

Technological description of aging resistance of paper and paper-board – comparison between cotton and wood pulps

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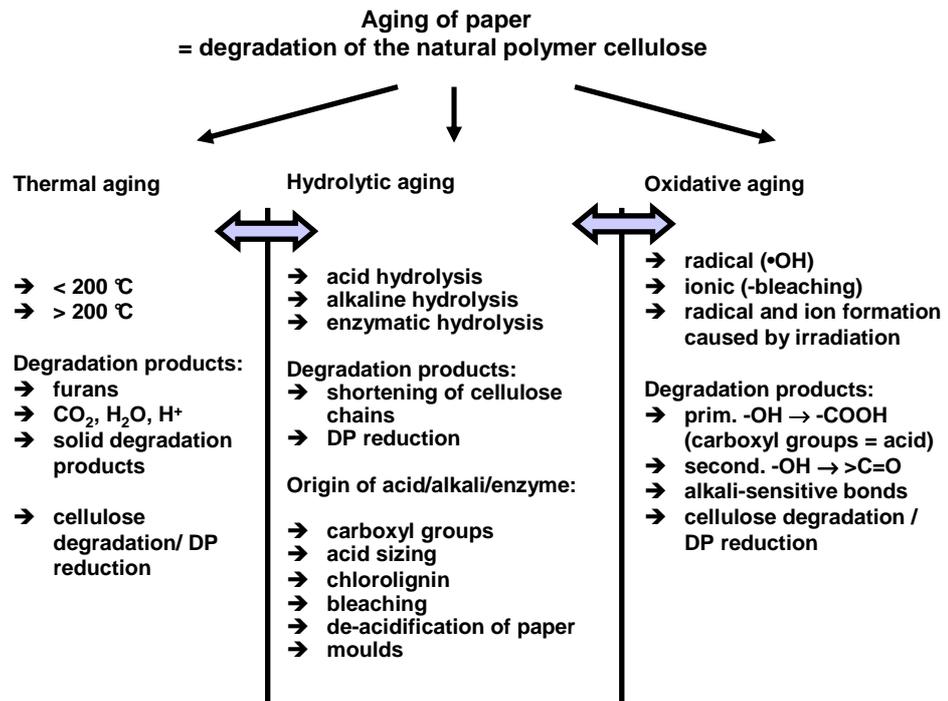
Summary

Objective	Identifying the fundamental differences in aging behaviour between cotton or cotton linters pulps and wood pulps to be expected during long-term archival storage
Procedure	<p>Published results on the aging behaviour of cellulosic pulps are summarised. Model calculations show how the permanence of paper is influenced by different parameters.</p> <p>Cotton or cotton linters pulps are assessed in comparison with highly bleached softwood and hardwood pulps.</p>
Results	<p>The aging process of cellulosic fibres is caused by the splitting of cellulose chains due to thermal (pyrolytic), hydrolytic or oxidative degradation. Molecular chains of cellulose are split and shortened; the degree of polymerisation (DP) is reduced. This affects the strength and, thus, aging resistance of papers produced from cellulose fibres. Depending on its origin and production process, cellulose has initial DP's in the range between 500 and 1200 in bleached pulp. It loses its bonding and strength effects in the paper at approximately 150 DP, causing the paper to fall apart when being touched or used.</p> <p>The rate of these degradation reactions depends mainly on temperature - provided that other detrimental influences are minimized. This makes it necessary to</p> <ul style="list-style-type: none">• reduce the exposure to high-energy light,• prevent infestation by enzyme-producing moulds,• use acid-binding fillers (like CaCO₃ as alkali reserve) in the paper to trap and render harmless any acid compounds formed by thermal or oxidative degradation, and• ensure that paper is produced in a so-called "neutral medium", i.e. without acid paper additives and production aids. <p>If these requirements are met, the aging behaviour is influenced by temperature, the initial DP, the moisture content of paper and pH reached. It must be born in mind, though, that degradation continues in the amorphous regions of cellulosic fibre structures up to the Level of DP (LODP). Cotton or cotton linters pulps have a higher degree of crystallinity than wood pulps, which means they will be degraded less under identical conditions.</p>

Aging processes and lifetime of paper

Aging mechanisms

The diagram below summarises the aging mechanisms of cellulosic fibres. In most cases, several different aging mechanisms are acting in parallel.



