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The Walter Burley Griffin Design Drawings of the City of Canberra

Conservation Work at the National Archives of Australia

by IAN BATTERHAM

ORIGINS OF THE PROJECT

The Walter Burley Griffin design drawings for the City of Canberra constitute one of the more important groups of records held by the National Archives of Australia. They are considered important, both as historical documents and as works of art.

Until recently the drawings were in a poor state of preservation, due to historical damage and, more recently, ill-advised treatment.

The project discussed in this article was set up to thoroughly investigate the nature of the drawings and their level of deterioration. Subsequently, a treatment method was devised and the drawings treated.

HISTORICAL BACKGROUND AND SIGNIFICANCE OF THE DRAWINGS

The federal capital design competition

In 1912 the Commonwealth Government of Australia held a competition to find a design for its proposed national capital. The competition was run by the Department of Home Affairs which established a board to judge the entries. The board consisted of a Chairman, John Montgomery Coane, a licensed surveyor and two other members, John Kirkpatrick, a Sydney architect and James A. Smith, a Melbourne engineer. Secretary of the board was Conway Inglis Clark, a Hobart Architect. Judging took place in Melbourne, the temporary seat of Government at that time.

In all, 137 entries were submitted and they came from all over the world including such far flung countries as Mexico, Paraguay, India, France, South Africa and Sweden. One of the last to reach the board was from an American, Walter Burley Griffin.

Walter Burley Griffin, a native of Chicago, was then 37 years old. He had studied architecture at the University of Illinois and later worked as an associate of Frank Lloyd Wright. He had recently married Marion Mahony Griffin née Marion Lucy Mahony, herself an architect, illustrator and furniture designer. Marion had graduated in architecture from the Massachusetts Institute of Technology, the second woman to do so. At the time of the competition Marion and Walter ran their own architecture practice in Chicago.

After much deliberating, the Board were unable to reach a consensus and came up with two separate reports. The Majority Report, agreed to by Kirkpatrick and Smith, gave first place to Griffin, second to Eliel Saarinen of Finland and third to D Alfred Agache of France. The Minority Report, put up by Coane, gave first ranking to an Australian syndicate consisting of Robert Charles Coulter, Charles Henry Caswell and Walter Scott Griffiths. The Majority Report was accepted by King O'Malley, Minister for Home Affairs, and Griffin was duly awarded first place. The entry which was placed first in the Minority Report was given an honourable mention.

When the judging was complete the unplaced entries were returned to their authors. The original drawings submitted by the three place getters and the first named in the Minority Report were retained by the Commonwealth Government – a condition of the competition rules. These drawings are now held by the National Archives of Australia as Commonwealth Record Series A710. The series contains 50 designs, 15 of which were submitted by Griffin.

The creation of the drawings

Essentially the design for the city of Canberra was Walter Burley Griffin's, but the drawings themselves were delineated by Marion. It is possible that it was her masterful renderings that clinched the first place for Walter.

Marion Mahoney Griffin has come to be recognised as an artist of considerable importance and her work is now widely admired. Marion's was a strong and idiosyncratic personality and she and Walter had interests extending to such areas as theosophy, anthroposophy and, if one recent commentator is correct, arcane and hermetic wisdom[1].

The style and technique of Marion's work was much influenced by Japanese decorative art which was much in vogue at the time. A first hand report of the methods she used to produce the Federal Capital Drawings has survived and reads as follows:

When I first worked with Marion she was making drawings on the silky Japanese vellum with a crow quill pen and brown ink. The hairy surface would catch the pen unless it barely skimmed the surface, in which case blot and finish for that sheet – start all over again. The Federal Capital drawings were made on linen tracing cloth, lithographed on window shade holland and rendered with water colour and photographic dyes. The next step was to lithograph them on satin, dip the satin in thin glue size and stretch it smooth on a board. When dry the rendering was done with the dyes, and when stripped from the board and lightly dusted with a soft cloth, enough of the size was removed to show the practically unchanged satin surface. Renderings so made are practically indestructible with ordinary care and can be ironed if they become mussed. In the case of the Canberra renderings they were completed in less than a week, but only try this method if time is not of the essence[2].

It appears from this description that there were three states of the drawings:

- The original monochrome drawings on tracing cloth.
- Lithographs on window shade holland with additional rendering in watercolour and photographic dyes
- Lithographs on satin dipped in glue size, with additional rendering in dyes.

The drawings held by the National Archives of Australia are those described as State 2. The State 1 drawings are with the Art Institute of Chicago. State 3 were kept by Marion and later exhibited in Europe, after which they disappeared.

A description of the drawings

Griffin submitted 15 drawings for the competition as follows:

- Plan of Central District – in two sections (Items 36 & 37)
  This is a rendering in black ink of Griffin's design onto a paper contour map of the site. The map itself was supplied as part of the kit sent to each competitor. The competition rules required each entrant to submit a version of their design drawn onto the map. The design was originally mounted on two stretchers 760 x 1525mm which were hinged together. Treatment of this item is not within the scope of this article.
- City and Environs (Item 38)
  This drawing on cloth is a rendering of the street plan for the city. Size: 760 x 1525 mm.
- Section A–B, Northerly Side of Water Axis, Black Mountain to Lake Park (Items 39–42)
  These four drawings are on cloth. The image takes up only a fraction of the surface area, being confined to a band running across the middle. The drawings

Fig. 1: City and Environs (Item 38)

fit together and form a section through the plan and were originally hinged together. Size of individual items: 760 x 1525 mm.

- Section B–A, Southerly Side of Water Axis, Government group (Item 43)
  This drawing is similar in appearance to Items 39–42 but stands alone. Size: 760 x 1525 mm.
- Section C–D, Easterly side of Land Axis, Ainslie to Red Hill (Items 44–47)
  These four drawings are similar in appearance to 39–42 and also fit together to form a complete section through the plan. They were originally hinged together. Size of individual drawings: 760 x 1525 mm.
- View from the summit of Mount Ainslie (Items 48–50)
  These three drawings were prepared as a triptych, on three separate stretchers which were originally hinged together. The image comprises a perspective of most of the city. The triptych is possibly the most aesthetically satisfying of all the Griffin items. The three parts are on cloth, their original sizes were, central panel: 760 x 1525 mm, outside panels: 760 x 760 mm.

A closer look at the drawings

When the Griffin drawings were originally created they were mounted onto stretchers in the manner of easel paintings, however, they were not framed, leaving them vulnerable to damage.

Closer examination of the objects themselves reveals that the 'window shade holland' described above is a simple tabby weave cotton fabric. Typical thread counts for the items were 30 x 29 threads per cm for Item 40 and 24 x 27 threads per cm for Item 38. In all cases the cloth had been given a cream primer wash which had not fully masked its weave.

The line images were transferred to the cloth using a black lithographic ink. Additions were first sketched in with pencil and then drawn in using a black drawing ink.

In addition it should be noted that:

- What colouring there is, has been done using watercolour and gouache.
- The colouring on Items 39–47 is restricted to the image area which consists of a small strip across the centre.
- Items 48–50 are coloured all over in pastel tones.
- Item 38 has an image in brown tones that covers most of its surface area. The image area also appears to have been varnished.

- Items 39–47 have bands of gold oil paint in 4 different tones running across their centre, the gold colour silhouettes the landscape and buildings.
- Items 39, 42, 44 and 47 have additional rectangular blocks of gold oil paint above and below the main image.
- Items 48–50 each have a thin border of gold oil paint.
- Items 38, 39, 43, 44, 48 and 50 have captions in red ink.

A physical history of the drawings

When the Griffin drawings arrived in Melbourne from Chicago in 1912 they passed into the custody of the Department of Home Affairs. The Board of Judges had decided to preserve the anonymity of the entrants and thus ensure a fair competition by giving each entry an identifying number. The Griffin drawings were numbered 29. This was stamped in the corner of drawings 37, 38, 42 & 47 in black ink.

By the time of the final closing date of the competition, 29 Feb 1912, 137 entries had been received. The entries were unpacked and displayed in the ballroom at Government House, Melbourne. After an initial selection process to eliminate the obviously unsuitable and invalid entries, a Departmental photographer copied the remainder.

These photographs are also held by the National Archives of Australia and reveal much about the early state of the Griffin drawings. For example, the photographs of the hinged triptych (Items 48–50) reveal that the drawing originally had substantial white borders. These borders are now missing and it appears that they were trimmed off during the conservation work carried out in the late '50's.

The photographs also show that at this early stage some of the objects had already been damaged. Items 45, 46 & 47 are seen to have tears which are consistent with puncture damage. These are still the only major tears in these items. It is possible to see the stretcher frame through one of the tears. From this image an approximate width of 65mm for the timbers can be determined. The photos of some of the items have some light coming through the back. These reveal that the objects were on keyed stretchers, the shadow of the keys being clearly visible.

One of the photographs gives an idea of the haste with which the Griffins prepared the drawings. It shows a version of the triptych (Items 48–50) simply on a single sheet of paper with apparently no colouring. Documentary sources reveal that the Griffins had not finished this item when the deadline for shipping to Australia had arrived. Griffin sent the paper copy of the item with instructions that

the finished item would follow. In fact, close scrutiny of the photograph allows the following inscription to be made out:

> KEY TO ACCOMPANYING PERSPECTIVE
> VIEW FROM SUMMIT OF AINSLIE
>
> SCALE AT PLANE OF INTERSECTION OF LAND AND WATER AXES
> - 1340' = 1"
> PERSPECTIVE DRAWING HAS BEEN DELAYED
> BY ACCIDENT WILL BE SENT BY NEXT SHIPMENT

The finished drawing arrived soon after and was presented for the judging. Unfortunately, it seems that the paper print was either destroyed or lost.

On 23 May 1912 in Melbourne, Walter D Bingle, chief clerk of the Department of Home Affairs opened an envelope containing the names of the competition winners before an assembly of officials and press. Subsequently, all entries were publicly displayed in Sydney and Melbourne. Those which had not achieved placings were then returned to their authors.

The early history of the drawings subsequent to the competition has been pieced together from files kept by the Department of Home Affairs. Of particular interest to us are the following:

In 1913 the Griffin drawings were removed from their stretchers, rolled up and placed in galvanized cylinders for storage.

Also in 1913 the following memorandum was sent by the Land and Property Office' to The Director of Commonwealth Lands and Surveys:

> *I am forwarding herewith for your information copy of a letter, dated 27th instant, received from the Honorary Secretary, Town planning Association of Australia, together with copy of the Minister's Minute thereon. I am having the plans cleaned and properly stretched on frames before they are taken to Sydney by Mr. Taylor. I may add that Mr. Griffin has expressed the opinion that the designs should not have been considered as plans, but as paintings, and treated as such, and states that they should never have been removed from the frames*[3].

The drawings were not taken off their stretcher frames again until conservation work in the 1950s.

In 1917 a set of slotted, zinc-lined chests was constructed to house the drawings.

In 1925 Mr C S Daley, Secretary of the Federal Capital Commission, pointed out the historical significance of the drawings and stated that they should be stored with the Archives of the Commonwealth.

From this time, documentary evidence about the drawings dries up and it was not until 1953 that they were heard of again. In November of that year the drawings were 'rediscovered' packed in five wooden crates in a Department of Works workshed in the Canberra suburb of Kingston. Staff of the Commonwealth National Library, Archives Division were concerned for the safety of the drawings and took them into custody on 6 November 1953. At that time the Griffin drawings were still on their original stretchers and some of them were hinged with removable hinges. The condition of the drawings was described as 'good'.

In 1957 the drawings were moved to plan cabinets in a non-air-conditioned Nissen hut in Parkes, ACT. In 1961 the Commonwealth Archives Office was established as an autonomous unit and the drawings became part of its holdings. The selfsame Nissen hut was given to the new body as a storage area and the drawings remained there until they were transferred to the Archives' new purpose built archival repository at Mitchell in the early 1980s, where they remain.

Previous treatment work

Soon after their 'rediscovery' in 1957, the Griffin drawings were sent to the Art Gallery of New South Wales for treatment. Because documentation from the time is scant, it is not known if all the Griffin drawings were sent at this time. We are only sure that the 'City and Environs' (Item 38) and the Triptych (Items 48–50) were sent. With hindsight, we can judge that the treatment method employed was an inappropriate one; the original tacking margins of all drawings, as well as the white borders of the triptych were trimmed off and the drawings were pasted directly onto Masonite with a starch paste.

In 1965 the objects were again sent to the Art Gallery of New South Wales for further treatment. This was probably to prepare them for an exhibition in the Albert Hall, Canberra the following year. On this occasion, the documentation records that all of the extant Federal Capital Design Competition drawings were treated.

The actual treatment work was sub-contracted to a commercial framing company in Sydney. The Art Gallery of New South Wales supervised the operation and provided the company with their brief.

The brief stated that the drawings were to be removed from their existing mounts and pasted onto chipboard. A layer of cartridge paper was to be first pasted to the chipboard to act as a barrier. Without being specific, the brief also stated that some drawings would require 'soaking' off their mounts and that drawings were to be retouched 'where practicable'. Stains, finger marks, dirt and mould spots were also to be removed. After treatment all items were to be placed in wooden frames.

Invoices provided on completion of the work describe it thus:

Objects were carefully stripped from their old supports without damage and remounted on to paper covered pyneboard panels.

This treatment description, which applies to all the items, is the only record we have of the conservation work that was carried out. It is therefore impossible to determine exactly what was done to particular items, nor is it possible to determine the state of individual items prior to treatment. Of particular note here is that one result of this conservation work was that the three parts of the triptych were attached to a single piece of chipboard.

It should be noted that since the time of this treatment work the field of conservation has progressed considerably. The principle of reversibility has been formulated to govern treatment procedures and also, we now know much more about the permanence and ageing characteristics of the materials we use.

Over the ensuing years the objects were further exhibited a number of times and photographically copied at least once. They were also examined by a number of conservators, resulting in various reports and treatment proposals. None of the proposals were acted upon and the objects remained as they were until the late 1980s when the treatment discussed herewith was commenced.

THE DECISION TO TREAT THE DRAWINGS

The Griffin drawings were very obviously the product of their chequered history. All of the drawings were generally very dirty and most had scuff marks, finger marks and losses of gold and other paint. Comparison to early photographs showed that many of the drawings had faded considerably, of particular note was the right-hand portion of the triptych which had lost much of its colour, as if wiped away by a damp cloth – it is not known when or how this happened. Some drawings had also sustained small tears other than those present at the time of the competition. Early inspection also revealed that the central bands of gold paint were extremely friable and poorly adhered to the cloth.

Because the objects had already been subjected to two traumatic and questionable conservation treatments, it was felt necessary that any further treatment should be very carefully researched before being applied.

