited in Houssni El-Saied 1998 p.156) demonstrated that paper made by traditional method, adding lime to the beating of the paper fibres resulted in a neutral paper due to the presence of calcium cations. Prior to 1980 calcium carbonate was already being used as a filler for paper, particularly in Europe where it was easily accessible in the form of chalk (Hubbe 2004 p.143). In the US, where it was only found in the form of marble and limestone, it was rarely used early on, due to the high level of energy required to grind it down. It was not until the advent of precipitated calcium carbonate (PCC) that it became commonly used (Hagemeyer 1984 cited in Hubbe p.143 2004). As paper moved to neutral and alkaline systems, calcium carbonate was increasingly used as a filler. It also provides the paper with increased brightness and its irregular particle structure gives the paper low gloss.

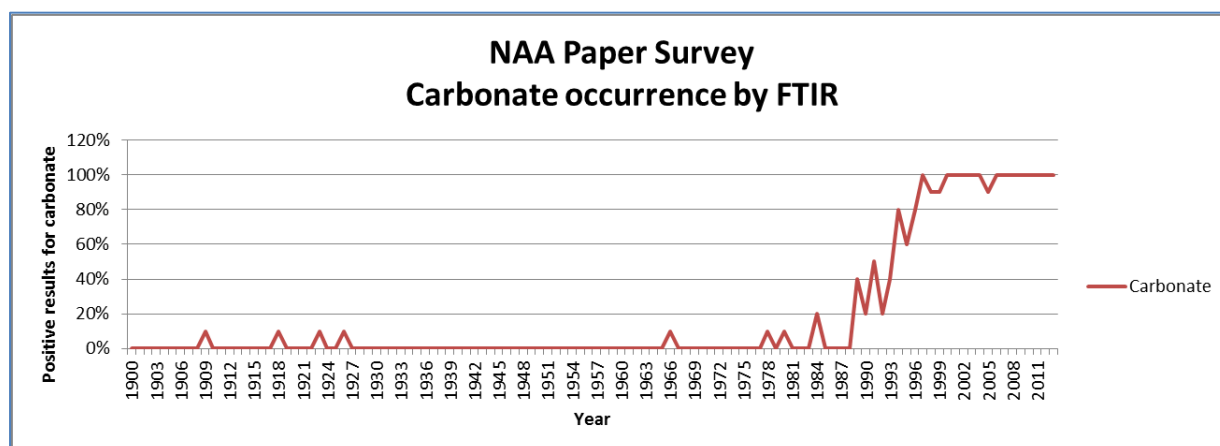
Carbonate fillers are vulnerable to acids, alum and other acidic chemicals, leading to the release of carbon dioxide and the formation of the corresponding salts (Eklund & Lindström 1991 p.255).

Methodology

The presence of carbonate was determined by FTIR spectroscopy. Carbonate has a distinctive FTIR spectrum, with peaks at 720, 870, 1420 and 1793 Cm^{-1} . The peaks are easily identified and generally visual analysis of the spectrum was sufficient to determine the presence of carbonate. If there was any doubt an integration was carried out in these regions. Any integration result above 0.000 was recorded as a positive. A typical positive carbonate spectrum is shown below.



Results and discussion



As predicted in early research, carbonate begins to be used around 1990. It was virtually universal by 1999. As was expected, due to the buffering effect of calcium carbonate, papers which tested positive for calcium carbonate were higher in pH (see Discussion and Conclusions below).

Alum

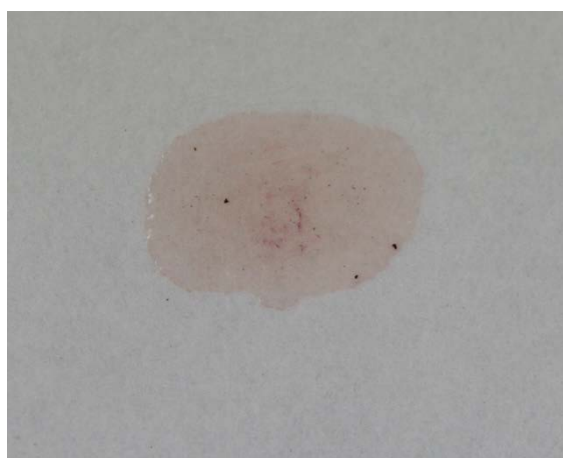
Background

Sizing agents are used to prevent excessive adsorption of liquids (such as ink) into the paper structure. Sizing is either added to the pulp slurry (internal sizing) or applying the size to the surface of the paper (surface size). Alum has been used as a sizing ingredient since the 15th century in the form of aluminium potassium sulphate. This was replaced by aluminium sulphate in the 19th century. It was used predominantly in rosin- alum sizing but was also

used in a range of papermaking processes. Alum acts as a mordant, binding primarily negatively charged pulp fibres, pulp fillers (such as clay) and size particles. Sodium rosinate and aluminium sulphate combine to form the water repellent aluminium resinate. In the presence of moisture the aluminium sulphate generates sulphuric acid. The ions of sodium sulphate and sulphuric acid combine to create the acidic product responsible for paper breakdown (El-Saied et al. 1998 p. 155). Alum rosin size performs optimally at a pH of 4 – 5.5 during the paper manufacturing process consequently resulting in low pH paper (Arnson 1982, cited in Thurn 2003 p.1). When mills made the transition from acidic to alkaline systems alum was excluded from the process but by the late 1980's alum was reintroduced in low levels to improve “runnability, sizing and retention” (Rose & Nitsche 1991, p.251) Rosin has little significance in the process of deterioration of paper but alum and its associated acidity has a major impact on paper permanence. Barrett's 1989 X-ray fluorescence analysis (cited in Bruckle 1993) found that “papers in good condition contained less aluminium.”

Methodology

The presence of alum was tested using an aluminon solution prepared and applied as per Browning (p. 318). The solution was applied using a glass pen nib, which allowed for the placement of a tiny spot of the test solution. Any colour change from light pink to darker pink was recorded as a positive. In some cases the aluminon solution can go a dark plum colour which apparently could indicate the presence of iron in the paper (Browning, p. 318).



