Effects of freeze drying on paper

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Abstract

Freeze drying is a practical and widely used method for drying water damaged paper [1]. The purpose of this investigation is to determine if mechanical strength and ageing stability is affected by freeze drying.

The investigation comprises three types of paper (groundwood paper, cotton paper, and coated paper) which have been freeze dried, air dried, and exposed to accelerated ageing. The effects of freeze drying on paper have been evaluated by the following indicators: moisture content, alkali reserve, folding endurance, tearing resistance, and zero span tensile strength.

The results indicate that freeze drying primarily influences paper characteristica such as moisture content, folding endurance, and tearing resistance. Freeze drying particularly influences mechanical strength of paper with low initial strength, whereas the influence by freeze drying on paper with high mechanical strength is relatively small.

The results also indicate that freeze drying in general influences the mechanical strength and ageing stability more than air drying. However the results of the investigation do not indicate that mechanical strength and ageing stability is influenced to such a degree that freeze drying in general should be characterized as unsuitable for drying paper when dealing with water damaged archival- and library materials.

Zusammenfassung

Gefriertrocknen ist eine praktische und weitverbreitete Methode, um wassergeschädigtes Papier zu trocknen. Diese Untersuchung will bestimmen, ob die mechanische Stärke und die Alterungsbeständigkeit durch Gefriertrocknung beeinträchtigt werden.

Die Untersuchung umfasst drei Arten von Papier (Holzschliffpapier, Baumwollpapier und gestrichenes Papier) die gefriergetrocknet, luftgetrocknet und beschleunigter Alterung ausgesetzt wurden. Der Einfluß von Gefriertrocknung auf Papier wurde anhand von folgenden Indikatoren bewertet: Feuchtigkeitsgehalt, alkalischer Puffer, Falzzahl, Reißfestigkeit und (zero span) Zugfestigkeit.

Die Ergebnisse zeigen, daß Gefriertrocknung in erster Linie Papiereigenschaften wie Feuchtigkeitsgehalt, Falzzahl und Reißfestigkeit beeinflußt. Besonders die mechanische Stärke von Papieren mit anfänglich geringer Stärke wird durch Gefriertrocknen beeinflußt, Papiere mit anfänglich großer mechanischer Stärke werden dagegen nur geringfügig beeinflußt.

Außerdem zeigen die Ergebnisse, daß Gefriertrocknung im allgemeinen die mechanische Stärke und die Alterungsbeständigkeit stärker beeinflußt als Lufttrocknung. Jedoch wird durch die Untersuchungsergebnisse nicht belegt, daß Gefriertrocknung die mechanische Stärke und die Alterungsbeständigkeit in einem Ausmaß beeinträchtigt, welches diese Methode allgemein als unbrauchbar für die Trocknung von wassergeschädigten Archivalien und Bibliotheksgut gelten lassen könnte.

Introduction

The technique of freeze drying which is based on the principle of sublimation - i.e. transformation of ice to vapour - has turned out to be a stable and effective method for drying water damaged archive and library materials [2].

Freeze drying uses the fact that a substance (water) can evaporate directly from the solid state (ice) without passing through a liquid state. In freeze drying water is converted to ice by freezing, subsequently ice is converted directly to vapour. This type of evaporation, characteristic of freeze drying, is called sublimation. The most commonly used method of removing water vapour when freeze drying is by condensation. Condensation is based on the principle of water vapour always moving from a warmer to a colder area.

Freeze drying systems consist in principle of a refrigerated condenser with a low vapour pressure and a freeze drying chamber with a higher vapour pressure. Water vapour is removed from the material by leading it from the freeze drying chamber to the condenser. Here the vapour condenses because of the lower pressure and as water it is no longer part of the process. The difference in vapour pressure, i. e. the driving force of the process, is created by the difference of temperature in the two chambers.