In making decisions concerning treatment, the following points were taken into account:

- The chipboard support was a major concern. It has been widely reported that chipboard gives off formaldehyde vapours[4 5 6], these vapours are a danger because they can oxidize in the atmosphere to create formic acid[7]. As any formaldehyde being given off by the chipboard would most certainly be penetrating the drawings, it was clear that the continued proximity of the drawings to the chipboard would endanger their survival. Furthermore, a cold extraction was carried out on the chipboard which gave a pH of 5.6, this level of acidity was judged of a magnitude sufficient to be a danger to the drawings.

- The cartridge paper lining the chipboard was also acidic. (cold extraction pH – 5.4). Again, this level of acidity was judged of a magnitude sufficient to be a danger to the drawings.
- The starch adhesive used to paste the drawings to the chipboard was becoming brittle and losing its adhesive strength. It was thought that if this were allowed to continue, the ultimate failure of the adhesive could lead to the drawings being damaged. The adhesive had also yellowed badly and it was thought possible that this yellowing could be transferring to the drawings themselves.
- The cartridge paper barrier was smaller than the object in some cases, leaving portions of drawings in direct contact with the chip board.
- All drawings had framing instructions written on the back. These were apparently written on to the drawings as part of the work done in the 50s or 60s. In many cases the writing was visible from the front. It was thought that if this writing were made accessible it may be possible to remove or reduce it.
- The triptych had not been properly aligned when it was mounted and parts of it overlapped.
- The chipboard supports made the objects extremely heavy.

Consideration of all these points led to the decision that to ensure the long term preservation of the Griffin drawings they needed to be removed from their chipboard supports.

Treatment

Which discipline?

When considering options for treating the Griffin drawings, it was realized that the drawings were unusual in that they did not fall readily into a single conservation discipline.

The drawings had initially been prepared in the manner of easel paintings and it was wished to return them, as much as possible, to this state. However, the conservation work of the '60's had reduced each drawing to a flat piece of cloth, so in some ways they resembled textile objects – especially given that large portions of the surface area were unpainted. Furthermore, the mounting method employed

in the '60's – pasting the drawings to supports – was more in line with techniques used for the mounting of paper objects, so paper conservation techniques were also to be considered.

In the end a combination of methods from all three fields was employed.

Cleaning

As a prelude to removal from the chipboard all the Griffin drawings were first surface cleaned. This was carried out using Mars Staedtler erasers, the standard rectangular shape (product No. 526 50) for general cleaning and the 'razor' pencil grip type (product No. 527 35) for finer work. These erasers are commonly used for cleaning paper items and are popular because they clean very well and they leave little microscopic debris in the fibre web. Small test areas were cleaned and examined microscopically, revealing that the surface of the cloth was unaffected by the action of the eraser. The objects proved to have a layer of fine dirt over their entire surface, which was easily removed by the eraser, unfortunately however, the heavier marking and staining was unaffected.

Removal of the drawings from the chipboard

A number of possible removal methods were evaluated before arriving at the most suitable one. The use of moisture to release the paste was considered, but rejected very early for two reasons; firstly, some of the colorants were water soluble and secondly, it was possible that the areas with gold paint would absorb the water at a different rate to the rest of the cloth and that the cloth would therefore tend to pucker around these areas. The use of chisels to pare down the chip board was also attempted but very quickly rejected as being labour intensive and too dangerous.

Examination of the starch paste suggested that the bond between the object and cartridge paper would be easily broken, due to the deterioration of the paste. It was therefore decided that the first major attempt at removal would exploit this weakness. The first item selected for treatment was Item 39, one of the cross sections through the city. This drawing had a red ink inscription, central bands of gold paint as well as additional blocks of gold, top and bottom.

A rectangular piece of 0.5 mm Mylar was cut and one of its corners rounded. Starting at a corner of the drawing that was already lifting, the rounded corner of the 'Mylar knife' was gently but firmly worked between the drawing and the cartridge paper, breaking through the paste layer as it went. Working this way

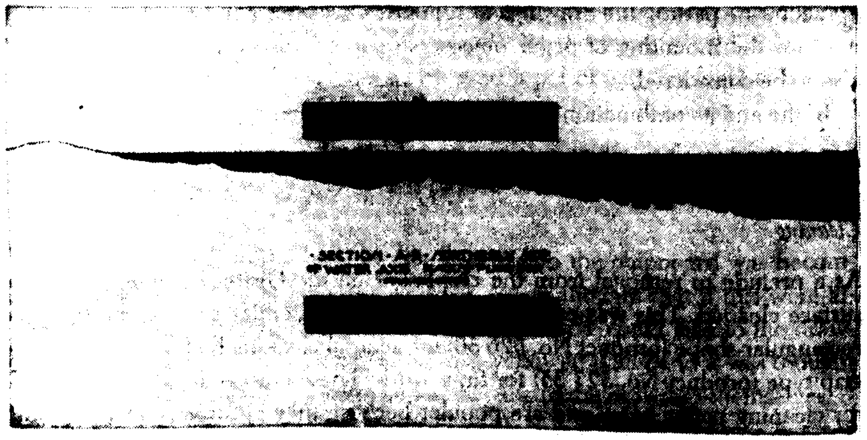

Fig. 2: Item 39

the drawing was released from the paper quite easily up to about 5 cm from the edge. However, at about 10 cm from the edge, the cartridge paper started delaminating in places. It was very difficult to move the Mylar knife through the delaminating paper and once it had started delaminating at one point, it tended to spread.

We persevered with this method, however, and eventually the whole lower section of the drawing was released from the chipboard, including the lower block of gold. By this time much of the cartridge paper was delaminating, making the process extremely slow and laborious.

Unfortunately, the whole method had to be abandoned when the area under the central gold bands was reached. Moving the Mylar knife under the gold paint caused a level of flexing and vibration sufficient to break the bond between the paint and the cloth. An attempt was made to consolidate the gold paint using 2 applications of 5% Beva 371 in toluene. Once this had dried, the Mylar knife was again tried with, unfortunately, no appreciable improvement. A different approach was, therefore, required.

Since the paper's natural inclination was to delaminate, it was decided to work with this rather than against it and to attempt to remove the drawing from the chipboard by splitting the paper. The tool selected for the job was a 23 cm-long icing spatula with a slightly sharpened tip. Starting from another point at the edge of the drawing, the paper was deliberately split and the spatula was worked through the paper. The method proved to be successful, leaving the friable central gold bands undisturbed. The additional layer of paper between the tool and

Fig.: 3 Removal of item 39 from the chipboard

the surface of the drawing, reduced the angle of flex and the amount of vibration to an acceptable level. With a great deal of care and a few grey hairs the spatula was worked under all of the friable gold paint and the drawing was free.

When it came to attempting removal of a second Griffin drawing it was decided to use the spatula method from the outset. To begin, the cartridge paper was split along the full length of the drawing using the spatula then, using firm but smooth strokes, the spatula was run through the paper. Each stroke went the entire length of the drawing, splitting the paper to a depth of about 1 cm. Within a couple of hours the drawing was released with no damage to the gold paint. After successful removal of two drawings in this way, this method was used for the remaining Griffin drawings.

Removal of the remaining paper and the adhesive

The next phase of the treatment involved the removal of the remaining paper and adhesive from the back of the drawings. As this could only be achieved through the use of water, a method had to be devised using a minimum of water to avoid distortion of the cloth and movement of the colorants.

Local applications of small amounts of water seemed to be the most appropriate way to proceed. The drawing was laid face down and a small area of the paper and starch residue, approximately 3–4 cm square, was lightly moistened with a cotton wool swab. After a few seconds the softened paper was scraped away with a septum elevator. The remaining adhesive was then swabbed away using a ball of dampened cotton wool. The cleaned area was then immediately patted dry with cotton wool and covered with a piece of spun bonded polyester, a blotter and a weight. This process was continued until all the remaining paper and the adhesive were removed. The drawings which were treated in this way did not distort and eventually dried extremely flat.

Attempted removal of the framing instructions

The written framing instructions on the reverse side of the drawing were now accessible. As stated earlier, these instructions were written on to the back of the drawings during the conservation work in the 50s or 60s. The writing appeared to be in either crayon or heavy pencil. Attempts to remove the writing using erasers had no appreciable effect. It was decided, however, not to attempt any other removal method, such as solvents, given the danger of driving the writing further into the cloth.

Mending

As mentioned earlier, Items 45, 46 & 47 were torn early in their history. Tears were repaired using a textile/easel painting conservation technique: a piece of Stabiltex grade 6–125 polyester cloth was painted with a layer of Beva 371 adhesive and allowed to dry. Patches were cut from this using pinking shears that were roughly 1.5 cm larger than the tear they were to cover. The patches were applied by activating the adhesive using a heated tacking iron, heated to the minimum softening temperature for Beva (68°C). During application the area underneath the patch was supported by a blotter and silicone release Mylar. Preliminary testing showed that application of the patches had no effect on the image on the obverse. Preliminary testing also showed that the colorants making up the image were unaffected by toluene and petroleum spirit, both of which can be used to release the Beva adhesive, the patches could therefore be safely removed if this was required in the future.

Mounting and framing

Because the National Archives of Australia wished to exhibit the drawings it was thought necessary to have them mounted and framed. In choosing a system for this, two factors were taken into account, firstly that the mounting method selected should be as simple and non-invasive as possible and secondly, that the system should match as closely as possible, the original used by Griffin.

The cotton support for the drawings was found to be quite strong and a full lining was thought unnecessary. It was therefore decided to strip line the drawings and attach them to wooden strainers.

Strainers were constructed of ash with recesses cut in them to take a piece of 5mm Foam-cor – so called 'blind-strainers'. In addition it was decided to use a 'nap lining' as an additional passive form of support for the drawings. In this method, commonly used in the mounting of textiles, the strainer with Foam-cor inserts is entirely covered with a piece of cloth. When the drawing is then mounted on the strainer, the nap of the support cloth and the nap of the cloth covering the strainer are in contact and the possibility of the drawing sagging on the strainer is thus reduced.

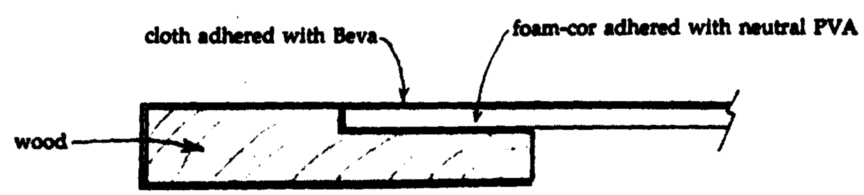

Fig. 4: The construction of the strainer

The raw timber of the strainer was first given three coats of acrylic varnish. Acid-free Foam-cor was then cut to size and glued in place using neutral PVA. Next, a piece of cotton drill cloth which had been thoroughly washed in deionized water was coated with Beva adhesive dissolved in petroleum spirits, and left to dry. To aid in the adhesion of the cloth to the strainer, the relevant surfaces of the strainer and Foam-cor insert were also coated in Beva adhesive. Because the edges of the Griffin drawings consist mainly of unadorned cloth, it was thought that the area of exposed wood at the edges of the strainer may tend to be visible through both the cloth covering and the drawing itself and result in a dark area around the edge. To avoid this, these areas of exposed wood were given a covering of white acid free paper before the cloth was attached. The cloth was then ironed over the strainer.

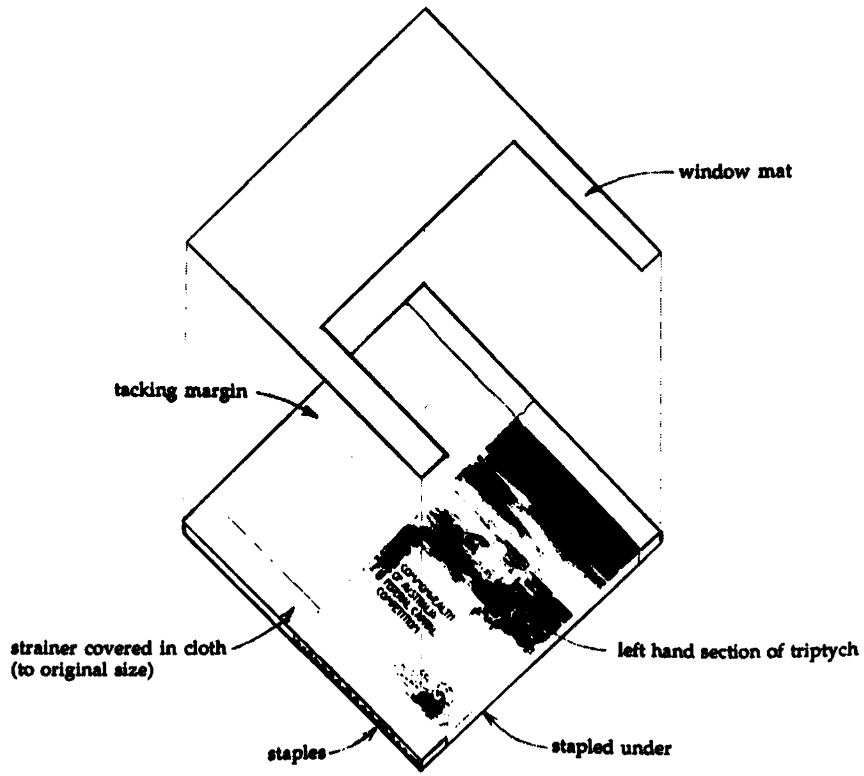

Fig. 7: The mounting system used for the sections of the Triptych

from the competition have also recently been loaned to the Centre George Pompidou in Paris for exhibition, and in the upcoming years, the Griffin drawings may be involved in another large scale exhibition that will tour within Australia and, possibly, the USA. It is therefore comforting to know that the utmost has been done for their preservation so as to prepare them for the dangers ahead.

Summaries

The Walter Burley Griffin Design Drawings of the City of Canberra; conservation work at the National Archives of Australia

The drawings submitted by Walter Burley Griffin and Marion Mahony Griffin for their winning entry in the Federal Capital Design Competition in 1912 are part of the holdings of the National Archives of Australia. The drawings are on cotton cloth and were originally mounted as easel paintings. The drawings were poorly treated in the years after the competition and they became much damaged and stained, more recently, ill advised conservation work also took its toll. The treatment of the drawings was an unusual project in that it fell across three conservation disciplines – easel paintings, textiles and paper. A combination approach to treatment was therefore developed.