Negative for Alum

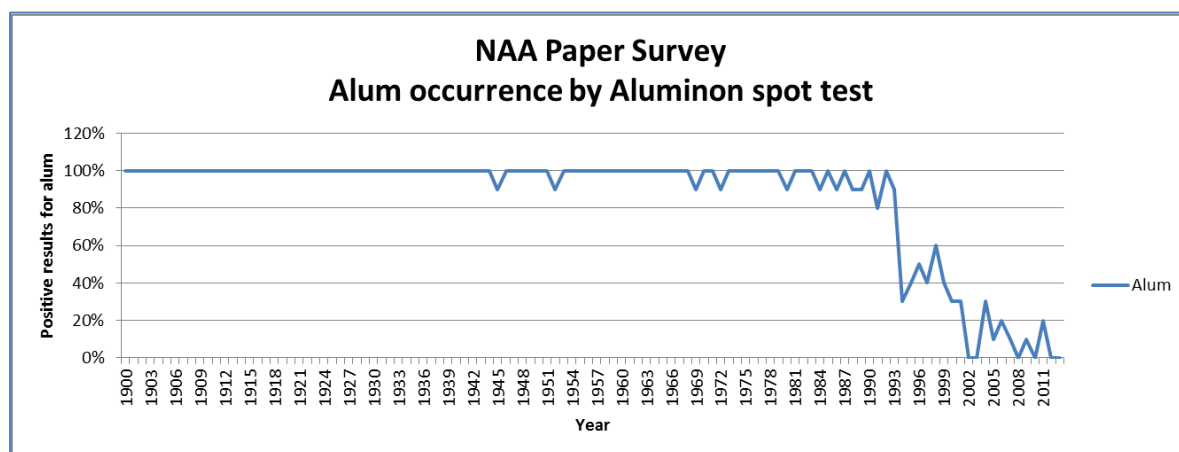


Positive for Alum



Strong positive for Alum
Possible Fe contamination

Results and discussion



Alum proved to be in almost every paper up until 1993 at which point it tapers off dramatically and appears to vanish in 2011. Although it was not specifically recorded, there was a trend in the results relating to the strength of the colour change. As a general rule the strength of colour of the spot test dropped off over the period under examination, most likely indicating that the quantity of alum in papers also dropped off over the period of the survey. This could conceivably mean that more recent papers would have better permanence than older papers, at least where permanence was a result of alum content. In a small number of cases the aluminon solution went a dark plum colour which apparently could indicate the presence of iron in the paper (Browning, p. 318). It is hoped to better explore the question of alum concentration and its effects on permanence as well as examining the prevalence of iron in further research.