Sublimation of ice can take place at atmospheric pressure and under vacuum. During vacuum freeze drying atmospheric air is removed at the beginning of the sublimation process. Controlling the process in vacuum freeze drying systems usually takes place by regulating the relation between the temperature in the freeze drying chamber and in the condenser and also by adjusting the pressure. Vacuum freeze drying systems are usually equipped with controls which make it possible to adjust the relation between temperature and pressure, thus sustaining optimal power in the chamber [3].

Materials used

Three types of material have been used in this study: groundwood paper, cotton paper, and coated paper. All three types of paper are widely represented in archives and libraries.

Paper 1	Fibre composition	75 % groundwood and 25 % softwood cellulose
	Filler	22 % kaolin clay
	Sizing	Alum rosin and casein
	pH extract	5,9
	Ash content, %	20
	Grammage, g/m2	80
	Producer	Unknown. Supplied by STFI
Paper 2	Fibre composition	100 % cotton
	Fillers	2-4 % calcium carbonate and 0,5-1 % titandioxide
	Sizing	Alkyl ketene dimer and polyvinyl alcohol
	pH extract	9,9
	Ash content, %	2,45
	Grammage, g/m2	80
	Producer	Tumba AB. Supplied by STFI
Paper 3	Fibre composition	100 % chemical cellulose
	Filler (base)	Calcium carbonate
	Sizing (base)	Alkyl ketene dimers
	Sizing (coating)	Styrene butadiene latex and carboxy methylcellulose
	Pigment (coating)	Kaolin clay
	pH extract	-
	Ash content, %	32
	Grammage, g/m2	80
	Producer	Grycksbo. Supplied by Grycksbo

The composition of the samples is listed in Table 1 (1).

Experimental

The samples have been divided into three groups according to basic compounds: groundwood, cotton, and coated paper, they have been dried by vacuum freeze drying (by warm and by cold chamber wall respectively) (2) and they have been air dried. Part of the dried material and also some untreated material has subsequently been subjected to accelerated ageing. (Figure 1)

The experimental treatment has been evaluated by reference, untreated material after accelerated ageing, freeze dried (by cold as well as by warm chamber wall) material before and after accelerated ageing, air dried material before and after accelerated ageing.

Test methods

Evaluation of the experimental treatment is based on the following:
· moisture content
· alkali reserve
· folding endurance
· tearing resistance
· zero span tensile strength (dry and wet determination)

All these tests are related to paper characteristics which are critical to the preservation of archive and library materials. The tests are determined according to relevant standards. [4, 5, 6, & 7]

The results of folding endurance are noted as the logarithm (to the base of 10) of the number of double folds, tearing resistance and zero span tensile strength is noted as tear index (nMm2/g) and zero span tensile strength index (Nm/g) respectively. The results of folding endurance, tear strength, and zero span tensile strength are noted as geometric mean (GM) based on machine direction (MD) and cross machine direction (CD) by using the following formula: *Geometric mean* $= \sqrt{\text{MD X CD}}$[8]

Accelerated ageing

Evaluating the effect of the experimental treatment on the ageing stability of the samples has been done by using thermal ageing on freely hanging sheets for 12 days at 90 °C and 50% RH. Accelerated ageing has been carried out according to the ISO 5630 Standard [9] with the modification of 90 °C/50% RH/12 days as these conditions produce a maximum effect within a limited time span [10]. The accelerated ageing has been conducted in separate runs to avoid interaction between the groups of different paper qualities.

Treatment of samples

Before freeze drying the samples were soaked in demineralized water in 90 ± 10 minutes and frozen individually in ziploc polyethylene bags at app. - 38 °C. The samples to be used for freeze drying by cold chamber wall were frozen in bags with 50 ± 10 ml of demineralized water and samples for freeze drying by warm chamber wall were frozen in bags with 400 ± 50 ml of demineralized water.

Cold chamber wall freeze drying took place in a system consisting of a drying chamber, two refrigerated condensers, a vacuum pump, and automatics for controlling temperature. Also an oasis with thermometers for measuring the relative humidity was placed in the drying chamber. The samples were taken out of the bags and placed individually on a perforated steel tray. The average RH at the end of the drying process was 30,4 %.