Les croquis de la ville de Canberra ébauchés par Walter Burley Griffin; travail de conservation aux Archives Nationales d'Australie

Les dessins que Walter Burley Griffin et Marion Mahony Griffin ont déposés en 1912 pour participer au concours relatif à la structure et à l'agencement de la capitale fédérale australienne font partie aujourd'hui de l'inventaire des Archives Nationales d'Australie. Les croquis sont dessinés sur toile de coton et étaient montés à l'origine sur des chevalets comme des tableaux peints à l'huile. Après le concours ils n'ont pas été suffisamment bien traités, ce qui a conduit à de graves détériorations et souillures; à une époque plus récente un traitement insuffisant de conservation a également contribué au mauvais état actuel des pièces. La restauration qui vient d'être réalisée était dans ce sens une entreprise extraordinaire du fait qu'elle englobait trois disciplines différentes de conservation: peinture sur toile, textile et papier. Il était indispensable de procéder selon les règles applicables à ces trois domaines.

Walter Burley Griffins Entwurfszeichnungen für die Stadt Canberra. Konservierung im Australischen Archiv

Die Zeichnungen, die Walter Burley Griffin und Marion Mahony Griffin 1912 für den Wettbewerb um die Gestaltung der australischen Bundeshauptstadt eingereicht hatten, gehören heute zu den Beständen des Australischen Archivs. Sie sind auf Tuch aus Baumwolle gezeichnet und waren ursprünglich wie Leinwand-Ölbilder montiert. Nach dem Wettbewerb waren sie wenig pfleglich behandelt worden, was zu starken Schäden und Verschmutzungen geführt hatte; auch unzureichende konservatorische Behandlung in neuerer Zeit trug zum schlechten Zustand der Stücke bei. Die jetzt durchgeführte Restaurierung war insofern ein ungewöhnliches Unternehmen, als es in drei verschiedene konservatorische Disziplinen reichte: Gemälde auf Leinwand, Textilien und Papier. Es war erforderlich, nach den Regeln aller dieser drei Bereiche vorzugehen.

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Fig. 5: The Triptych in 1912

100mm-wide tacking margins were cut from Stabiltex grade 6-125 polyester cloth and adhered to the edges of the back of the object. They were adhered to a depth of about 1 cm using Beva film which was cast by making up a 50/50 solution in toluene and painting it on to a release layer of silicone treated paper. The margins were applied in a similar fashion to the mending patches, described at point 5.6 above.

The two edges of the Stabiltex tacking margins were prepared as follows: the edge to be adhered to the drawing was 'tapered' by the removal of three threads along its long dimension. This reduced the hardness of the cut edge and thus reduced the risk of it showing through on the front. The unsecured edge of the tacking margin was protected from fraying by sealing it using an ultrasonic welder.

The margins were adhered with a tacking iron. A good bond was ensured by the application of digital pressure on the bonded area as the adhesive cooled. Bond strength was constantly double checked. The drawing was then attached to the strainer using a staple gun and copper staples and strips of cover weight acid-free paper were used to protect the tacking margin from the staples. The drawings were placed in simple pine frames with a semi circular profile. The frames were limed and varnished with an acrylic varnish. They were glazed with Perspex, and a spacer was inserted to separate the Perspex from the drawing.

The Triptych (Items 48-50)

Treatment of the triptych presented some unique problems. As already stated, the triptych had originally been mounted on three separate strainers but was now

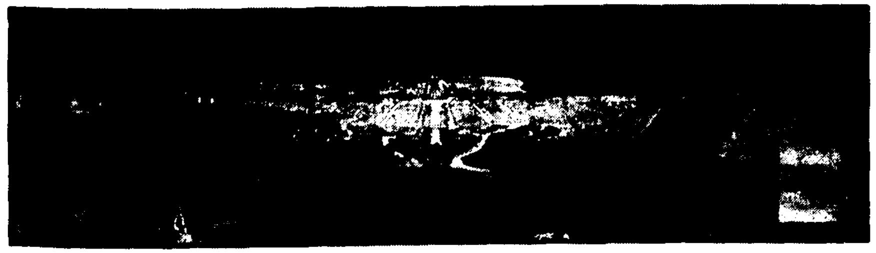

Fig. 6: The Triptych prior to treatment

mounted on a single piece of chipboard. Also, its original white border areas had been removed during previous conservation work. It was thought extremely desirable to try as far as possible to reverse these changes and restore it to its initial state. This involved once again treating it as three individual pieces. Three strainers were prepared, one 1525 x 765mm and two 765 x 765mm, the original dimensions of the drawings prior to the removal of their borders. The three sections of the triptych were removed from the chip board and tacking margins added using the method described above.

Because the objects were smaller than the strainers they were to be attached to, the new tacking margins had to be long enough to make up the difference. Stapling the drawings in place was quite difficult because positioning was critical and there was nothing stopping them from sliding around. Also, on the edges where the sections butted together, the staples had to be applied at the back.

When mounting was complete, the three strainers were placed in a single frame. To simulate the effect of the missing cloth borders, and to disguise the unsightly tacking margins they were covered with a window mat of a similar tone to the bare cloth of the drawings. The edges of the window were painted gold to simulate the effect of the original gold border which was mostly lost.

CONCLUSION

The conservation work described in this article was timely. In recent years there has been a growing level of interest in the material associated with the 1912 Federal Capital Design Competition. This includes not only the Griffin material but all entries in the competition. When viewed as a whole this group of drawings presents a unique view of the state of urban design before the First World War.

At the time of writing, drawings from the competition, including the bulk of the Griffin drawings, are on display in a joint National Archives of Australia/National Library of Australia exhibition entitled 'An Ideal City ?' which focuses on the design competition and examines many of the non-winning entries. Drawings

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Harrison, Peter.: *Walter Burley Griffin, Landscape Architect.* Canberra: National Library of Australia, 1995.

Wigmore, Lionel: *The Long View: A History of Canberra, Australia's National Capital.* Melbourne: F. W. Cheshire, 1963.

Much anecdotal information about the discovery of the drawings in the 1950s and their subsequent history was gleaned from discussion with Peter Harrison, retired Town Planner for NCDC. These discussions took place in 1989 and 1990. Sadly, Mr Harrison has since passed away.

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The Impact of Lignin on Paper Permanence

A Comprehensive Study of the Ageing Behaviour of Handsheets and Commercial Paper Samples*

by P. BÉGIN, S. DESCHÂTELETS, D. GRATTAN, N. GURNAGUL, J. IRACI, E. KAMINSKA, D. WOODS & X. ZOU

Introduction

Existing international standards have the following specifications for permanence:

- the paper must have a minimum cold extract pH of 7.5;
- it must contain an alkaline reserve equivalent to at least two percent calcium carbonate; and
- the lignin content of the paper must not exceed one percent[1–3].

The restriction on lignin derives from the observation that many papers made from mechanical pulps have poor permanence. It had been thought that this instability was caused by the presence of lignin, which constitutes about 16 to 24% of the components for hardwoods and about 25 to 31% for softwoods. The major component is cellulose which, historically, is regarded as having greater stability. Recent evidence suggested that assumptions about lignin may not be correct[4–14]. However, at that time, not enough scientific data had been accumulated to be certain since there were remaining questions about the role of lignin in paper exposed to air pollutants[3].

While previous studies into the permanence of lignin-containing papers have concentrated on the retention of physical properties, this research project also emphasizes changes in chemical properties.

* The following text is Part 1 of the Canadian Co-Operative Permanent Paper Research Project: *The Impact of Lignin on Paper Permanence. Final Report.* Ottawa: Pulp and Paper Institute of Canada, Canadian Conservation Institute 1998. Some more technical data on the samples under research can be found there and, moreover, the standard deviation to any of them.

EXPERIMENTAL

Samples

A series of handsheets was prepared from a variety of pure pulps ranging from mechanical pulps to rag pulps. The sheets were made with and without the presence of an alkaline reserve (2% calcium carbonate). Table 1 summarizes the various handsheets used in the research project.

A series of commercial paper samples that are representative of the various grades of paper currently available and proposed for development was also aged using the conditions established for the handsheet experiments. Table 2 summarizes the different commercial paper samples that were examined.

Table 1: Pulps used for the preparation of handsheets

Species	Pulp Type	g/m²	Moisture content (%)	cold extr. pH (0.1N NaCl)	acidity (mmols /100g)	$CaCO_3$ (%)	Code*
Spruce	TMP	58.9	9.4	6.24	3.7		H7TS
		59.0	9.7	8.94		1.71	H9TS
		60.4	9.1	4.19	21.6		H4BS
	BCTMP	59.7	9.9	6.87	1.8		H7BS
		59.2	9.4	9.05		1.99	H9BS
	bleached kraft	62.6	7.1	4.90	2.8		H4KS
		60.3	7.5	6.35	0.3		H7KS
		59.8	7.0	9.47		1.91	H9KS
Aspen	BCTMP	60.8	9.0	6.65	1.5		H7BA
		58.9	9.0	9.05		1.89	H9BA
	Bleached Kraft	60.5	6.7	6.40	0.6		H7KA
		59.8	7.0	9.54		2.05	H9KA
Cotton	Rag	60.8	6.0	5.41	0.7		H4RC
		58.8	6.4	6.56	0.4		H7RC
		59.7	5.9	9.65		2.53	H9RC

* The coding system for the handsheet samples works as follows:

- the first letter represents the type of sample; H stands for handsheets;
- the number represents the acidity/alkalinity of the samples; 4: acidic; 7: neutral, non buffered; 9: alkaline, buffered;
- the second letter represents the pulp type;
  T: TMP, i.e. thermomechanical pulp;
  B: BCTMP, i.e. bleached chemi-thermomechanical pulp;
  K: bleached kraft;
  R: rag;
- the third letter represents the species; A (aspen), S (spruce), C (cotton).

Table 2: Commercial paper samples included in the research project

Sample description	g/m²	Moisture content (%)	pH*	acidity*	$CaCO_3$ (%)	Code**
Alkaline fine paper: 60% softwood bleached kraft, 25% hardwood bleached kraft, 15% aspen BCTMP, 15% filler (precipitated $CaCO_3$)	72.2	6.0	9.53		13.89	C9BM
Alkaline fine paper: 85% softwood + 15% hardwood bleached kraft, 15% filler (precipitated $CaCO_3$), starch, alkyl ketene dimer sizing	70.8	6.1	9.52		10.97	C9KM
Acid fine paper: 50% hardwood bleached kraft, 50% softwood bleached kraft (post-industrial), 4% filler (clay), alum-rosin sizing, starch	71.5	6.0	4.75	6.4		C4KM
Alkaline recycled fine paper: 25% softwood bleached kraft, 75% recycled (including 10% post-commercial), 15% filler (precipitated and ground $CaCO_3$), alkyl ketene dimer sizing, starch	85.7	5.5	9.27		15.43	C9FR
Alkaline cotton: 100% cotton, 8.5% filler (precipitated $CaCO_3$)	64.4	5.5	9.41		7.25	C9RC
Acid Whatman filter paper: 100% cotton, ashless	86.0	5.4	4.62	0.5		C4RC
Light-weight coated paper: 50% groundwood + 50% bleached softwood kraft, 12% filler (precipitated $CaCO_3$ and clay)	56.1	5.2	8.79		11.67	C9GM
Acid newsprint: 100% TMP, alum-rosin sizing	44.6	8.5	4.17	13.4		C4NM
Alkaline newsprint: 90% TMP + 10% bleached kraft, 7% filler (precipitated $CaCO_3$)	39.5	7.1	8.88		6.72	C9NM
Recycled newsprint: 70% TMP, 30% recycled newsprint, alum-rosin sizing	43.5	7.8	4.46	10.8		C4NR

* for method cf. Table 1

** The coding system for the commercial paper samples works as follows:

- the first letter represents the type of sample; C stands for commercial paper;
- the number represents the acidity/alkalinity of the samples; 4: acidic; 7: neutral, non buffered; 9: alkaline, buffered;
- the second letter represents the pulp type;
  B: BCTMP, i.e. bleached chemi-thermomechanical pulp
  K: bleached kraft
  F: fine paper made from bleached kraft pulp (virgin and recycled)
  G: light-weight coated (groundwood + bleached kraft)
  R: fine rag;
- the third letter represents the species or origin:
  M: mixed hardwood and softwood
  R: recycle fibre (post-consumer)
  C: cotton.

Handsheet preparation

Handsheets made from six different pulp types were prepared using CPPA standard C.4[15]. The pulps were thoroughly washed with tap water for the production of the neutral (non-buffered) samples. The acidic handsheets were prepared by adding alum to the pulp suspension just before the formation of the handsheets. The amount of alum addition was controlled by adjusting the pH of the pulp suspension to 4. For the preparation of alkaline (buffered) handsheets, the amount of calcium carbonate required to produce an alkaline reserve of 2% for each pulp type was determined by measuring the ash content of test handsheets containing increasing amounts of calcium carbonate. This predetermined amount of calcium carbonate was added to the pulp suspension before mixing in a British disintegrator. This was then followed by the standard handsheet preparation procedure.

Accelerated ageing procedure

The accelerated ageing of the papers was carried out in controlled temperature and humidity chambers (ESPEC PRA-3GP). The samples were suspended in sheet form, in the dark, and exposed to a temperature of 80°C and a relative humidity of 65%[16]. During the accelerated ageing, specimens were removed at intervals of 5, 20, and 50 days. After ageing, the papers were conditioned for testing according to CPPA standard A.4[17].

PHYSICAL PROPERTIES

Zero-span tensile strength

Fibre strength is an important parameter that affects paper failure. Properties such as tensile strength, tear strength and folding endurance are highly dependent on fibre strength[18]. The dry zero-span tensile strength gives a good indication of the strength of fibres in the dry state[19]. The Pulmac apparatus was used to measure the dry zero-span tensile strength of the samples[20].

Tear strength

Tear strength is often used as a criterion for printing and writing papers as well as for certain permanent paper standards. The tear test is sensitive to a number of

factors including fibre length, fibre strength, and interfibre bonding[18]. For well-bonded sheets, the tear index is proportional to the square of fibre strength[21]. The tearing resistance of all the paper samples was measured with an Elmendorf tear tester using CPPA standard D.9[22].

Stress/strain curve of paper

The stress/strain curve of paper was obtained using a constant rate of elongation apparatus (Instron tensile tester) using CPPA standard D.34[23]. This allowed us to determine tensile strength, stretch, and the tensile energy absorption (TEA) for the work to rupture. For well-bonded sheets, the tensile strength is proportional to fibre strength[24]. The tensile strength of paper is not very sensitive to accelerated ageing[25]. However, the TEA is somewhat more sensitive, therefore, in this report, we focus primarily on the TEA data.