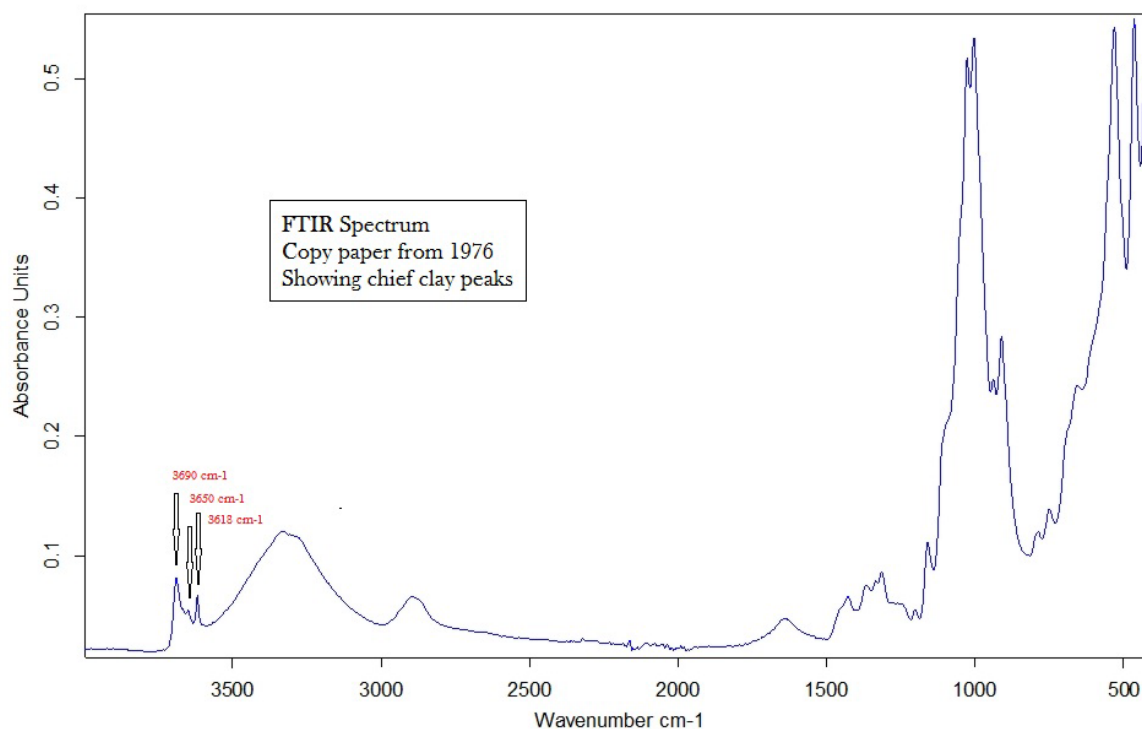
Clay

Background

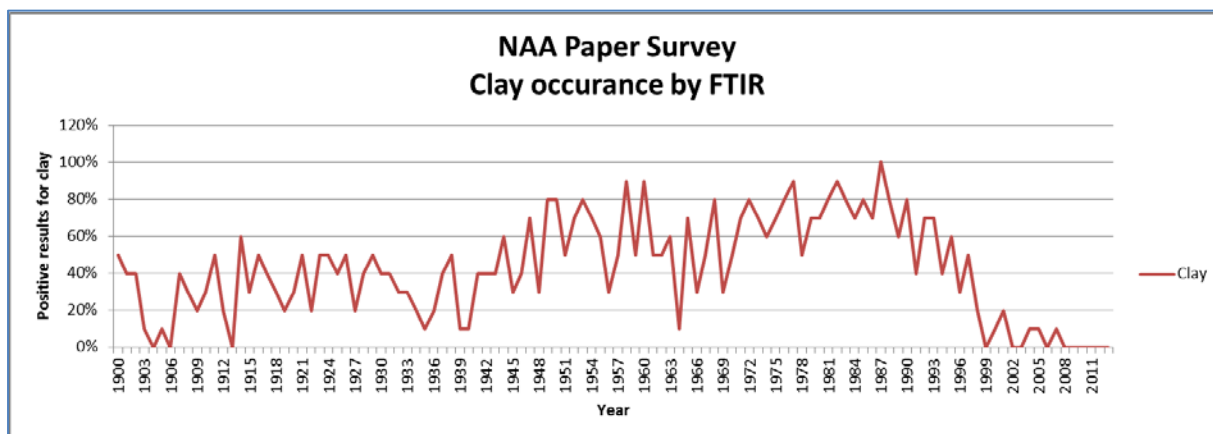
Kaolin clay is the most commonly used filler which improves smoothness, gloss, optical properties and printability of the paper sheet. These improvements do however come at the expense of mechanical properties. The use of filler results in a sheet which contains fewer fibres per unit grammage and blocks fibre to fibre bonding. Although bonding between cellulose and filler is relatively good, filler to filler bonding is poor (Eklund & Lindstrom 1991 p.235).

Methodology

The presence of clay was determined by FTIR spectroscopy. Kaolin clay ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) has a distinctive FTIR spectrum, with peaks at 3618, 3650 and 3690 cm^{-1} . The peaks are easily identified and generally visual analysis of the spectrum was sufficient to determine the presence of clay. If there was any doubt an integration was carried out in these regions. Any integration result above 0.000 was recorded as a positive. A typical positive clay spectrum is shown below.



Results and discussion



The occurrence of clay in paper is highly erratic across the testing period. There is a slight increase beginning around 1945 which is difficult to explain. The one clear observation to be made is the sudden drop in usage around 1996 and total absence after 2008. This can easily be explained by the increased use of carbonate, which would serve the same purpose as clay.

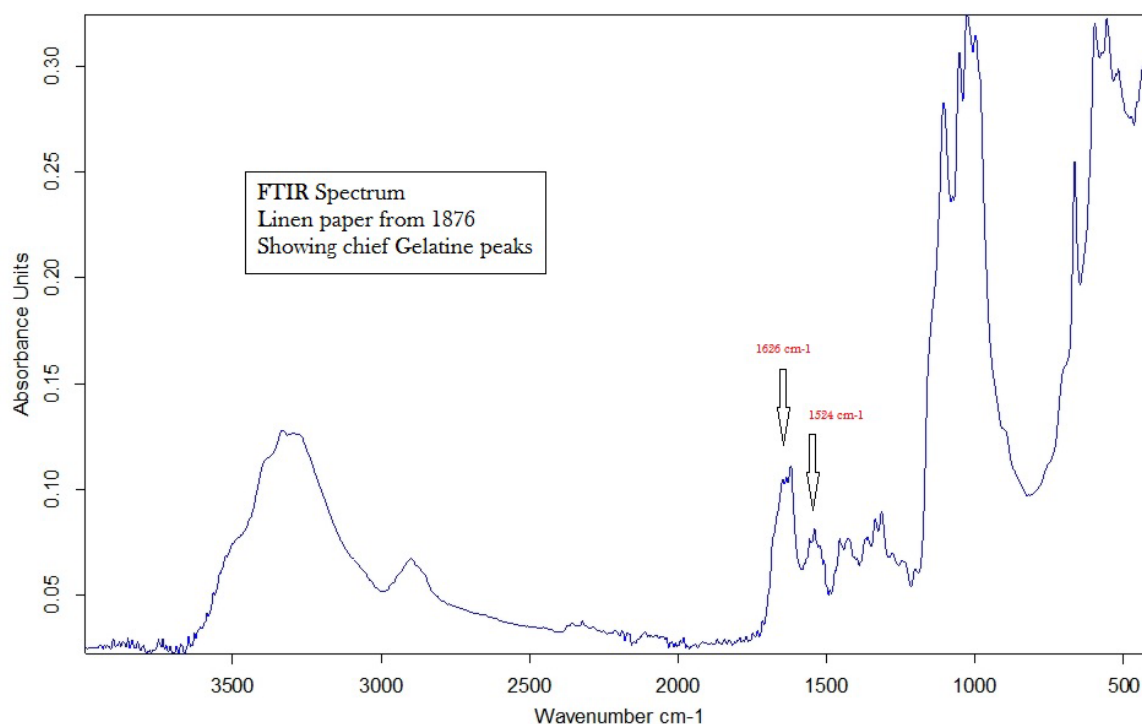
Gelatine

Background

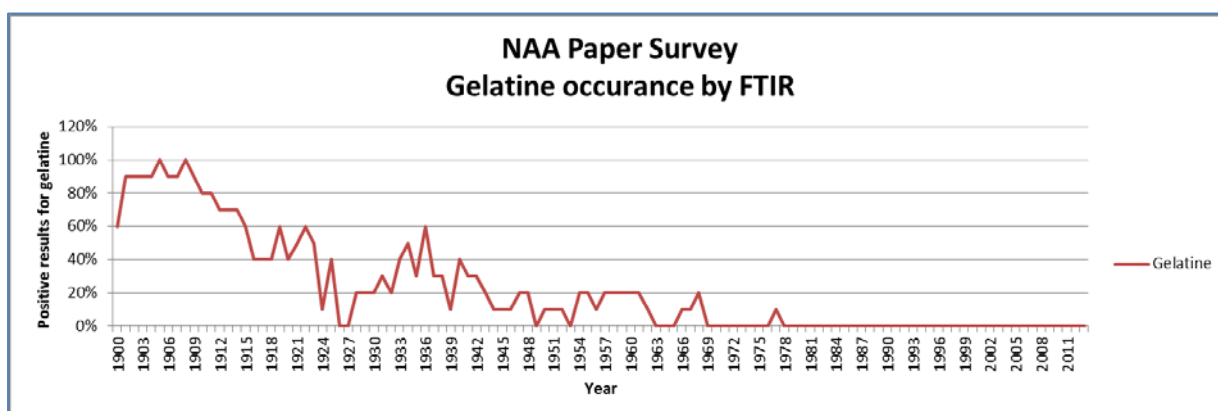
Gelatine was a common paper size in the 19th century but became less common in the 20th. Studies have been carried out that suggest gelatine may be beneficial to permanence (Baker, 1997; Barrett & Mosier, 1995; Wilson & Parks, 1983 & Courts, 1980). Although the mechanisms are not fully understood, its effects appear to relate to aiding in the control of the pH of the paper sheet and buffering moisture content.