Freeze drying by warm chamber wall took place in a vacuum tank to which the following were connected: a vacuum pump, a vacuum gauge, and two electric thermometers for the registration of relative humidity. The samples were taken out of the bags and

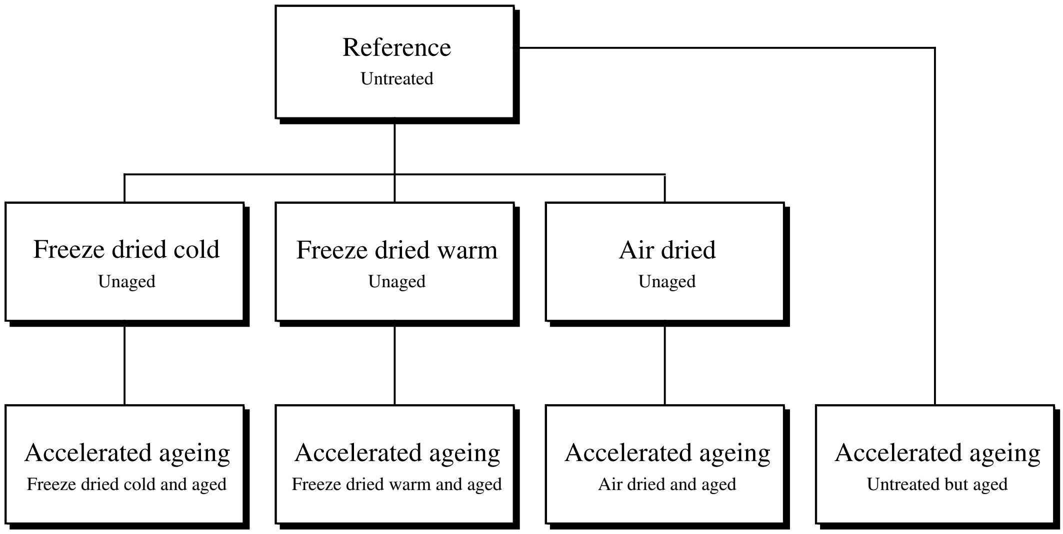

Figure 1: Experimental set-up

placed individually on a steel tray. The average RH at the end of the drying process was 4,8 %.

Before air drying the samples were soaked in demineralized water in 90 ± 10 minutes. Drying took place in a sealed room at 14 - 18 °C. The samples were placed individually on a drying rack. The average RH was 27 % at the end of the drying process.

Results and discussion

Generally the results of the study indicate that freeze drying particularly influences moisture content, folding endurance, and tearing resistance. The results also indicate that freeze drying and accelerated ageing influences the various samples differently regarding moisture content, folding endurance, and tearing resistance. The influence of the experimental treatment on alkali reserve and zero span tensile strength is relatively insignificant. Some of the results of the study are presented as follows. The accuracy of the results is given as 95 % confidence limits.

Groundwood paper

The experiments show that freeze drying alum rosin-sized groundwood paper with a high level of fillers and low mechanical strength (represented by Paper 1) particularly reduces the folding endurance (Figure 2). The results also show that the folding endurance after accelerated ageing is reduced significantly when freeze dried by warm chamber wall and when air dried.

The reduction of folding endurance and zero span tensile strength, dry determination (Figure 3), indicates a possible acid-catalyzed hydrolysis of cellulose (a reduction of the degree of polymerisation of cellulose) caused by alum.

The study also indicates that tearing resistance (Figure 4) is generally increased by freeze drying and by air drying. The increase of tearing resistance presumably indicates that the fibre-fibre bonds in the sample are strengthened as a result of the aqueous treatment. Regarding moisture content (Figure 5) the experiments show an increase and this increase is significant after accelerated ageing. The changes in moisture content are generally assumed to influence the mechanical strength of the samples. But it is not possible in this study to show any relation between changes in moisture content and changes in folding endurance, tearing resistance, and zero span tensile strength.