Folding endurance

The folding endurance test has high variability but it is a very sensitive test to monitor the effects of accelerated ageing. The reason for this is that folding endurance is proportional to the eighth power of fibre strength[18]. The folding test was done with the M.I.T. apparatus using CPPA standard method D.17P[26]. A tension of 500g was used instead of the normal 1000g for all of the samples. This was done to ensure that a reasonable fold value could be obtained for papers with a wide range of strength properties.

Brightness

The brightness of the samples was measured at a wavelength of 457nm using CPPA standard E.1[27].

CHEMICAL PROPERTIES

Acidity

The cold extraction pH of the paper was measured in both deionized water (CPPA standard G.25P[28]) and in a 0.1N sodium chloride solution[29]. In both cases, the final pH readings were recorded after nitrogen had been bubbled through the

Table 3: Testing data, part I

		Zero span breaking length(km) ageing (days)				Tear index (mNm^2/g) ageing (days)				TEA index (mJ/g) ageing (days)			
		0	5	20	50	0	5	20	50	0	5	20	50
H4RC		14,93	15,18	14,39	13,22	20,48	20,17	16,90	14,18	1051	977	895	861
H4KS		15,14	14,52	13,00	11,18	27,67	25,28	18,01	11,28	1017	879	821	621
H4BS		11,69	11,31	10,28	8,84	7,69	6,97	5,89	4,67	694	594	464	359
H7RC		15,30	15,43	15,56	15,43	21,67	20,50	20,86	19,29	871	811	896	874
H7KS		15,94	15,36	15,33	14,56	27,71	27,46	26,21	22,61	967	821	800	801
H7BS		12,38	12,08	12,29	11,63	8,97	8,14	8,36	7,95	660	546	601	568
H9RC		15,15	14,85	14,99	15,00	22,18	21,31	20,77	20,13	769	784	724	670
H9KS		15,71	15,93	15,87	15,41	24,78	22,92	21,78	22,12	690	600	610	556
H9KA		13,73	13,59	13,65	12,97	5,28	5,08	4,81	5,14	398	335	377	360
H9BA		12,67	11,89	11,93	12,01	3,07	3,03	2,71	2,91	158	170	176	143
H9BS		11,98	12,32	12,36	12,76	8,38	7,66	7,60	7,44	651	551	668	631
H9TS		11,46	11,68	11,48	11,28	8,61	8,14	7,77	7,11	574	507	583	413
C9BM	MD	15,69	15,72	15,74	15,89	7,64	7,37	7,49	7,05	622	634	593	569
C9BM	CD	9,90	10,05	10,36	10,30	8,77	8,43	8,41	8,09	647	584	666	570
C9KM	MD	15,37	15,25	14,90	14,82	6,05	6,13	6,17	6,35	1175	710	722	858
C9KM	CD	9,77	10,50	10,35	10,27	6,27	6,68	6,27	6,07	1171	1294	1279	1218
C4KM	MD	13,30	12,68	11,74	9,87	6,34	5,37	4,26	3,14	955	787	603	404
C4KM	CD	10,70	9,94	8,30	7,58	6,70	5,86	4,80	3,49	1236	1028	760	507
C9FR	MD	11,73	10,80	10,89	11,41	8,22	8,69	8,32	8,19	562	455	428	470
C9FR	CD	8,51	9,04	8,95	9,11	9,13	8,32	8,30	8,28	753	886	847	816
C9RC	MD	15,08	15,24	15,38	15,00	8,78	8,40	8,48	8,16	1272	1396	1401	1187
C9RC	CD	10,23	10,43	10,50	10,48	9,39	9,06	9,07	9,06	1815	1773	1734	1805
C9GM	MD	13,07	13,16	13,17	13,64	3,95	4,05	4,20	4,04	542	498	551	513
C9GM	CD	7,22	7,20	6,90	7,70	5,24	4,90	5,04	4,99	358	286	305	318
C4NM	MD	16,85	16,97	14,96	15,28	5,50	4,74	4,15	3,06	517	403	442	322
C4NM	CD	6,49	6,17	5,19	5,38	9,41	8,01	6,39	5,34	444	428	322	261
C9NM	MD	15,86	16,25	16,08	15,94	5,46	5,26	5,28	5,08	488	539	492	436
C9NM	CD	8,15	7,12	7,36	7,62	7,45	6,82	5,89	6,59	311	260	255	313
C4NR	MD	14,82	14,99	14,76	14,21	3,74	3,40	3,36	3,11	379	322	316	303
C4NR	CD	5,50	5,46	5,45	5,20	5,55	5,44			329	322	307	264
C4RC	MD	11,48	10,81	9,02	7,81	5,82	5,62	4,91	3,48	409	351	275	155
C4RC	CD	9,41	6,96	6,61	5,25	5,59	5,84	5,08	3,83	320	300	289	176

solution to remove carbon dioxide. When the extraction is carried out in deionized water, most of the hydrogen ions remain in the fibre wall. The sodium chloride provides a more equal distribution, by ion exchange, of the hydrogen ions between the interior of the fibre wall and the external solution where the pH

Table 4: Testing data, part II

		MIT Fold Number (500g) ageing (days)				DP ageing (days)				Brightness (%) ageing (days)			
		0	5	20	50	0	5	20	50	0	5	20	50
H4RC		4647	4083	3158	1726	1930	1476	1104	741	84,84	83,32	80,08	73,49
H4KS		2216	1588	773	273	2190	1772	1154	812	87,65	82,31	74,56	64,52
H4BS		609	285	116	12	1316	985	549	317	73,87	63,15	49,89	40,20
H7RC		2897	2307	1620	1450	1932	1701	1532	1277	85,26	81,55	79,47	77,94
H7KS		2516	2433	1715	1528	2361	2201	1967	1588	85,69	81,81	77,89	73,71
H7BS		471	479	455	259	1247	1219	1182	1133	71,94	64,07	54,13	45,86
H9RC		636	603	391	453	1882	1705	1625	1522	86,08	84,37	83,00	81,84
H9KS		6	5	6	5	2324	2200	2120	1949	87,47	83,42	79,98	77,89
H9KA		1866	2555	1666	1541	1937	1806	1713	1591	85,25	81,30	78,05	76,43
H9BA		19	18	17	10	1882	1776	1580	1488	78,96	71,96	65,90	59,38
H9BS		538	359	294	256	1253	1168	1168	1100	73,76	63,81	56,57	48,55
H9TS		791	428	1153	694	1184	1141	979	879	54,95	52,08	47,47	41,69
C4RC	MD	38	24	17	6	1188	853	599	383	91,75	89,76	85,95	71,99
C4RC	CD	22	12	11	5								
C4KM	MD	998	739	346	24	1425	1113	757	521	84,34	80,07	75,04	68,77
C4KM	CD	713	452	201	45								
C4NM	MD	988	634	267	103	1239	920	685	508	51,48	43,71	38,26	33,20
C4NM	CD	49	52	29	15								
C4NR	MD	385	241	173	96	1226	1084	887	711	53,31	47,00	42,08	36,94
C4NR	CD	28	29	22	19								
C9RC	MD	3797	3880	3695	3050	1606	1449	1414	1337	79,12	78,00	76,86	74,78
C9RC	CD	2477	2798	2741	2335								
C9KM	MD	996	972	695	894	1262	1300	1203	1227	85,17	80,94	78,90	77,72
C9KM	CD	603	564	784	753								
C9FR	MD	1042	635	708	729					85,03	83,40	81,44	81,08
C9FR	CD	395	617	701	508								
C9BM	MD	680	627	525	563	1824	1835	1749	1764	83,11	79,75	76,61	73,58
C9BM	CD	237	204	323	190								
C9GM	MD	1187	1113	1027	913					69,76	65,84	62,29	59,58
C9GM	CD	697	730	763	786								
C9NM	MD	1070	890	918	733	1728	1684	1603	1464	70,89	65,42	60,03	55,24
C9NM	CD	233	120	130	191								

is measured. It is argued that the pH value so determined is a more accurate indication of the acidity of the paper[29].

The measurement of the total amount of acid, including strong to very weak acids is accomplished using an iodometric method[30]. This method can also be used to determine the total acid group content of the paper. For the acid group content determination, the iodometric method is carried out after the sample has been acid washed to ensure that all acidic functional groups are in the acid form. This measurement can detect changes in acidic functional groups such as carboxylic and sulphonic acid groups, but it does not differentiate between them.

Alkaline reserve

The amount of alkaline reserve in the papers was measured by the method outlined in ASTM standard D 4988-89[31]. The procedure was modified by determining the endpoint of the titration potentiometrically rather than by the use of an indicator. Also, instead of breaking up the samples in a blender and subsequently boiling them for one minute, the samples were cut into small pieces (5mm x 5mm) to which the water and 0.1N HCl was added. This sample solution was then left overnight and the titration was performed the following day. This modification allowed the pH and alkaline reserve to be determined on the same sample therefore reducing the amount of sample used.

Degree of polymerization

The average degree of polymerization (DP) of the samples was determined by viscosity measurements using cadoxen solvent[32, 33]. Cadoxen rather than cupriethylenediamine (CED) was chosen because it is odourless, colourless, relatively stable, and the cellulose in cadoxen solution is less readily degraded by atmospheric oxygen[34, 35]. The samples of paper were pretreated with sodium borohydride to stabilize oxidizing groups to prevent possible solvent induced degradation[36]. The lignin-containing samples were treated by a mild acid-chlorite delignification to remove some of the lignin prior to the borohydride stage[37]. The average values of DP were calculated from the intrinsic viscosity (η_i) of the cellulose solution using the following equation[35]:

$$DP = \left(\frac{\eta_i}{1.84 \times 10^{-2}}\right)^{1.316}$$

RESULTS AND DISCUSSION

As can be seen from the Tables 1 to 4, there are significant differences in some of the initial properties of the samples. Therefore, it is sometimes useful to look at the

percent retention of the strength properties in order to compare the samples on a similar basis.

The determination of the average degree of polymerization (DP) is easily accomplished for the chemical pulps because they are highly soluble in cadoxen. The mechanical pulps are more difficult to analyze due to their low solubility in cadoxen. Delignification of the mechanical pulps by the acid chlorite method improved the solubility. However, complete removal of the lignin was avoided to minimize the damage to the cellulose[37]. The presence of the remaining lignin is in part responsible for the lower DP values determined for the mechanical pulps, particularly for the spruce samples[38]. Another reason for the lower DP values for the mechanical pulps is the presence of a larger amount of hemicellulose in these pulps as compared to the kraft ones. Treatment of pulps by the acid chlorite method produces holocellulose, i.e. all of the cellulose and hemicellulose is retained and only the lignin is removed[37]. Thus wood or mechanical pulp treated in this fashion results in a 70% yield pulp comprised of about 30% hemicellulose and 70% cellulose. On the other hand, bleached kraft pulp has only about 10% hemicellulose and 90% cellulose because a large portion of the hemicellulose is solubilized during the cooking and bleaching processes[39]. Since the hemicellulose fraction is of lower molecular weight and has a lower DP (200–250), the average DP of the acid chlorite bleached mechanical pulp is lower than the average DP of the bleached kraft pulp. Therefore, the DP values of the mechanical pulps can be considered as "apparent" DP values.

The emphasis of the DP determination should not be placed on comparing DP values from various pulp types, but rather on the change in the DP of a particular sample during accelerated ageing. The rate at which the cellulose molecules depolymerize is a valuable tool in determining the relative stabilities of different papers because the fibres become increasingly weaker as the depolymerization progresses. This rate can be determined using the following equation derived for polymer degradation in general[40] and recently applied to the degradation of cellulose during ageing [25]:

$$kt = \left(\frac{1}{DP_t} - \frac{1}{DP_0}\right)$$

Where: DP_t = the degree of polymerization at time t
DP_0 = the initial degree of polymerization
k = the rate constant for glycosidic bond breakage (day-1)
t = time (days)

Rate constants of bond breakage can be calculated from the slope of the lines of the plot of $1/DP_t$ - $1/DP_0$ against time.

Handsheets

Effect of Acidity

Three of the six pulp types used in this project were chosen to study the effect of acidity on the stability of the papers. Acidic, neutral (non-buffered), and alkaline (buffered) handsheets of cotton linter (rag), bleached kraft spruce, and BCTMP spruce were chosen because they covered the three pH ranges of interest and they also included both lignin-containing and lignin-free pulps.

The pH of the three acidic samples are significantly different even though they were prepared under identical conditions. This is due to the differences in the total acid group content for each of the three pulp types (Table 1).

The fibre strength of the papers, as measured by zero-span tensile (Fig. 1) shows a significant reduction in stability for the acidic handsheets. The neutral and alkaline handsheets demonstrate the best stability. The acidic bleached kraft spruce (H4KS) and acidic BCTMP spruce (H4BS) sheets show the largest decrease in fibre strength during the accelerated ageing. The higher retention of zero-span strength of the acidic rag handsheet may be attributed to its higher initial pH.

The retention of the tensile energy absorption (TEA) shows results that are similar to the ones for zero-span tensile.

The retention of tear strength is highest for the alkaline and neutral handsheets. This property decreases more rapidly for the acidic papers. The tear strength loss is larger for the bleached kraft spruce (H7KS) than it is for the BCTMP spruce (H7BS). As well as fibre strength, other factors such as fibre length and interfibre bonding can influence the tear strength of handsheets. This can give results for the acidic sheets that differ slightly from the other strength tests.

The plot of $1/DP_t - 1/DP_0$ against ageing time at 80°C and 65% RH (Fig. 2) shows the effect of the acidity of the sample on its degradation rate as indicated by the slopes of the lines. The alkaline samples show the lowest degradation rate followed closely by the neutral samples. Degradation for the acidic samples is more pronounced with the acidic BCTMP (lowest pH) showing the fastest rate. These results are similar to the ones for the strength properties and confirm that acidity is an important cause of paper degradation[25]. As expected, the addition of an alkaline buffering agent such as calcium carbonate is effective in slowing down the rate of degradation.

Effect of Lignin

In order to isolate the effect of lignin, the stabilities of the six pulps, including lignin-containing and lignin-free, were examined in the neutral and alkaline pH ranges.