Methodology

The presence of Gelatine was determined by FTIR spectroscopy. Gelatine has a distinctive FTIR spectrum with peaks at 1524 and 1626 cm^{-1} . The peaks are easily identified and generally visual analysis of the spectrum was sufficient to determine the presence of gelatine. If there was any doubt an integration was carried out in these regions. Any integration result above 0.000 was recorded as a positive. A typical positive gelatine spectrum is shown below.



Results and discussion



From a peak early in the century, a spill over from the strong popularity of gelatine as a size in the 19th century, gelatine usage quickly drops off and becomes minimal by 1943. By 1969 it had virtually vanished apart from a single example in 1977. Clearly other sizing systems must have taken over from gelatine in the second half of the century.

Optical brighteners

Background

The presence of optical brighteners in paper is of potential concern for permanence. The history and properties of this class of chemical is discussed by Mustalish (2000). She points out that optical brighteners, due to their strong water solubility, may interfere with conservation treatments or leave tidelines after water based work. Ian Batterham asked Ms Mustalish in 2000 if she thought optical brighteners were of concern in relation to paper permanence and she stated that since they absorb and radiate different wavelengths of light they may well accelerate light-based deterioration.

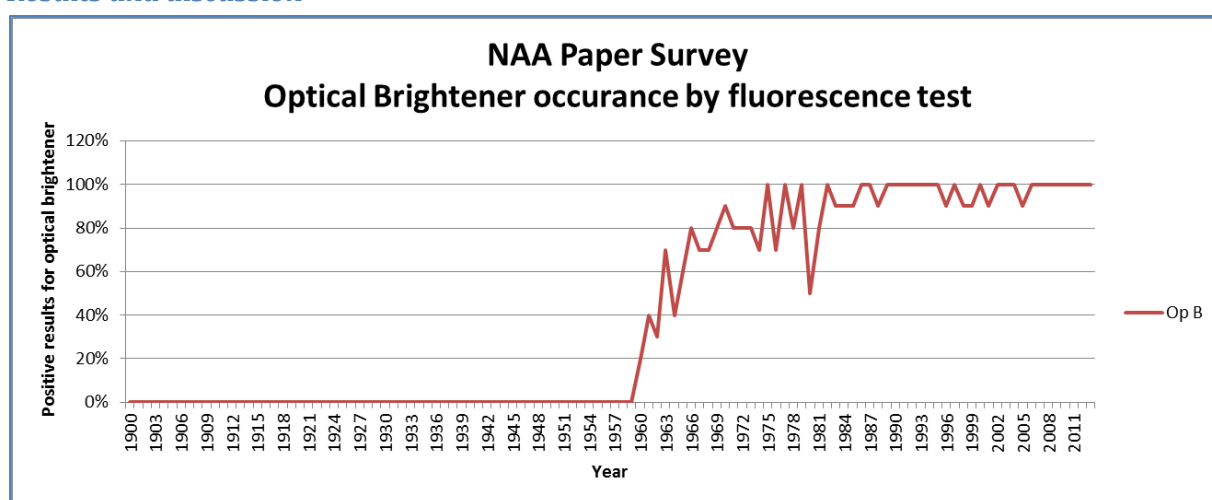
Henry Wilhelm on *Wilhelm Imaging Research*, his website dedicated to the assessment of modern photographic printing products, states that optical brighteners can yellow over time and has the following words appended to all his reviews of printing papers: "When long-term image permanence is an important consideration - or may eventually become an important consideration - fluorescent brighteners should be avoided".

Breathing Colour, manufacturers of high end printing papers, make reference on their website to anecdotal evidence that optical brighteners "have been known to decompose over time and can cause yellow stains to appear on your prints."

Methodology

The presence of optical brighteners was determined by a simple visual test. The paper was held under a UV source emitting light at wavelength 366 nm and if it exhibited any fluorescence then a 'yes' was recorded for the presence of optical brighteners.

Results and discussion



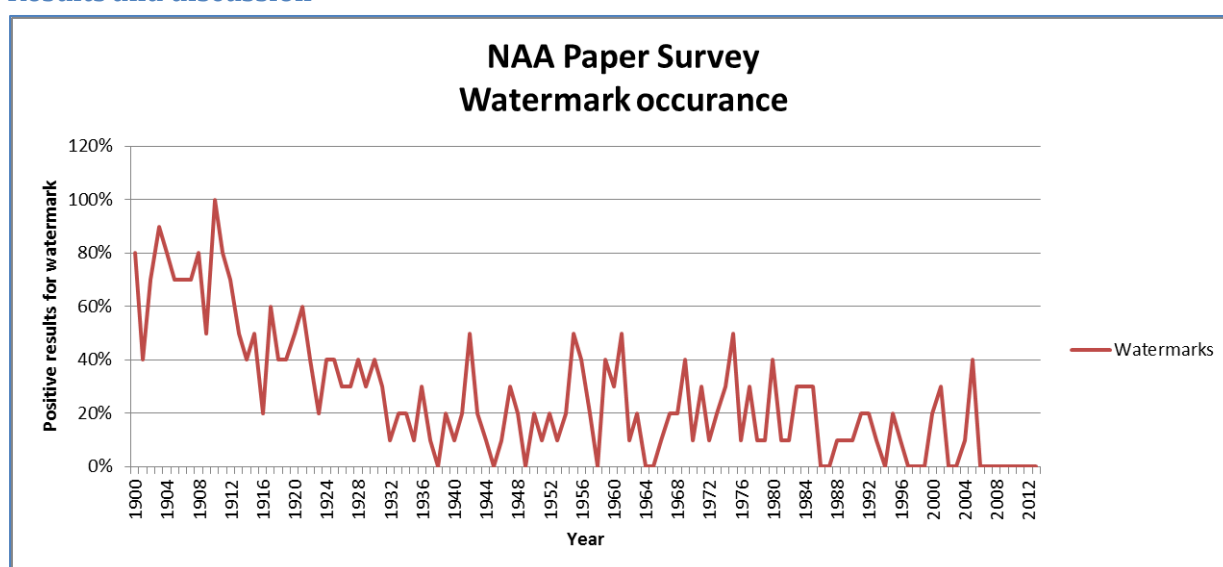
This graph is fairly easy to interpret. Fluorescent materials first appear in papers around 1960 and within 20 years virtually all paper included such materials. These results should be approached with a little caution as it is possible that there are paper additives that fluoresce but which were not specifically added as optical brighteners.