Cotton paper

Paper 2 of this study is neutrally sized cotton paper with a high calcium carbonate content, and with good mechanical strength. Experiments on this paper show relatively limited effects regarding folding endurance (Figure 6) and zero span tensile strength (Figures 7 & 8) when freeze dried, air dried, and subjected to accelerated ageing.

Other results of the study show that the tearing resistance (Figure 9) is increased by freeze drying and by air drying. The largest increase of tearing resistance occurs after freeze drying and the tendency is most significant after accelerated ageing. This increase presumably indicates that the fibre-fibre bonds in the samples are strengthened as a result of the aqueous treatment.

The increase of tearing resistance after accelerated ageing might in part be due to the aqueous treatment in part to crosslinking in cellulose fibres and sizing (alkyl ketene dimer and polyvinyl alcohol) caused by the accelerated ageing process.

Coated paper

Paper made from chemical pulp coated with calcium carbonate (Paper 3) shows indications of reduced folding endurance (Figure 10) when freeze dried and air dried. The reduction is particularly pronounced after freeze drying by cold chamber wall and accelerated ageing.

This study also reveals that tearing resistance (Figure 11) is increased by freeze drying, air drying, and accelerated ageing. It is worth noticing that tearing resistance is increased in untreated

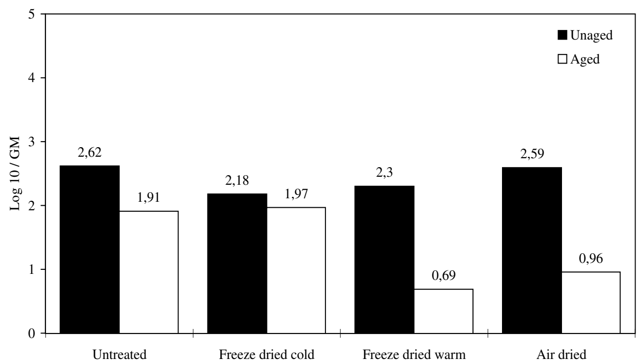

Figure 2: Paper 1. Folding endurance. Before and after accelerated ageing.

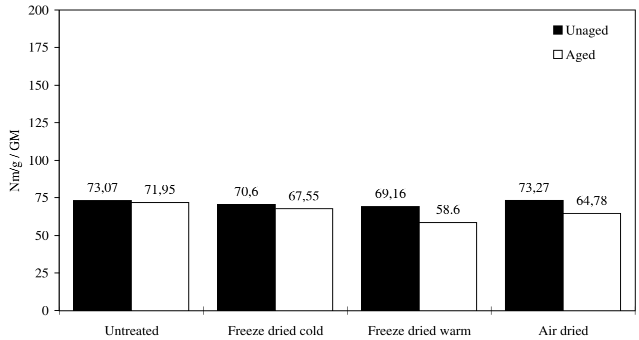

Figure 3: Paper 1. Zero span tensile strength, dry determination. Before and after accelerated ageing.

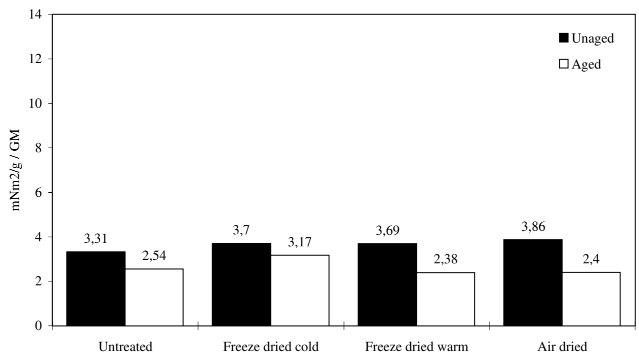

Figure 4: Paper 1. Tearing resistance. Before and after accelerated ageing.