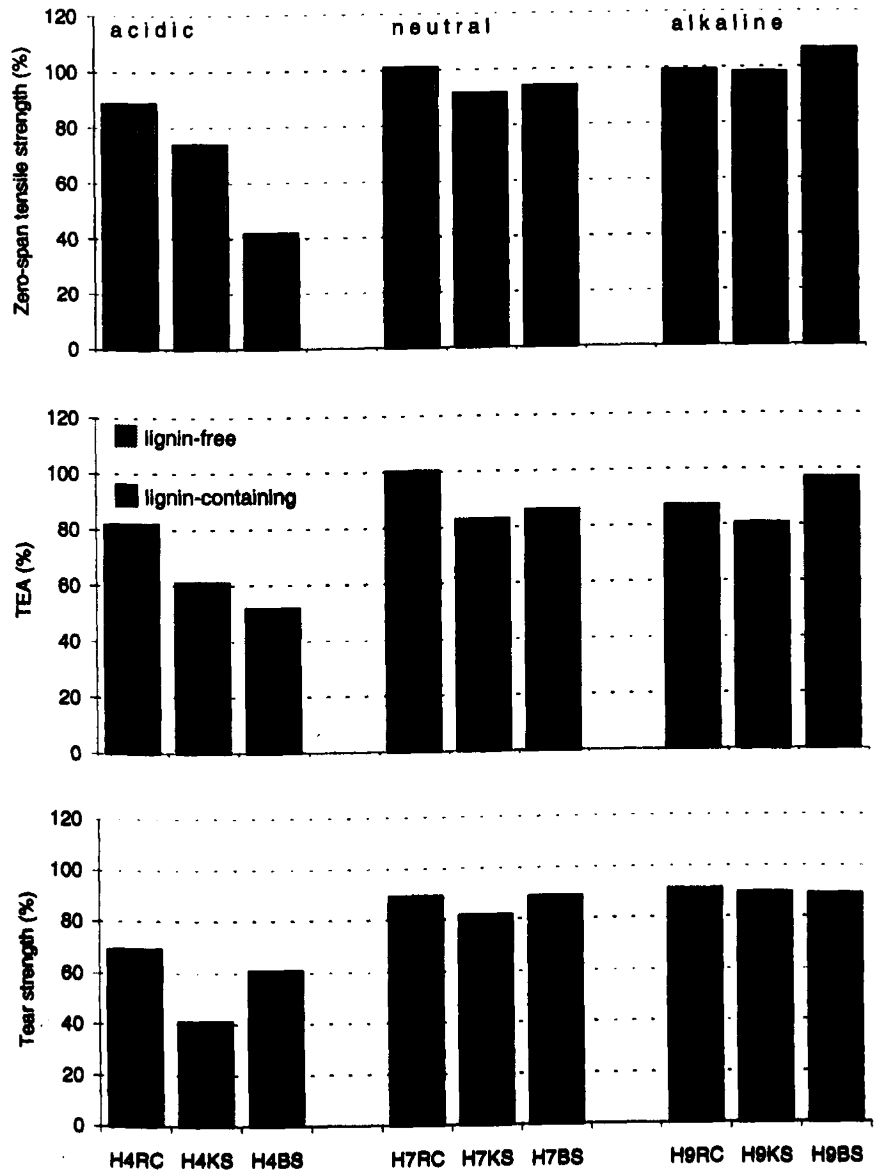

Fig. 1: Retention of physical properties after 50 days of ageing at 80°C and 65% RH (handsheets)

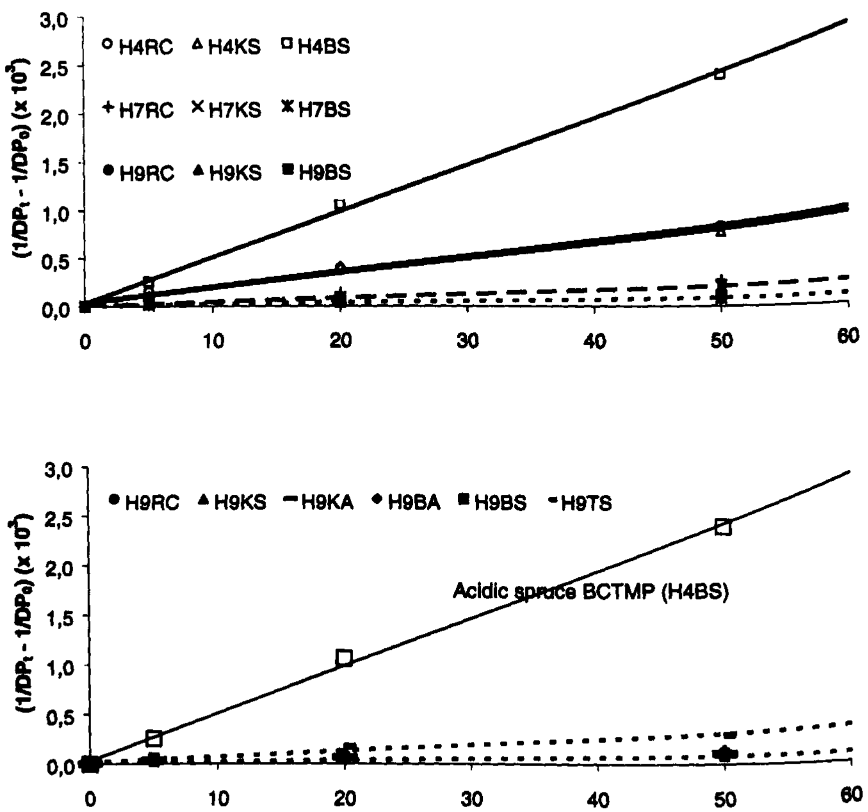

Fig. 2: (1/DPt - 1/DP0) versus ageing time (days)

The neutral samples gave results that were more variable in the amount of initial property retained after accelerated ageing. This may be a result of the varying initial pHs of these papers, for this reason, only the graphs for the alkaline samples are shown and discussed.

The changes with accelerated ageing in the physical properties (Fig. 3) including zero-span tensile, internal tearing resistance, and tensile energy absorption (TEA) show good strength retention for the alkaline handsheets regardless of the pulp type used to make them.

The plot of $1/DP_t$ -$1/DP_0$ against ageing time (Fig. 2) shows that the alkaline samples of rag, kraft, and BCTMP have similar degradation rates during acceler-

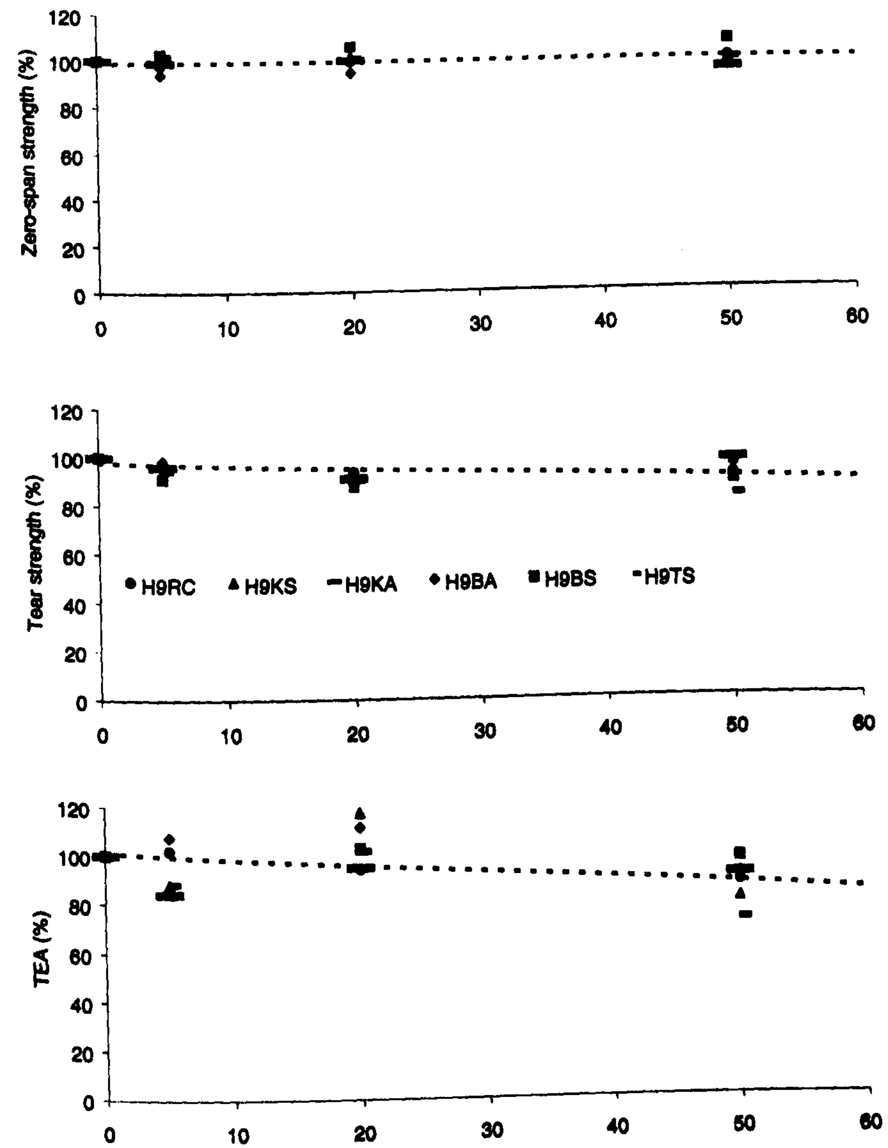

Fig. 3: Retention of physical properties with ageing time (alkaline handsheets)

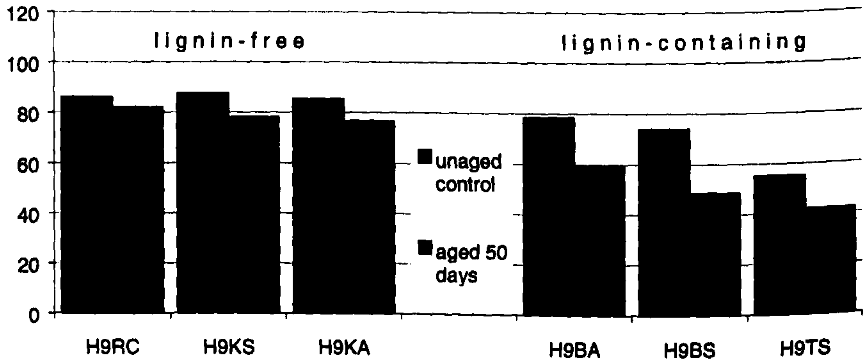

Fig. 4: Change in brightness (% reflectance) after 50 days of ageing at 80°C and 65% RH (alkaline handsheets).

ated ageing regardless of species or presence of lignin. The rate of DP loss is higher for the alkaline TMP pulp. However, all of the alkaline handsheets have a significantly lower degradation rate than the acidic handsheets as shown by the slope of the acidic spruce BCTMP sample (H4BS).

The brightness values (Fig. 4) show that lignin-containing pulps start with a lower brightness value and lose this property more quickly during accelerated ageing in the dark than the bleached chemical and rag pulps.

Commercial papers

The retention of the physical and chemical properties including zero-span tensile strength, internal tearing resistance, tensile energy absorption (TEA), folding endurance, and rate of bond breakage are compared for acid and alkaline commercial papers (Fig. 5 and 6). The data show that, similar to the handsheets, the alkaline commercial papers are more stable than the acidic ones.

There is no significant difference in the mechanical and chemical stabilities of the lignin-containing and lignin-free alkaline commercial papers. The alkaline newsprint sheets are quite stable in terms of both mechanical and chemical properties even though they are made in large part of TMP pulp. These commercial papers contain significantly more calcium carbonate than the TMP handsheets. The larger loss of properties for the TMP handsheets may be caused by

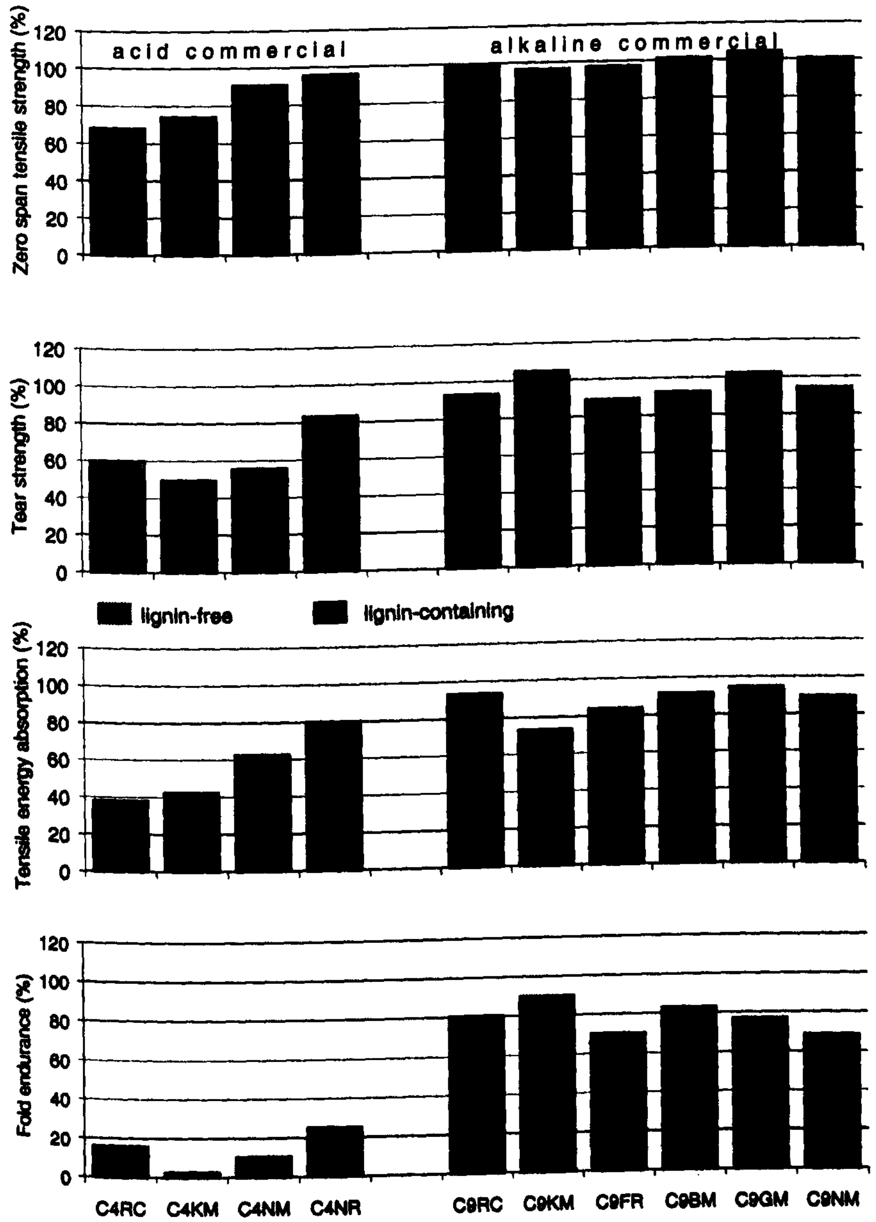

Fig. 5: Retention of physical properties after 50 days of ageing at 80°C and 65% RH (commercial papers).