Watermarks

Background

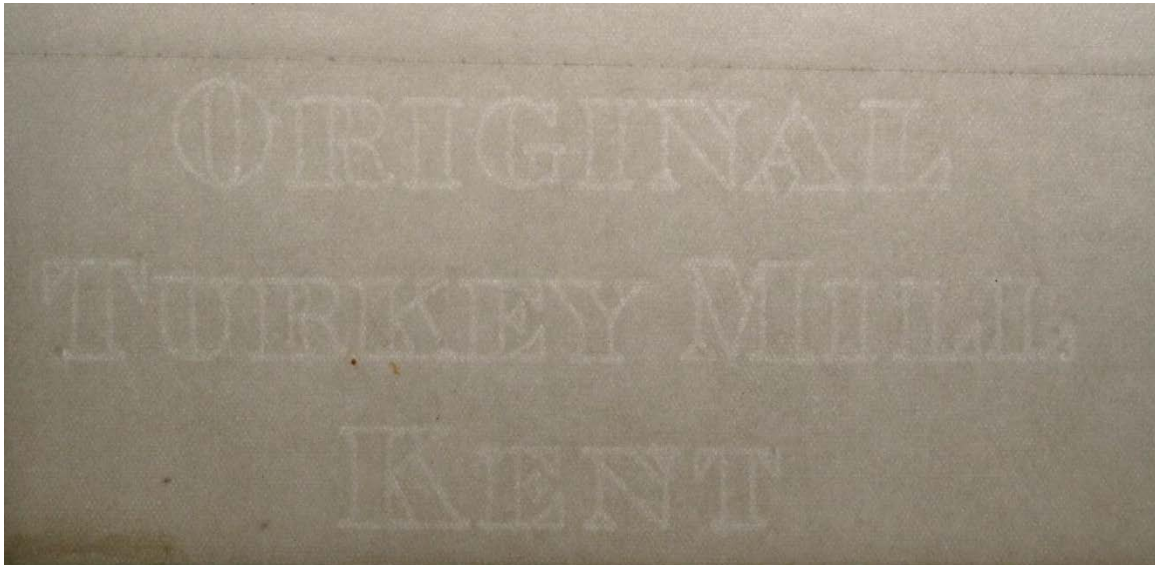
The chief value of a watermark is that it allows the paper to be traced to a specific paper mill. The types of watermark found amongst the NAA collection would therefore give a good indication of where papers were being sourced and manufactured at different times during the 20th century. It would also allow paper quality to be linked to a readily discernible identifier, and thus allow anybody to know the quality of a sheet simply by noting its watermark and referring to the results of this survey. Also, a watermark gives a paper an air of quality and it was hoped that there may be a correlation between the presence of a watermark and properties of the paper sheet.

Results and discussion

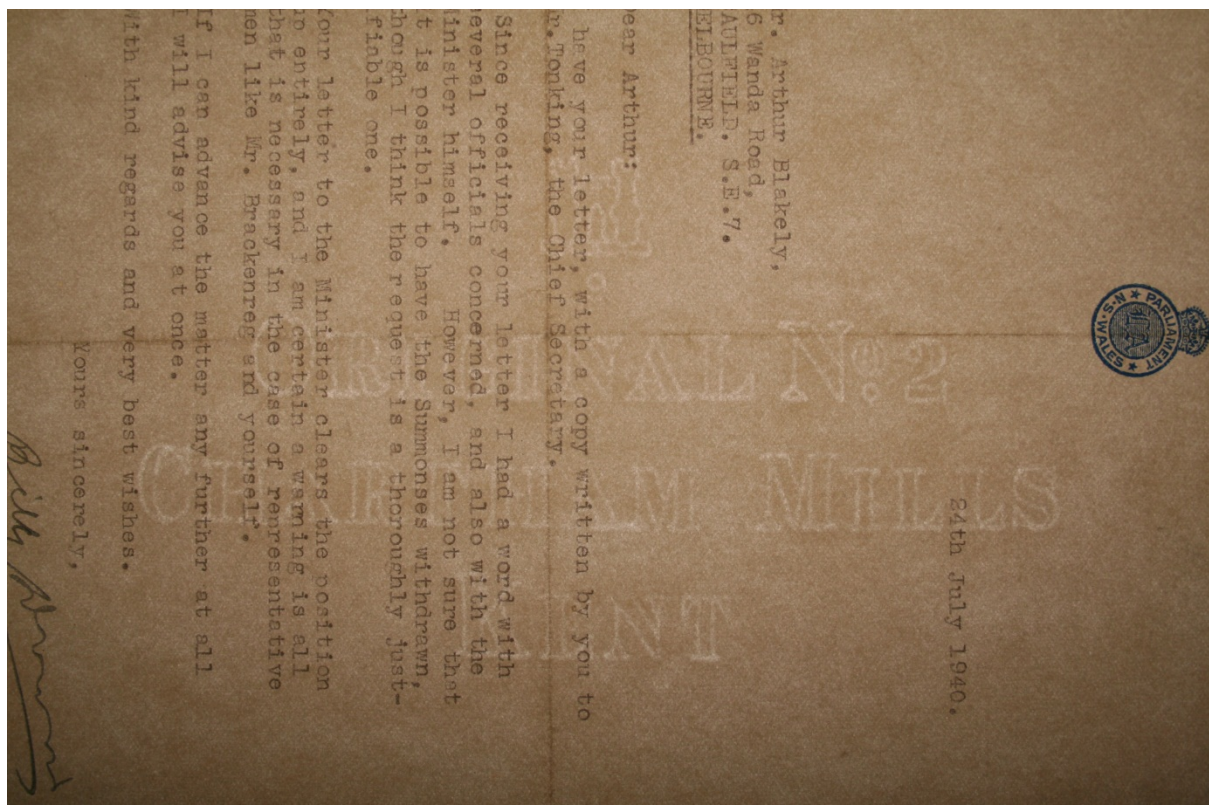


The presence of a watermark is not directly related to permanence. However, there was always the perception that a watermarked paper was of higher quality than a non-watermarked one. Such a correlation is not borne out by this study. The slow loss of watermarks over the century is an indication of a change in attitude and a change in manufacturing process. The introduction of high speed paper machines made the application of a watermark more problematic, at the same time the public became less interested in paper quality, as paper usage increased.