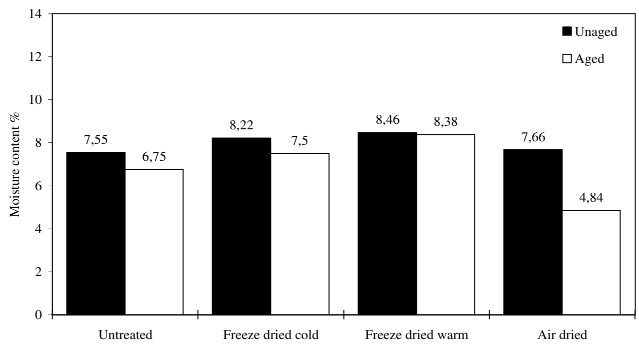

Figure 5: Paper 1. Moisture content. Before and after accelerated ageing.

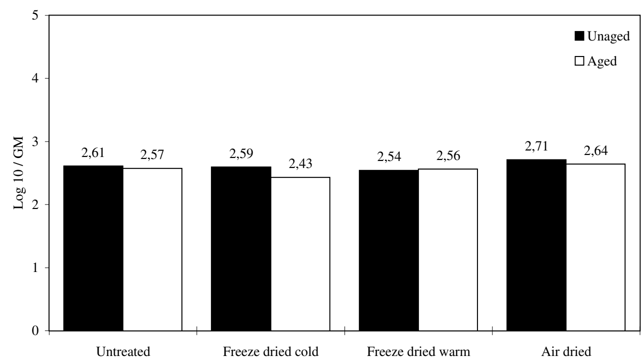

Figure 6: Paper 2. Folding endurance. Before and after accelerated ageing.

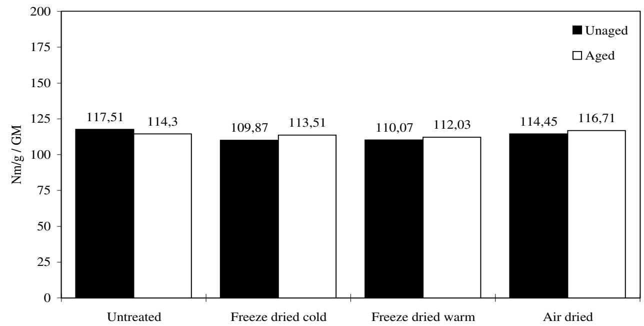

Figure 7: Paper 2. Zero span tensile strength, dry determination. Before and after accelerated ageing.

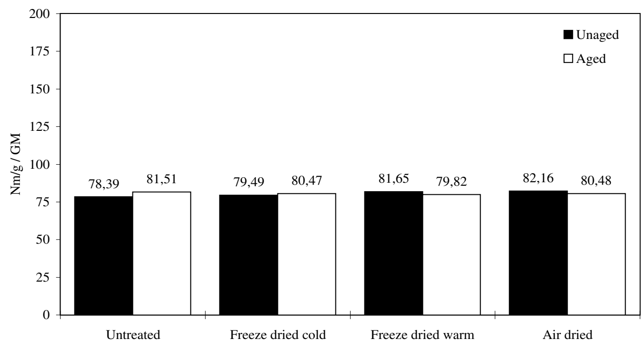

Figure 8: Paper 2. Zero span tensile strength, wet determination. Before and after accelerated ageing.

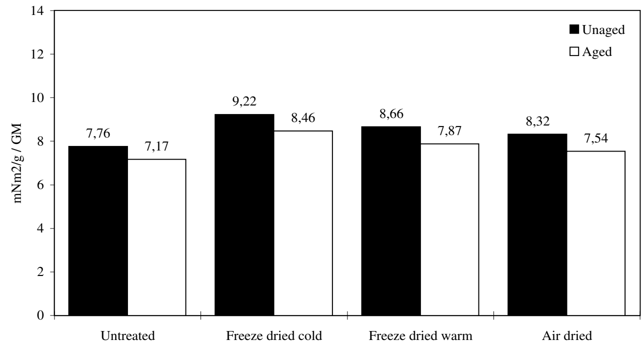

Figure 9: Paper 2. Tearing resistance. Before and after accelerated ageing.

material after accelerated ageing. This increase after accelerated ageing might suggest that fibre bonding strength in the samples is increased not only as a result of crosslinking in cellulose fibres [11] and in sizing substances in the coating (styrene butadiene latex) and the base (alkyl ketene dimers) respectively - but it is also increased as the result of a softening of the size in the coating.