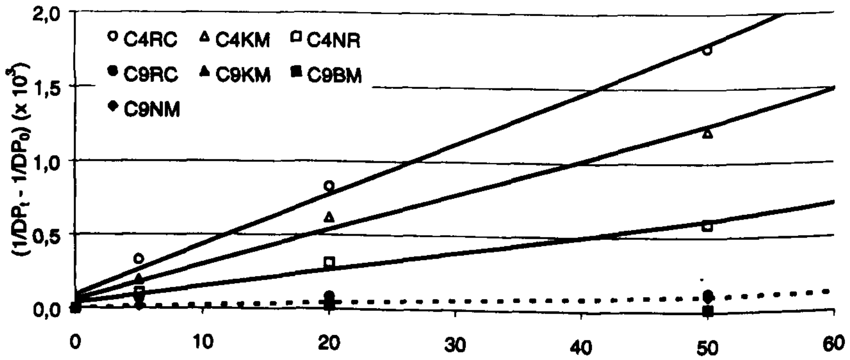

Fig. 6: $(1/DP_t - 1/DP_0)$ versus ageing time (commercial papers)

a non-uniform distribution of calcium carbonate within the sheets. Due to the poor retention properties of the kraft and rag pulps, more calcium carbonate (e.g. twice more than that for TMP) must be added to these pulp suspensions during sheet formation to get the same 2% calcium carbonate in the dry sheets. This produces a more uniform calcium carbonate distribution in the bleached kraft and rag sheets. In the case of TMP, the calcium carbonate is easily retained during the formation of handsheets due to the presence of a large amount of fines. The reduced amount of calcium carbonate required for the formation of the TMP handsheets could result in a less effective neutralization by the calcium carbonate and non-uniform distribution of the alkaline reserve.

The effect of accelerated ageing in the dark on brightness (Fig. 7) also gives results that are the same as for the handsheets. The high-lignin content papers (C9GM and C9NM) start at lower brightness and decrease more than the other alkaline papers.

CONCLUSIONS

The permanent paper research project examined the ageing behaviour of a comprehensive set of handsheets (prepared from six pulp types) and ten commercial papers. The results confirmed that acidity is the most significant factor that affects the stability of paper during accelerated ageing. The addition of calcium carbonate as a buffering compound is an effective way of improving the stability. This research shows that lignin does not have a negative impact on the ageing stability of mechanical and chemical properties of paper if the paper is buffered with a

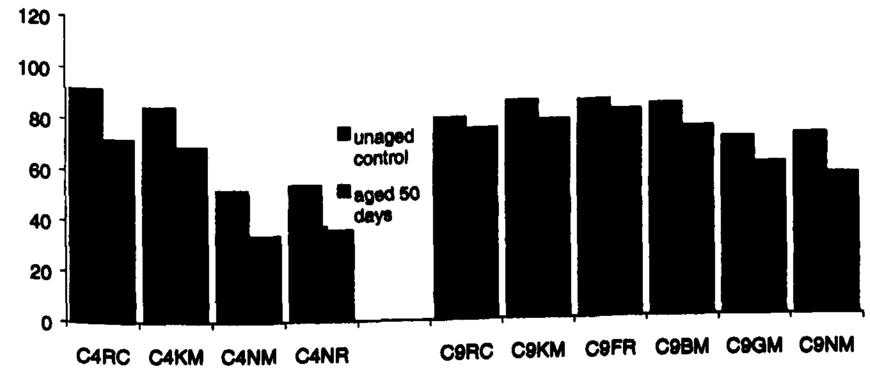

Fig. 7: Change in brightness (% reflectance) after 50 days of ageing at 80°C and 65% RH (commercial papers)

sufficient amount of calcium carbonate. However, the stability of the optical properties of papers made predominantly from high-yield pulps is negatively affected by the presence of lignin.

SUMMARIES

The Impact of Lignin on Paper Permanence

The accelerated ageing of handsheets and commercial papers at 80°C and 65%RH confirms that acidity is the most significant factor that affects paper stability. The addition of a buffering compound such as calcium carbonate is an effective way of improving the stability. This research shows that lignin does not have a negative impact on the ageing stability of mechanical and chemical properties of paper if it is buffered with a sufficient amount of calcium carbonate. The stability of the optical properties of papers made predominantly from high-yield pulps is negatively affected by the presence of lignin.

L'impact de la lignine sur la durabilité du papier

Un vieillissement accéléré de feuilles de laboratoire ainsi que de papiers en vente dans le commerce réalisé à une température de 80°C et une humidité ambiante de 65% confirme que l'acide est le facteur qui exerce la plus grande influence sur la durabilité du papier. L'addition d'une substance tampon, comme p. ex. le carbonate de calcium, est une possibilité effective pour améliorer la stabilité. L'étude démontre que la lignine n'a pas d'effet négatif sur la stabilité du vieillissement des propriétés mécaniques et chimiques du papier lorsque celle-ci est suffisamment amortie par une substance tampon comme le carbonate de calcium. La stabilité des propriétés optiques de

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Permanence of Paper 1

Problems and Permanency of Alum-Rosin Sized Paper Sheets from Wood Pulp

by HOUSSNI EL-SAIED, ALTAF H. BASTA & MONA M. ABDOU

Introduction

In the National Book Organization (Dar El-kuteb, Egypt), Restoration, Conservation and Micro-Films Research Center, there are increasing concerns by workers in the paper conservation field about the rapid deterioration of old and rare books, documents and manuscripts. Such heritage concerns have resulted in an increased demand for "permanent paper", i.e., good strength and optical permanence.

Permanent paper is paper that can have a reasonable life expectancy exceeding 200 year[1]. Most modern papers have a reasonable life expectancy of about 50 years.

Rasch et al.[2] proposed that the folding endurance after 75 hrs. at 100°C should be termed the *permanency factor.* The natural and accelerated ageing process of paper, which is connected to the degradation of its cellulosic substrate is related to two factors:

- Internal causes of deterioration, e.g., acidity of paper as a result of paper additives and /or inks[1,3–5] and
- External causes of deterioration, e.g., light, moisture, polluted air[6–7]. As a consequence of the ageing process, oxidized group (carboxyl and carbonyl) are formed in the cellulose chains[8].

Sizing of paper constitutes one degradative component in paper; internal causes of deterioration[1]. The sizing agents are used in most modern writing and printing papers to provide resistance to excessive surface wetting, penetration through the structure, and excessive adsorption of aqueous liquids. Rosin size and papermaker's alum are always used together for sizing of paper[9]. The reaction of alum and rosin varies according to the physical and chemical conditions in the paper making process. It was thought that aluminium sulfate (alum) combines with the sodium rosinate to form aluminium resinate (the water-repellent size), and with the ions of sodium sulfate and sulfuric acid. The acidic material is responsible for deterioration, i.e. decreased paper permanence[10].

Literature concerned on permanence showed that direct dyes protect cellulose, however, acid dyes are harmful. Anthraquinonoid dyes have been reported to produce "photoendering" of cellulose[11]. When paper is impregnated with Kymene (epichlorohydrin type wet-strength resin), followed by moderate drying and hot pressing, the deterioration of the treated paper sheet will be prevented when subjected to accelerated heat ageing. Also, Jozef et al.[12] showed that paper with good permanency was manufactured by ancient papermaking method under alkaline conditions, whereas calcium cations (from lime added to beating) act as an agent to maintain the neutral character of paper (pH ~7.0). It was also found that rosin-sized paper has a lower thermal decomposition temperature than unsized and alkyl ketene dimmer (AKD)-sized papers.

In the present work the effect of artificial ageing (dry thermal ageing method) on the properties of different alum-rosin sized paper sheets have been studied, in order to find out the suitable (optimum) sizing conditions, i.e., pH of sizing medium, for producing paper sheets from wood pulp having acceptable optical and mechanical permanences and to be used for in-house restoration. The polynominal equation which gives the relation between the time of thermal ageing and pH-values of the prepared papers with the optical or quality number of the mechanical measurements was also proposed.

EXPERIMENTAL

Materials

Paper substrate: Paper grade kraft soft wood pulp sample was delivered from Rakta Paper Mill – Alexandria, Egypt. The pulp was analyzed as follows :

- α-Cellulose estimation was carried out according to Merkblatt IV/29 Zellchming (German Association of Cellulose Chemistry & Engineering).
- Pentosan was estimated according to Jayme and Sarten[13].
- Lignin estimation was carried out according to the method of the Institute of Paper Chemistry[14].
- Ash content was determined by ignition in a muffle furnace at 400°C for one hour, then at 850°C for 45 minutes.

Sizing agents

- Rosin: The used rosin size was prepared by reacting 100 kg rosin with 6 kg NaOH and 6.5 kg Na_2CO_3, and stabilizing the size with 3.5 kg Casein.
- Alum ($Al_2(SO_4)_3 \cdot 16\ H_2O$) was used as a precipitant of rosin.

Preparation of handsheets

The purpose of the present work is an attempt to reduce the amount of alum used in sizing, which causes a problems on paper permanency[10]. This is done by carrying out laboratory study in the sizing of the pre-beaten kraft soft wood pulp, till 43 SR, in systems containing :

- sample 1: unsized control,
- sample 2: only alum: 5.6% based on dry pulp,
- sample 3: a high alum-to-rosin ratio (2 : 1),
- sample 4: an alum-deficient system having a low alum-to-rosin ratio (0.67 : 1), a
- sample 5: adjusting the pH of alum-deficient system by 0.6% sodium silicate to ~ 7.0.

The change in the amount of prementioned additives was performed to change the pH-value during paper sheets formation (pH 3.65–7.0).

Handsheets from the prementioned system were prepared according to the Scandinavian standard method (S.C.A.). The prepared and thermal aged paper sheets were chemically analyzed (α-, β- and γ-celluloses, carbonyl content, and caustic soda solubility[15-17]) and tested for optical, mechanical and quality number of mechanical measurements[18,19]. The hydrogen-ion-concentration of a cold aqueous extract[20], degree of polymerization (DP), and water resistance[21] of the prepared sheets were also estimated. The properties of paper sheets prepared from unsized wood pulp were measured for comparison.

The mechanical measurements were carried out after conditioning the prepared sheets at relative humidity 65% and temperature 18 –20°C.

Ageing of paper sheets

Sized paper sheets prepared at different pH's were artificially aged using dry thermal accelerated ageing in an oven at 100°C for several cycles of heating (3,6 & 12 days).

papiers faits principalement à base de pâte chimique à haut rendement est influencée négativement par la présence de la lignine.

Der Einfluß von Lignin auf die Dauerhaftigkeit von Papier

Eine beschleunigte Alterung von Laborblättern und im Handel erhältlichen Papieren bei 80°C und 65% rF bestätigt, daß Säure der Faktor ist, der den stärksten Einfluß auf die Dauerhaftigkeit von Papier hat. Der Zusatz einer Puffersubstanz, z.B. Calciumcarbonat, ist eine effektive Möglichkeit, dieselbe zu verbessern. Die Untersuchung zeigte, daß Lignin keinen negativen Einfluß auf die Alterungsstabilität von mechanischen und chemischen Eigenschaften des Papiers hat, wenn dieses ausreichend mit Calciumcarbonat gepuffert ist. Die Alterungsstabilität der optischen Eigenschaften von Papier, das überwiegend aus Hochausbeute-Zellstoff hergestellt ist, wird hingegen durch das Vorhandensein von Lignin negativ beeinflußt.

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The artificial ageing for 72 hours at 100°C is considered to be approximately equal to 25 years under ambient conditions[22].

POLYNOMINAL CORRELATION AND REGRESSION EQUATION

In order to correlate the permanence (optical or mechanical) of sized-paper sheets (Y) and the independent variables, X's (time of ageing, X_1 and pH's of sized paper preparation, X_2), the following polynominal models were proposed;

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{12}X_1X_2 \quad \text{or}$$

$$Y = b_0 + b_1X_1 + b_2X_2 + b_{11}X_1^2 + b_{22}X_2^2 + b_{12}X_1X_2$$

The regression constant, b_0, the coefficients, b_1–b_{12}, determination coefficient (R^2) and standard error of estimation (SE) of the models were obtained using multiple regression analyses[23, 24]. The most appropriate regression equation is that possessing a relatively high R^2 and minimum SE.

RESULT AND DISCUSSION

Table 1 represents the chemical constituents of the kraft soft wood pulp and Table 2 shows the chemical and physical analysis of handsheets made from it. Table 3 shows the percentage composition of the sizing used on the papers under experimentation.

Effect of ageing time on chemical composition of the aged sheets

Cellulose fractions

For α-cellulose, Fig. 1a shows that thermal ageing decreases the percentage content of unsized and sized paper sheets. The extent of the decrease in case of rosin and/or alum sized paper sheets (samples 2 and 3) is higher than with the unsized ones; while minimizing the amount of alum and adding sodium silicate during sized paper preparation (sample 4 and 5) reduce this decreasing effect in α-cellulose.

For β-cellulose, the degradation of cellulose as a result of thermal ageing was reflected in an increase of its percentage. This value gradually increased with increasing the period of thermal heating from 3 to 12 days (Fig. 1b). While, for the variation of the γ-cellulose (the most degraded cellulose fraction) as a function of ageing time (Fig. 1c), it can be seen that γ-cellulose content was increased first till ageing time about 6 days and then decreased at 12 days, but this value is still higher than the γ-cellulose of unaged paper.

As can be clear from Fig. 1b and 1c, as the case of α-cellulose, the addition of sodium silicate reduces the bad effect, i.e. the increase of the percents of β- and γ-celluloses as a result of alum-rosin addition.

The above results are attributed to the speculation that, during thermal ageing, the hemicellulose containing paper is oxidized to produce additional carboxylic acid groups[33], in addition to release free acid as a result of thermal decomposition of aluminium sulfate in sized paper[26]. Both produce a high acidity in the paper, and consequently increase the degradation of cellulose long chains, via cleavage at the glucosidic linkage between the C_1 and oxygen[10].