Examples of watermarks found



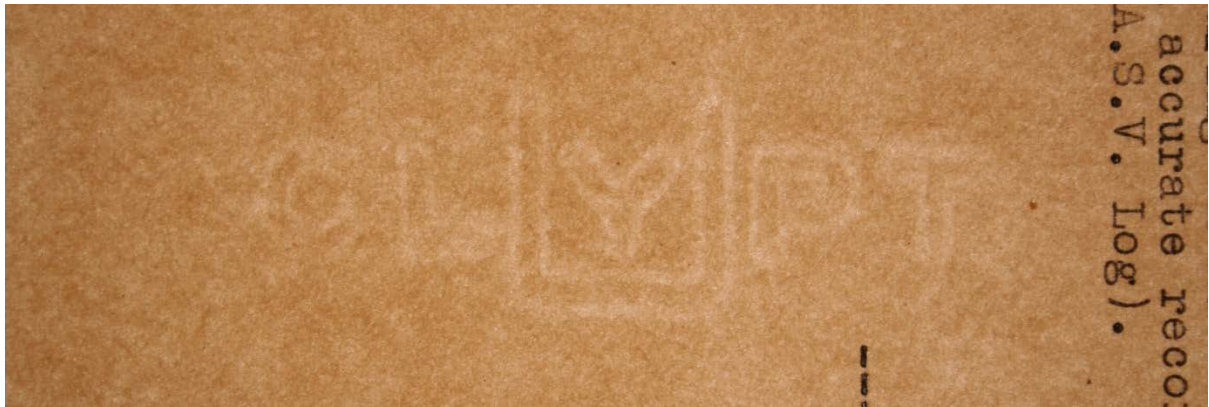
Original Turkey Mill Kent – very common from 1900 to 1940



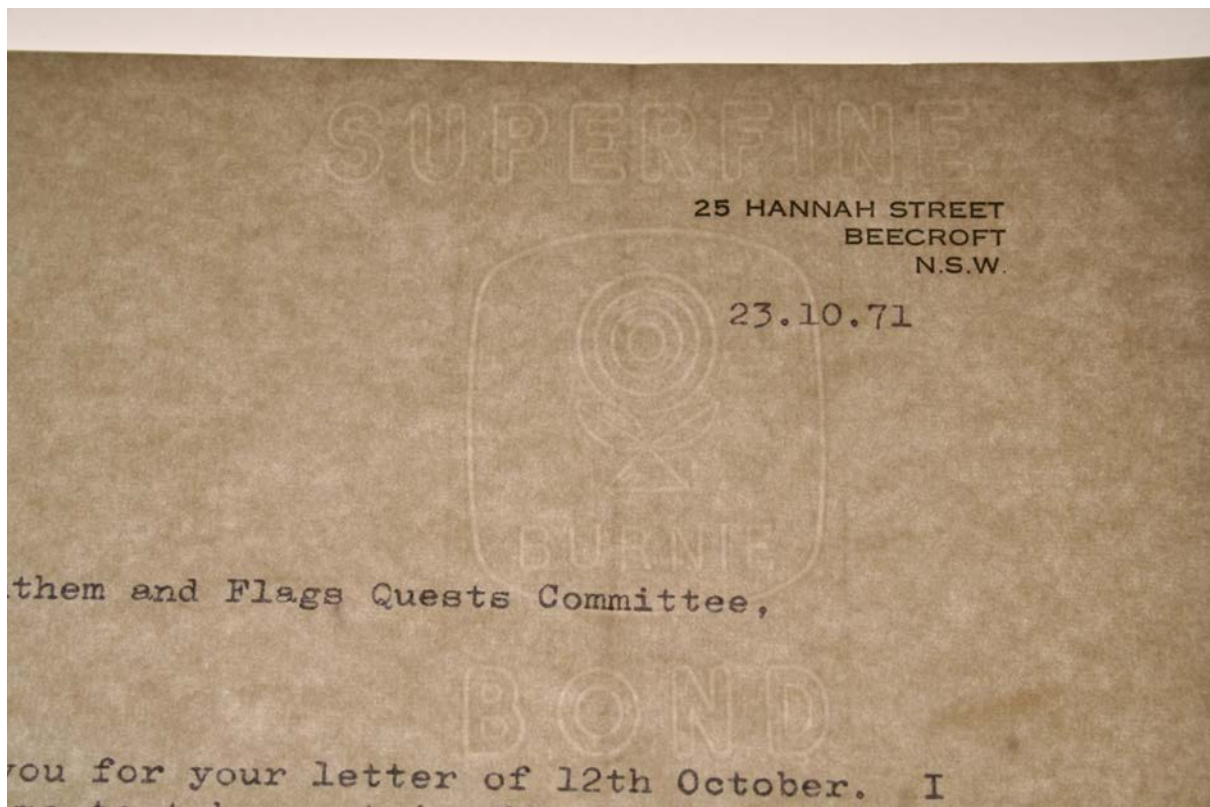
Original No. 2 Chartham Mills Kent – in use from 1955 to present



From 1911 – the word 'Linen' has little to do with paper quality



U-Clypt Australian-made paper from 1944 – the first commercial use of eucalyptus in papermaking



Burnie Bond, made in Tasmania, from 1971

Paper dimensions

Whilst not directly related to paper quality, a note was taken during the survey of the size of the sheet of paper being tested. From this it was possible to see trends in paper sizing came in went.