Presumably the presence of especially butadiene in the test material might be a cause of crosslinking in the coating. Increase of tearing resistance in untreated material after accelerated ageing could indicate that thermal ageing is not suitable for evaluating the ageing

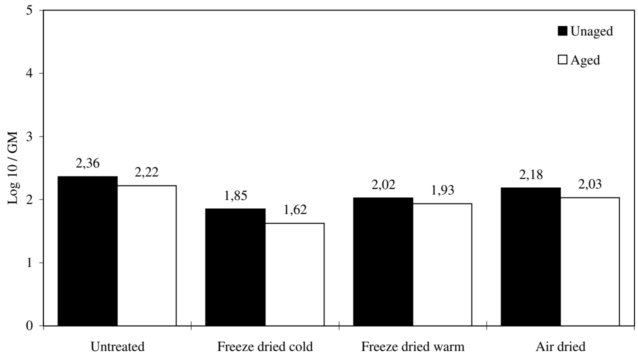

Figure 10: Paper 3. Folding endurance. Before and after accelerated ageing.

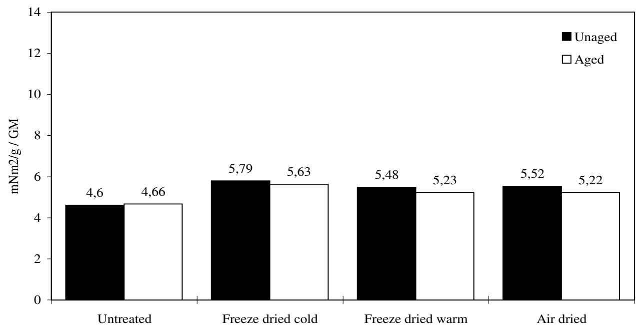

Figure 11: Paper 3. Tearing resistance. Before and after accelerated ageing.

stability of coated paper, as an increase in temperature might influence the size in the coating thus causing thermal ageing to deviate significantly from the process of natural ageing [12].

Retention of mechanical strength

An evaluation based on retention (3) (Table 2) shows that freeze drying particularly reduces the folding endurance. This is most significant in Paper 1 & Paper 3, whereas freeze drying has a relatively insignificant effect on folding endurance in Paper 2.

When looking at the retention of mechanical strength it also becomes clear that the ageing stability of Paper 1 and partly of Paper 3 is reduced more by freeze drying than by air drying whereas the ageing stability of Paper 2 is only insignificantly effected by freeze drying as well as by air drying. The retention does not indicate that freeze drying by cold chamber wall reduces the mechanical strength more than freeze drying by warm chamber wall and vice versa. The retention of mechanical strength does indicate however that freeze drying in general reduces mechanical strength more than air drying. Also retention of moisture content shows that freeze drying by warm chamber wall does not lead to over drying (based on a low RH in the drying chamber of app. 5 % at the end of the process).

An evaluation of the results of this study might be conducted on the basis of different criteria as a standardized method for evaluating freeze dried paper does not exist. One criterion might be to relate the results of the study to ISO 9706. [13] To relate the process of freeze drying paper to a paper standard aimed at defining minimum specifications of initial strength might seem arbitrary, but if the test material after freeze drying and accelerated ageing is compatible to the specifications of initial strength and thus ageing stability, then it is also fair to assume that freeze drying does not affect the tested qualities of paper in any critical way.