Table 1: Chemical analysis of bleached kraft soft wood pulp (%)

α-cellulose	Pentosans	Lignin	Ash
87.2	6.90	traces	0.16

Table 2: Properties of the produced paper sheets (%)

α-cellulose	84.50	Brightness	89.00
β-cellulose	6.89	Whiteness	88.40
γ-cellulose	4.10	Opacity	67.50
Carbonyl content (mM /100g sample)	13.60	Number of double folds	250
DP	862.67	Tear factor	128.30
Alkali solubility	6.28	Burst factor	84.50
		Breaking length (m)	4467

Table 3: Kinds of examined papers

Sample No.	Sizing Agent (% based on the weight of dry pulp)			pH of sizing system
	Rosin	Alum	Sodium silicate	
1	-	-	-	-
2	-	5.6	-	3.65
3	2.74	5.6	-	4.80
4	2.74	1.84	-	6.75
5	2.74	1.84	0.6	7.0

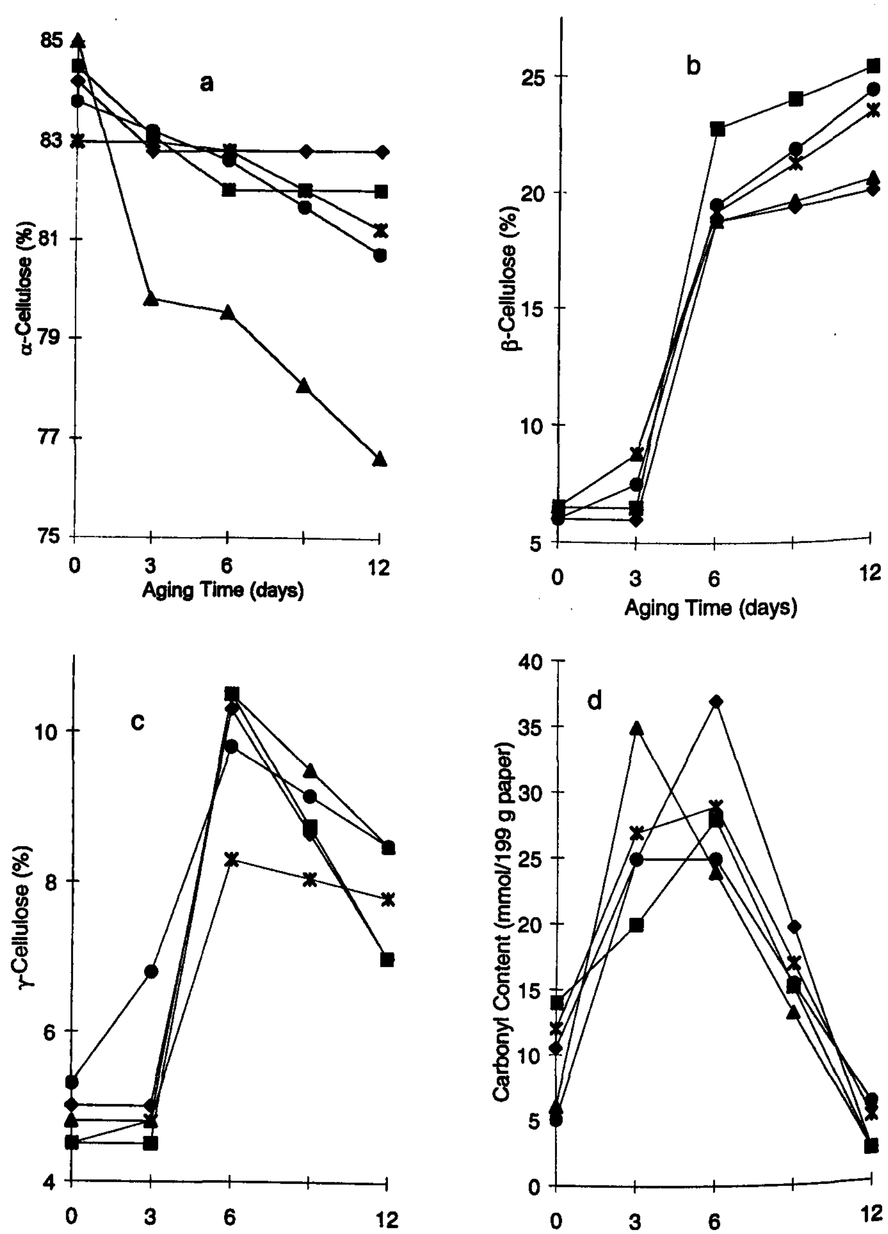

Fig. 1: Effect of aging time on chemical composition of unsized and sized paper sheets

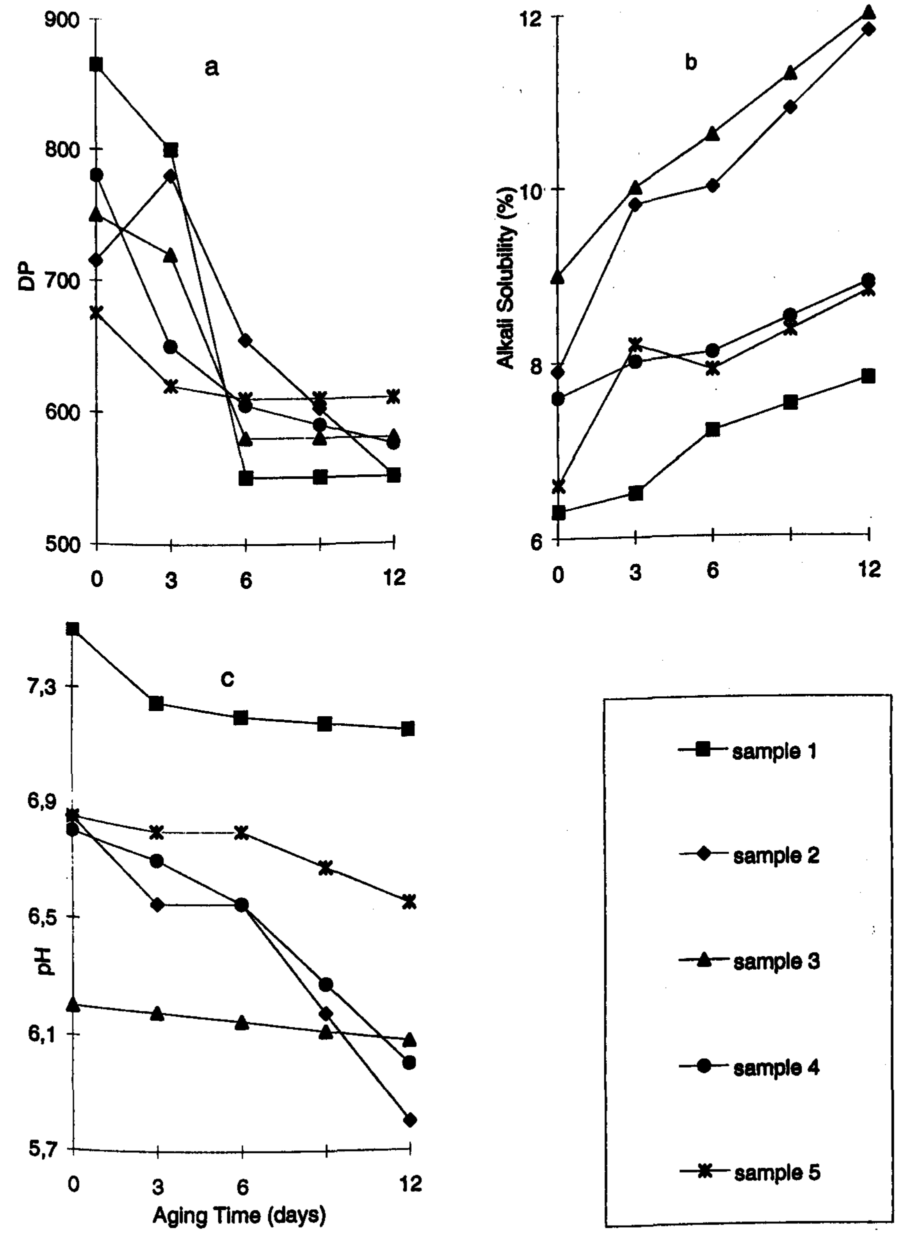

Fig. 2: Effect of aging time on DP, alkali solubility and pH (cold aqueous extract) of unsized and sized paper sheets

Carbonyl content

From Fig. 1d it is clear that the formation of carbonyl content during thermal ageing increased with increasing ageing time up to 6 days. Prolonging the thermal ageing to 12 days led to a decrease in carbonyl content: most probably due to the crosslinking of the radicals or carbonyl groups, created from thermal oxidation of hydroxyl groups (present in cellulose and hemicelluloses of wood pulp), with a neighbouring carbohydrate chain, to form hemiacetal bonds[26] as the next reaction step. This reaction (crosslinking) involves dehydration and may be catalyzed by a high acidity in the cellulosic material. This supposition may explain the observed decrease in the carbonyl content as a result of crosslinking in case of sized paper samples prepared at pH ~ 7.0 (samples 4 and 5), which is mostly lower than that observed in other paper samples (samples 1– 3).

Summing up the above results, the thermal ageing has a profound degradation effect on hemicellulose and acidic preparation of sized-paper sheets. To identify the effect of sizing agent at different pH's on the extent of cellulose degradation the rates of glycosidic bond breakage from the values of degree of polymerization (DP), alkali solubility and the hydrogen-ion-concentration of the aqueous extract of the pre-aged paper samples as a function of ageing time must be examined.

Degree of polymerization

From Fig. 2a it is obvious that, for the case of unsized and sized paper sheets, except the case of using alum alone as sizing agent (sample 2), the chain depolymerization initially proceeds quickly and after a certain time it slows down (at 6–12 days); for the case of sample 2 the chain breakage (depolymerization) increased gradually with increasing the ageing time from 3 to 12 days. This thermal decomposition of paper is attributed to the oxidation which causes a decrease in viscosity, whereas the viscosity of cellulose solution is related to the length of cellulose chains[27].

In case of studying the kinetic reaction rate of chain scission, the depolymerization of cellulose during ageing can be considered as a first order reaction, and this represented by the following equation :

$$kt = \ln(1-\frac{1}{DP_t}) - \ln(1-\frac{1}{DP_0}) \qquad \text{(I)}$$

where k is the rate constant for glycosidic bond breaking (days^{-1}), DP_0 and DP_t are the average degree of polymerization initially and after time t.

In the early stage of hydrolysis when DP_0 and DP_t are large, the equation (I) becomes

$$kt = \frac{1}{DP_t} - \frac{1}{DP_0} \qquad \text{(II)}$$

i.e., the gradient of the plot of $1/DP_t - 1/DP_0$ against time equal to k represents the rate of bond breakage. This value was calculated by using the least square method to the equation (II). The passage of the produced straight lines nearly to the origin (intercept ~ zero) confirms that the kinetic reaction rate of chain scission is a first order.

The values of the reaction rate constants, the correlation coefficient and the intercept are calculated from applying the least square method that are recorded in Table 4. It is obvious that unsized and acidic preparation of sized paper sheets (pH 3.65- 4.8: samples 1–3) have a higher degradation rate than neutral sized papers (pH 6.8 – 7.0: samples 4 and 5).

Table 4 : The kinetic parameters of glycosidic bond cleavage

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
correlation coefficient of the linear relation	0.87959	0.97977	0.87569	0.90419	0.98413
k x 10^5 (day^{-1})	3.533	5.858	3.546	2.630	1.545
Intercept	0.000067	-0.000025	0.0000236	0.0000922	0.0000084

Alkali solubility

From Fig. 2b it becomes clear that the alkali solubility of all aged paper samples increased gradually with increasing ageing time from 3 to 12 days. The percentage of alkali solubility as a function of ageing time in the case of sized papers, especially acidic preparation-sized paper sheets, is higher than with the unsized ones. This may be due to, in addition, the higher rate of glycosidic bond breaking in the case of sized paper than with unsized sheets (Table 4); the alkali extraction led to destroy the weak bonds in the sizing of cellulose fibers, and the precipitated rosin acid is converted to soluble sodium rosinate.

Hydrogen-ion-concentration (pH-value)

The pH of the cold aqueous extracts of paper hand-sheets, made from unsized and sized wood pulp, as a function of ageing time are illustrated in Fig. 2c. It is

The polynominal correlation which describes the dependence of the mean of total changes in the optical properties of the tested paper samples (Y) on the independent variables (time of ageing, X_1, and pH's of preparation system, X_2), is proposed as follows:

$$Y = 9.38 - 3.42X_1 - 1.508X_2 + 0.154X_1^2 + 0.179\,X_2^2 + 2.43\,X_1X_2$$
$$(R^2 = 0.99999 \text{ and } SE = 2.27 \times 10^{-3})$$

Mechanical properties

In the definition of permanence as mentioned before, it is important to specify the end-use requirements for the paper. For most end use applications, in addition to optical permanence, the retention of strength properties, i.e. "mechanical permanence", is of importance since book pages have to remain intact during handling. In this work, the mechanical permanence has been studied by measuring the change in number of double fold, tear, burst and breaking length as a function of thermal ageing time at 100°C. The results are given in Fig. 4a to 4d.

From Fig. 4a it can be seen that for unsized and sized papers the number of double-folds decrease with increased of ageing time. The loss of double folds, i.e. embrittlement, during thermal ageing is due to a decrease in fiber strength as a result of cellulose depolymerization by acid-catalyzed hydrolysis[28]. This view is emphasized from the results in Fig. 2.

Decreasing the acidity of the papermaking process from pH 4.8 (sample 3) to pH 6.75 (sample 4) or to pH 7.0 (sample 5), both resulted in an increase of double folds, i.e. in improved mechanical permanences of thermal aged papers[2]. From Fig. 4b and 4c it is clear that the change in the tear and burst factors of sized and unsized paper sheets as a function of ageing time is in similar trend with double folds.

Fig. 4d shows that, as with other strength properties, the increase in ageing time up to 6 days is accompanied by a decrease in breaking length of all examined samples. The only difference was observed at prolonged heating time (12 days); even if the breaking length of tested sheets began to increase, its value remains low compared to that of unaged paper. This unexpected result may be attributed to the following reasons

- Thermal auto-crosslinking in cellulose material with the formation of hemi-acetal bonds[26],
- Decrease of sizing efficiency as result of prolonged heating time.