Foolscap

This was a standard size from 1900. It becomes uncommon after 1968 and was last used in 1978.

Quarto

This came in a number of variations, the short dimension varying between 192mm to 207mm and the long dimension varying between 242mm and 262mm. It was a standard size from 1900. It becomes uncommon after 1976 and was last used in 2007. Between 1976 and 2007 most occurrences come from North America where the size remained a standard.

A4

This first appears in 1965 but does not become common until 1970, after which it is almost the only paper size.

A5 and B5

These were used infrequently after 1971.

Junior Legal (approx. 8"x5", 203.2x127mm)

This was used infrequently between 1901 and 1956.

Kings (approx. 8"x6.5", 203.2 x 165.1mm)

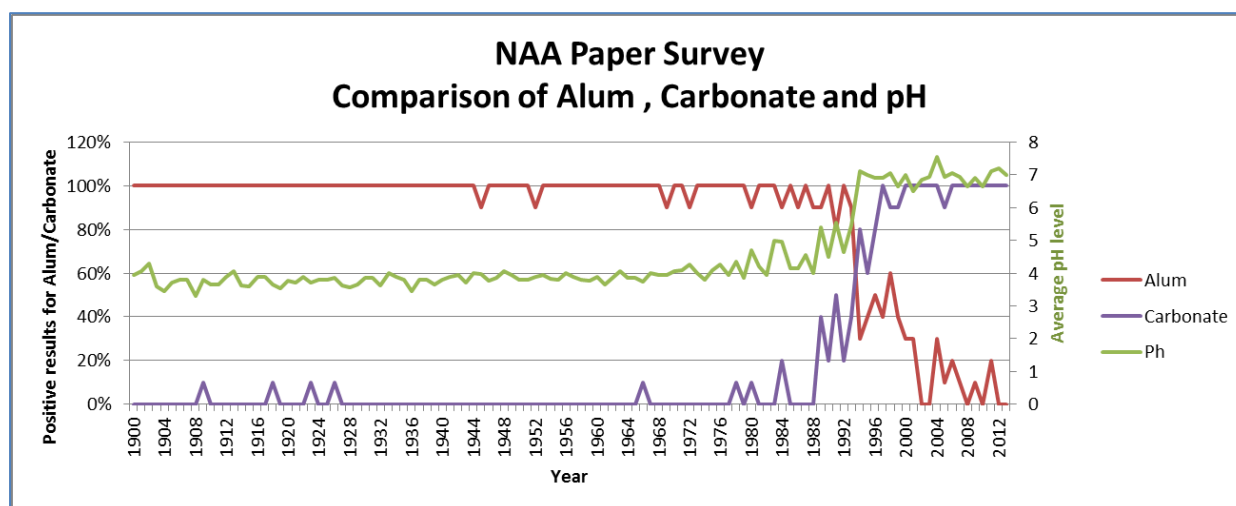
This was used infrequently between 1909 and 1995.

Letter (approx. 8.5" × 11", 215.9 × 279.4mm)

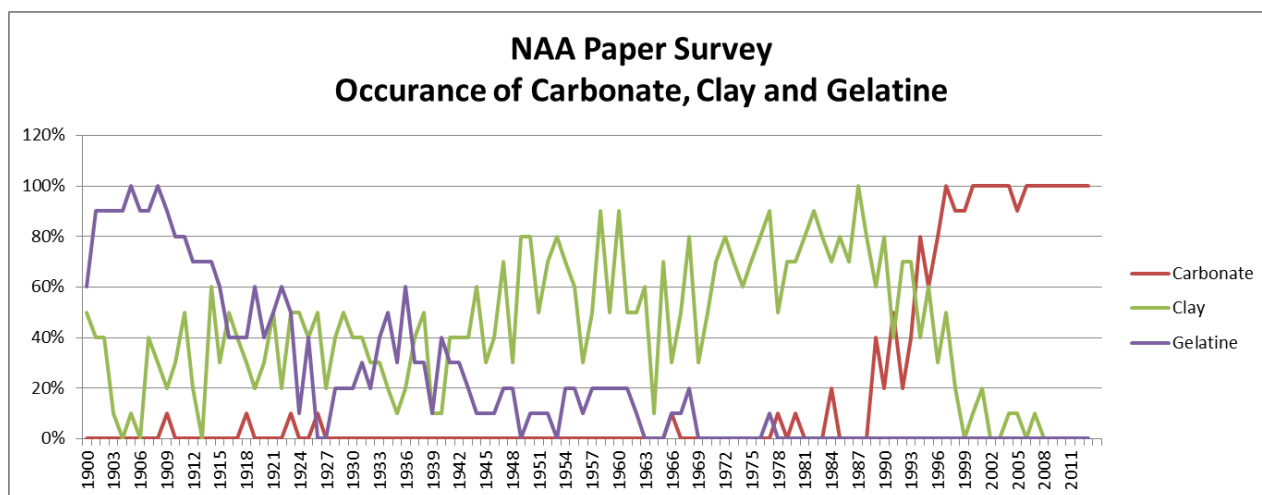
This was used infrequently between 1921 and 2007.

5. Discussion and conclusions

Discussion



From this graph it seems clear that towards the end of the 20th century a major change in papermaking occurred, one which will have a major impact on paper permanence. At almost the same time alum ceased to be used as a sizing agent and carbonate became an always present paper additive. These two factors led to all paper being neutral or alkaline.



From this graph a possible set of trends in sizing and fillers can be seen. Early in the 20th century gelatine is more common than clay whilst carbonate is almost unknown. As gelatine drops off clay becomes more common and remains so until late in the century. Although this seems clear graphically, it may not indicate a direct link as gelatine and clay perform different tasks. The link may be that a third agent, for example rosin, which we have not directly looked for in this study, may have taken over from gelatine as a size. In this scenario the use of clay may have been increased to simply bulk up the papers.

At the end of the century it seems very clear that there is a link between the drop in the use of clay and the increase in the use of carbonate. This latter link is easily understood as clay and carbonate perform the same function.