ISO 9706 defines minimum specifications for paper permanence in terms of pH, tearing resistance, alkali reserve, and lignin content. ISO 9706 also states that tests for mechanical strength have shown that if a paper matches the required minimum specifications the retention of tearing resistance after accelerated ageing according to ISO 5630-3 [14] will be a minimum of 80 % (in both paper directions) compared to its initial strength.

When evaluating the results of the experimental treatment based on folding endurance, tearing resistance, and zero span tensile strength, including the fact that retention after accelerated ageing ought to be a minimum of 80 % of the initial strength (Figures 12 & 13), then Paper 1 shows that retention of at least one of the tested characteristics after freeze drying, air drying, and accelerated ageing falls under this limit of 80 %. Paper 3 shows that the retention of folding endurance after freeze drying by cold chamber wall and accelerated ageing is less than 80 % of the initial strength.

Paper 2 shows that the ageing stability is affected only insignificantly by freeze drying and air drying. In this paper the retention of folding endurance, tearing resistance, and zero span tensile strength after freeze drying, air drying, and accelerated ageing is minimum 80 % of the initial strength.

To summize: mechanical strength and ageing stability of different paper qualities is affected differently by freeze drying, and folding endurance and ageing stability of particularly groundwood paper and coated paper may be affected critically by freeze drying. The study does not show which of the two freeze drying methods has the most pronounced effect on mechanical strength or ageing stability although it seems as if the tested paper remains more flat after freeze drying than after conventional drying.

When assessing the results of the study and also freeze drying as a method for conservation each individual situation and existing alternatives must be taken into consideration. When dealing with water damaged paper the study shows that freeze drying is particularly suitable for drying cotton paper and paper with high initial strength, as mechanical strength and ageing stability is affected insignificantly compared to conventional drying. If microbiological infection, ink, and colour etc. do not present a problem the study shows that groundwood paper and paper with a low initial strength as well as coated paper if possible should be dried conventionally as mechanical strength and ageing stability may be affected critically by freeze drying.

Conclusion

The investigation shows that it is possible to determine changes in the mechanical strength of paper as well as in the ageing stability caused by freeze drying, and that mechanical strength and ageing stability is affected differently in different paper qualities.

The study indicates that freeze drying particularly affects mechanical strength and ageing stability in groundwood paper and coated paper whereas the same characteristics are only affected insignificantly in cotton paper. The results particularly reveal that freeze drying reduces the folding endurance of groundwood paper and coated paper, and also that the ageing stability of groundwood and of coated paper is reduced significantly, whereas fibre-fibre bonds are generally strengthened by freeze drying. The strengthening is particularly pronounced in coated paper after accelerated ageing. It is also shown that freeze drying in general has a relatively limited effect on the fibre strength and buffer capacity of the material used. There does not seem to be an indication as to which of the two freeze drying methods effects mechanical strength and ageing stability the most, although it seems as if the tested paper remains more flat after freeze drying by cold chamber wall.

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Notes

(1) Paper 1 and Paper 2 are included as test material in an EU research project, specification on this may be found in Deventer, R. van, Havermans, J. & Kolseth, P., *The Effects of Air Pollutants on the Accelerated Ageing of Cellulose Containing Materials - Paper*, EC/DGXII/STEP Project CT 90-0100, BU3.94/1068/JH, TNO Centre for Paper and Board Research, Delft, 1994, Part 2, pp. 60 & 65.

(2) Freeze drying by cold chamber wall allows adjusting the RH in the drying chamber to 50 % for example. This cor responds to the equilibrium moisture content of paper. When freeze drying by warm chamber wall, the drying process also takes place by sublimation, but it is not possible to adjust the RH in the system. Typically the RH in the system will be 5 % at the end of the drying process.

(3) The retention (%) is calculated by dividing the actual value by the reference value.

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Biography

Søren Carlsen, graduated from The School of Conservation, Copenhagen, as conservation technician (B. Sc) in 1986 and conservator (M. Sc) in 1997.

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