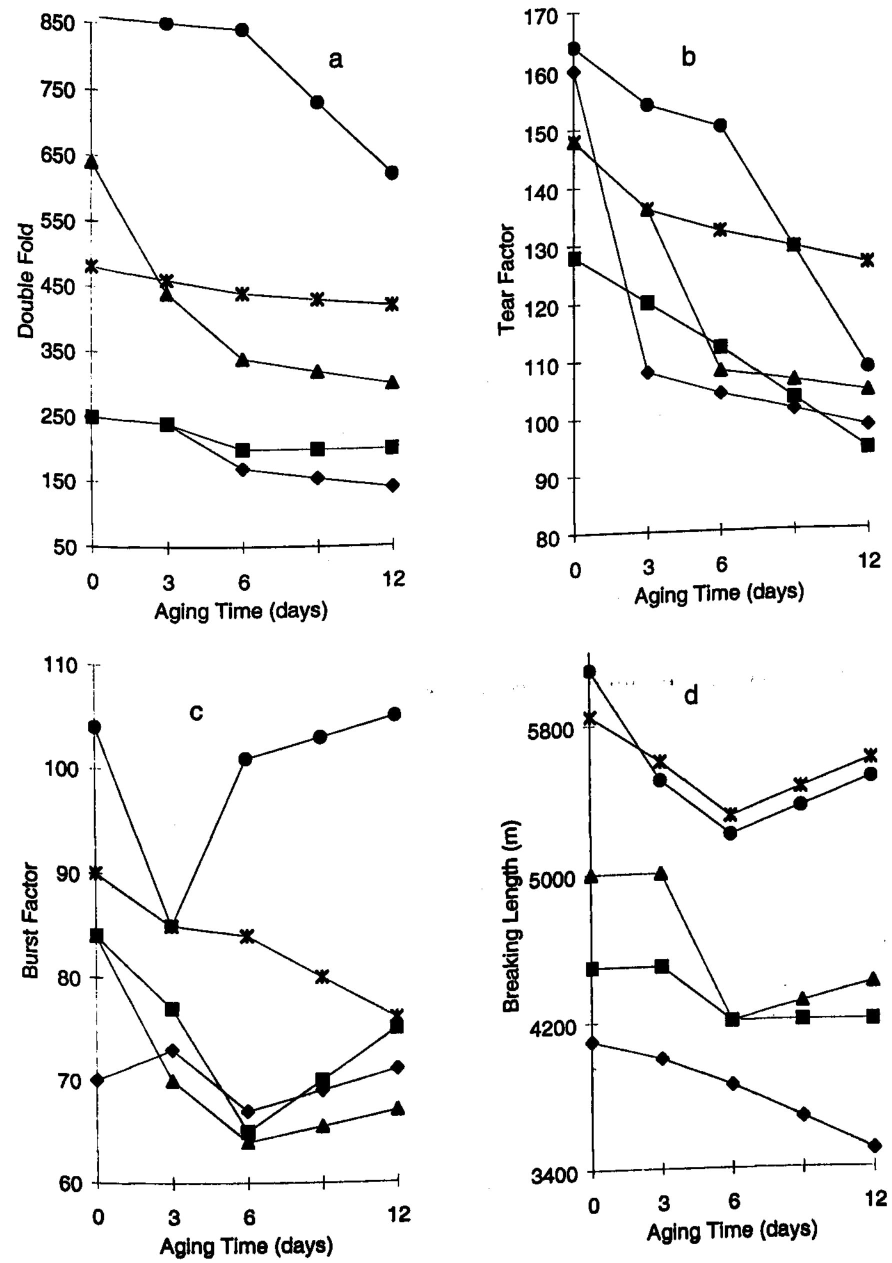

Fig. 4: Effect of aging time on mechanical properties of unsized and sized paper sheets.

clear that the pH-value of most tested papers, especially alum-rosin sized paper sheets, decreased during thermal ageing. This observation emphasizes the opinion that water-extractable low polymeric carbohydrate containing acidic groups are formed upon heat treatment of the cellulosic material.

Fig. 2c also shows that the addition of sodium silicate with alum-rosin sizing agent minimizes the decrease in the pH-value, compared with unaged ones. These results may be related to the fact that addition of sodium silicate leads to decrease the extent of rosin acid and aluminium rosinate formation, whereas the reaction of the rosin to form aluminium rosinate or rosin acid is governed by the total acidity of the papermaking system and by the amount and availability of aluminium ions. In other word, the addition of sodium silicate reduces the amount of rosin acid or aluminium rosinate in pulp fibers, and consequently decreased the release of free acid during ageing.

Optical properties

Fig. 3a shows that the brightness of different tested paper sheets decreased with increasing the time of thermal ageing. This yellowing tendency could be explained as result of some physical changes and also of chemical degradation taking place in the paper sheets. The functional groups of the aged papers affect yellowing; there is an exponential relation between the reducing carbonyl groups of cellulose and the post colour-number.

Fig. 3a also shows that the brightness of paper containing only alum (sample 2) is relatively lower compared with rosin-added systems (sample 3). This protective effect of rosin is attributed to the ability of rosin to react with alum to form aluminium rosinate, thus reducing the amount of unreacted alum and the acidity of the dry sheets. Due to the same reason, decreasing the amount of added alum from 5.6% (sample 3) to 1.84% (sample 4), with the same amount of rosin (2.74%), and the addition of 0.6% sodium silicate to this system (sample 5), both improved the brightness property.

Fig. 3b illustrates that the whiteness decreased considerably during thermal ageing. The addition of rosin with alum, minimizing the amount of alum added, or the addition of sodium silicate (sample5) decreases the deleterious effect of alum.

For the case of opacity measurements, Fig. 3c shows that the opacity changes with changing pH and changing time of ageing. The alum-added paper sheets have a relatively high opacity compared with other examined samples. This is attributed to the action of alum in settling the fine fraction down, thus a tighter (less porous) sheets are obtained.

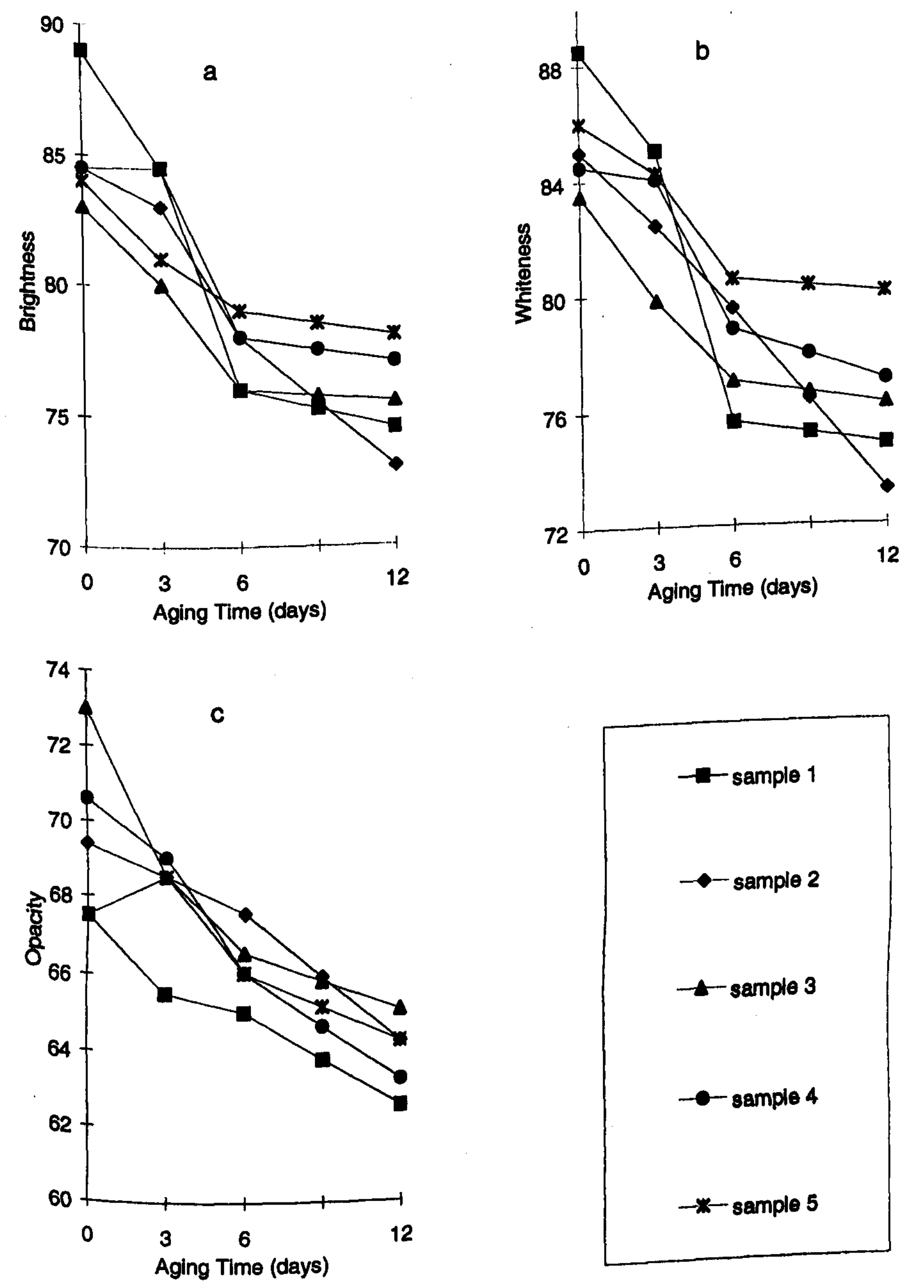

Fig. 3: Effect of aging time on optical properties of unsized and sized paper sheets

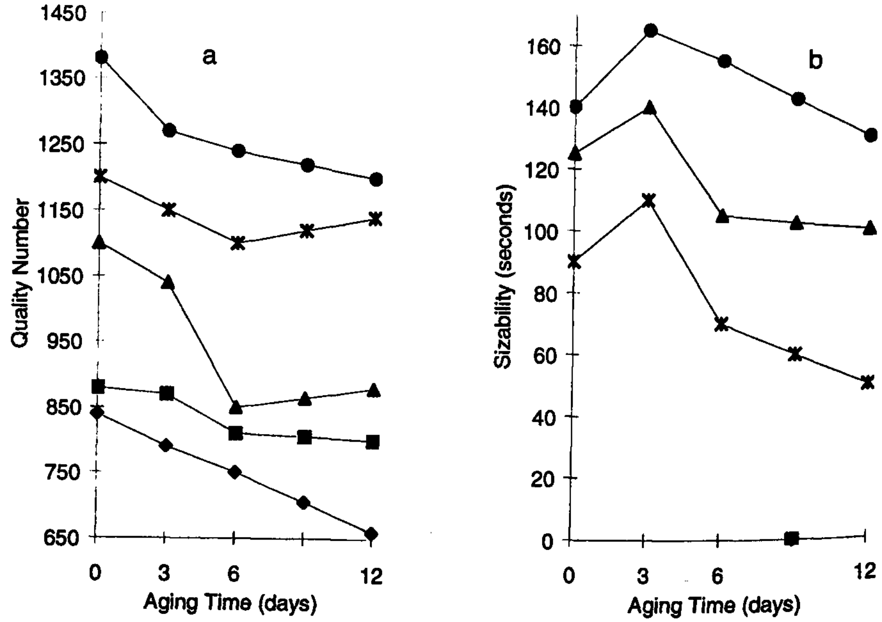

Fig. 5: Effect of aging time on quality number of mechanical properties and degree of sizing of unsized and sized paper sheets.

These reasons are emphasized in the decrease of carbonyl content (Fig. 1d) and sizability (water resistance: Fig. 5b) of paper aged for 12 days compared to the values for 6 days.

The polynominal regression correlating the time of ageing (X_1) and pH's of sizing system (X_2) with the quality number of the mechanical measurements (Y) is represented as follows:

$$Y = 716.547 - 79.435X_1 + 30.840X_2 + 4.645\,X_1^2 + 14.693\,X_2^2 - 1.726\,X_1X_2$$
$$(R^2 = 0.99999 \text{ and } SE = 0.46503)$$

From all the above results it can be concluded that paper sheets made from low level alum/rosin-sized wood pulp or sodium silicate-rosin/alum-sized wood pulp both resist the artificial ageing, i.e. relatively high optical and mechanical permanences are retained, compared with sheets prepared from conventional rosin and/or alum-sized pulp. The polynominal models are demonstrating the importance of ageing time on the optical and mechanical permanence rather than variable pH, and the mechanical properties of examined samples are more affected than optical properties.

SUMMARIES

Permanence of Paper 1. Problems and Permanency of Alum-Rosin Sized Paper Sheets from Wood Pulp

Dry thermal ageing in the presence of air were applied to different alum-rosin sized wood pulp paper sheets. The change in the percentage of alum or adding sodium silicate in the sizing systems was carried out to vary the pH of the sample sheets in the range from 3.65 to 7.0. The changes in chemical composition, mechanical and optical properties, degree of sizing, in addition to the rate of glycosidic bond cleavage as a result of thermal ageing were measured. The results obtained show that neutral sized paper sheets have a higher optical and mechanical permanence compared with acidic sized papers.

The polynominal models which correlate the time of ageing and pH's of sizing system with the mean values of optical changes or quality number of mechanical measurements were also proposed.

Durabilité du papier 1. Problèmes et durabilité des feuilles de papier à base de pâte mécanique collées avec de la résine d'alun.

Différentes sortes de papier à base de pâte mécanique collées avec de la résine d'alun ont été soumises à un vieillissement thermique accéléré avec de l'air chaud. La variation des pourcentages d'alun ou l'addition de silicate de sodium dans le système de collage ont conduit à des variations de valeur du pH allant de 3,65 à 7. On a mesuré les variations de la composition chimique, des résultats mécaniques et optiques, du degré du collage et de l'étendue de la dissociation chimique des liaisons glucosidiques comme conséquence du vieillissement. Les résultats mettent en évidence que le papier traité de façon alcaline pour le collage présente des qualités optiques et mécaniques de durabilité supérieures à celui qui a subi un traitement acide.

Par ailleurs on présente des modèles polynomes qui établissent une corrélation entre la durée du vieillissement et le pH du système de collage avec les valeurs moyennes des variations optiques et des caractéristiques mécaniques.

Dauerhaftigkeit von Papier 1. Probleme und Dauerhaftigkeit von Blättern aus Holzstoff, die mit alaungefälltem Harz geleimt sind

Verschiedene mit alaungefälltem Harz geleimte Holzstoffpapiere wurden thermisch bei Umluft gealtert. Durch den Zusatz von Alaun in verschiedenen Prozentsätzen oder von Natriumsilikat zum Leimungssystem führte zu pH-Werten zwischen 3,65 und 7. Es wurden die Veränderungen der chemischen Zusammensetzung, der mechanischen, der optischen Werte, des Leimungsgrad und des Ausmaßes der Spaltung von glykosidischen Bindungen als Folge der Alterung gemessen. Die Ergebnisse zeigen, daß neutralgeleimtes Papier im Vergleich zu saurem eine bessere optische und mechanische Dauerhaftigkeit aufweist.

Es werden zudem polynomen Modelle vorgestellt, welche die Alterungsdauer und das pH des Leimungssystems in Korrelation zu den Mittelwerten der optischen Veränderungen und den mechanischen Kennzahlen setzen.

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