Conclusions

The conclusions of the study can be summarised as follows:

- Office paper was universally acidic until around 1992 when it moves to the alkaline.
- This alkalinity can be credited to a stop in the use of alum and the introduction of carbonate as an additive, both of which occurred at around this time.
- There is a slight but consistent rise in alkalinity over the period 1900-1992.
- Gelatine sizing, common in the early part of the century, vanishes around mid-century.
- Clay was a fairly common filler during most of the 20th century. Although common its use from year to year was quite variable, there was however a clear increase in its use beginning around 1940 and continuing until 1996. Clay vanishes from use around 2008.
- There may be a link (perhaps indirect) between a drop in the use of gelatine as a size and a rise in the use of clay filler, which both happen around 1940.
- A watermark appears to be no indicator of paper quality.
- Optical brighteners (fluorescing agents) first appear in 1960 and are universal by 1984.
- Identifiable Australian made paper (bearing the U-Clypt watermark) first appears in 1942.

6. Further work

This survey has provided some very useful information but raised some further questions:

- What has replaced clay, gelatine and alum as paper size/filler? Candidates could include Aquapel, cellulose ethers, resins etc.
- What are the effects on permanence of the new additives?
- How quickly is alkalinity from carbonate filler used up?
- Is there a link between alum concentration, pH and permanence?
- When was rosin sizing used in papermaking? (not tested in this survey)
- What can we learn about paper quality, trade and usage from watermarks?
- What more can we learn about the history of paper in Australia, generally and particularly since WWII?

For the latter question we could consult a range of sources:

- Monographs or journal articles about papermaking in Australia
- Website - Papermaking in Australasia to 1900: <http://home.vicnet.net.au/~paper/>
- APPM Shoalhaven – corporate archives
- APPITA (Australian Pulp and Paper Industry Technical Association) Journal
- TAPPI Journal and library for information on the history of the paper trade
- CSIRO Forest Industries Division
- Noel Butlin Archives – for a history of the paper industry in Australia
- NLA Collection
- NAA Collection

In the NAA and NLA we could do keyword searches, for example:

- Paper
- Paper import
- Papermaking (or Paper Making)
- Paper Mill
- Pulp
- APPM (Associated Pulp and Paper Mills)
- APPM (Australian Pulp and Paper Manufacturers),
- APM (Australian Paper Manufacturers Limited),
- Australian Newsprint Mills Pty Ltd (ANM),
- APMEU (Australian Paper Mills Employees Union)

Bibliography

- Baker, W., 1997, The Role of Gelatin in Paper Permanence, Part II, Phase One: Gelatin as a Relative Humidity Buffer, Thesis, University of Texas at Austin

- Barrett, T. & Mosier, C., 1996, 'The role of gelatin in paper permanence', JAIC 34/3 pp. 173-186, 1995.
- Begin, P. Deschâtelets, S, Grattan, D, Gurnagul, N, Iraci, J, Kaminska, E, Woods, D, Zou, X., 1998, 'The Impact of Lignin on Paper Permanence: A comprehensive Study of Ageing Behaviour of handsheets and commercial paper samples', Restaurator, vol. 19,no.3, pp. 135-154.
- Breathing Color, <http://www.breathingcolor.com>, accessed May 2013.
- Browning, B.L., Analysis of Paper (second edition), 1977, Marcel Dekker, New York.
- Bruckle, Irene, 1993, 'The Role of alum in Historical Papermaking', Abbey Newsletter, vol. 17, no 4, Sept 1993, accessed 2 Feb 2013, <http://cool.conservation-us.org>.
- Commonwealth Tariff Board, 1943, Report on the Manufacture of Paper and Paper Boards, National Archives of Australia, Commonwealth Record Series B11. Items 2&3.
- Courts, A., 1980, 'Properties and uses of gelatin', Applied Protein Chemistry, ed. R.A. Grant. London, Applied Science Publishers, pp.1-29.
- Hubbe, Martin A., 2004, 'Acidic and Alkaline Sizings for Printing, Writing, and Drawing Papers', The Book and Paper Group Annual, No. 23, pp. 139-151.
- El-Saied, A.H. Basta & Abdou, Mona. M., 1998, 'Permanence of Paper 1: Problems and Permanency of Alum-Rosin Sized Paper Sheets from Wood Pulp', Restaurator, vol.19, no. 3, pp. 155-170.
- McCrady, Ellen, 1991, 'The Nature of Lignin', Alkaline Paper Advocate, vol. 4, no.4, viewed 9 Feb 2013, <http://cool.conservation-us.org/byorg/abbey/ap/ap04/ap04-4/ap04-402.html>
- Mustalish, R. A., 2000, Optical brighteners: history and technology, Tradition and innovation: advances in conservation: contributions to the Melbourne Congress, 10-14 October (2000) pp. 133-136.
- Rawson, J., 1953, 'A history of the Australian paper making industry 1818-1951' Masters Research thesis, School of History, The University of Melbourne.
- Robertson, P. & Trace K., 1983, "Government Involvement in the Development of Australian Manufacturing since 1945", Business and Economic History, 2nd series, 12, pp.109-123, viewed 4 Feb 2013
www.thebhc.org/publications/BEHprint/v012/p0109-p0123.pdf
- Rose, Gerard R & Nitsche, Carmen I., 1991, 'The Effect of aluminium on the Permanence of Alkaline Papers', Proceedings of the Paper Makers Conference, TAPPI, Seattle, viewed 2 Feb 2013 <http://www.tappi.org/Bookstore/Technical-Papers/Conference-Papers/1991/PM91/Effect-of-Aluminum-on-the-Permanence-of-Alkaline-Papers-1991-Papermakers-Conference-Proceedings.aspx>
- Sinclair, E.K., 1990, The Spreading Tree: A History of APM and AMCOR 1844-1989, Allen & Unwin Sydney
- Trafela, T., Strlic M, Kolar, J., Lichtblau, D.A., Anders M, Pucko Mencigar D. & Pihlar B. 2007, 'Nondestructive Analysis and Dating of Historical Paper Based on IR

Spectroscopy and Chemometric Data Evaluation', Analytical Chemistry, Vol. 79, No.16, August 15, pp. 6319-6323.

- Wilhelm Imaging Research, www.wilhelm-research.com, accessed May 2013
- Wilson, W.K. & Parks E.J., 1983, 'Historical survey of research at the National Bureau of Standards on materials for archival records' Restaurator 5(3-4) pp191-241.