The subsequent quantitative analysis of aging mechanisms serves to identify and evaluate all relevant influences. Model calculations are used to highlight differences in aging properties.

Laws and equations – life prediction of paper

The life of paper or paperboard suitable for archival storage can be roughly predicted by means of the following equations and assumptions¹ :

1. Degradation reaction of cellulose chains due to aging processes: marked by the decrease in DP (Degree of Polymerization, DP of cellulose). The equation describes the decrease in initial DP₀ of the initial cellulose

$$\frac{1}{DP_t} - \frac{1}{DP_0} = k \cdot t$$

where

¹ X. ZOU, T. UESAKA and N. GURNAGUL: Prediction of paper permanence by accelerated aging: I: Kinetic analysis of the aging process, II: Comparison of the prediction with natural aging results Cellulose 3, 243 - 267 und 269 - 279 (1996) Nr. 4

DP_0 is the initial DP of the cellulose used (fibrous raw material for papermaking),

DP_t is the DP after the reaction time t (life),

t : is the reaction time (life), and

k : is the temperature-dependent rate constant of cellulose splitting

- Cellulose degradation follows a first-order reaction - the Arrhenius rate equation describing the relationship between the rate constant k and the activation energy, temperature and the chemical conditions summarised by the pre-exponential factor A :

$$k = A_a \cdot e^{-E_a/R \cdot T}$$

where:

k : equilibrium constant of cellulose degradation (published value)

A : pre-exponential factor (value determined by the moisture content and pH of paper)

E_a : activation energy of the degradation reaction (published value)

R : gas constant ($R = 8,314 \text{ J/mol} \cdot \text{K}$)

T : reaction temperature, storage temperature

- Secondary conditions:

Approximate calculation of DP by means of the limiting viscosity number (LVN) measured in the pulp and the pre-exponential factor A_a obtained from published test results. The DP's calculated by the various authors differ significantly. We have used the algorithm published by IMMERGUT et al., which gives a pessimistic forecast.

$$LVN = Q' \cdot DP^\alpha \rightarrow DP = (LVN/Q')^{1/\alpha}$$

according to [MARX and FIGINI 1978 or GRUBER and GRUBER 1981]

where

$$Q' = 0,42 \text{ and } \alpha = 1 \text{ for } DP < 950 \rightarrow DP = LVN/0,42 \text{ or}$$

$$Q' = 2,28 \text{ and } \alpha = 0,76 \text{ for } DP > 950 \rightarrow DP = (LVN/2,28)^{1,316}$$

or

$$DP^{0,85} = 1,1 \cdot LVN \rightarrow DP = (1,1 \cdot LVN)^{1/0,85} = (1,1 \cdot LVN)^{1,176}$$

according to [EVANS and ELLIS 1987]

or

$$DP^\alpha = 0,75 \cdot LVN \rightarrow DP = (0,75 \cdot LVN)^{1/\alpha} \text{ with } \alpha = 0,965$$

[according to IMMERGUT et al., 1953]

Calculation of A_a :

$$A_a = A_{a0} + A_{a2} \cdot c(\text{H}_2\text{O}) + A_{a5} \cdot c(\text{H}_2\text{O}) \cdot c(\text{H}^+)$$

where $c(\text{H}^+) = -\lg(\text{pH})$ of the aqueous extract and $c(\text{H}_2\text{O})$ – equilibrium moisture content of paper and constants for:

$$A_{a0} = 4,54 \cdot 10^9 \text{ 1/d, } A_{a2} = 2,83 \cdot 10^{12} \text{ 1/d and } A_{a5} = 9,85 \cdot 10^{16} \text{ l/(mol} \cdot \text{d)}$$

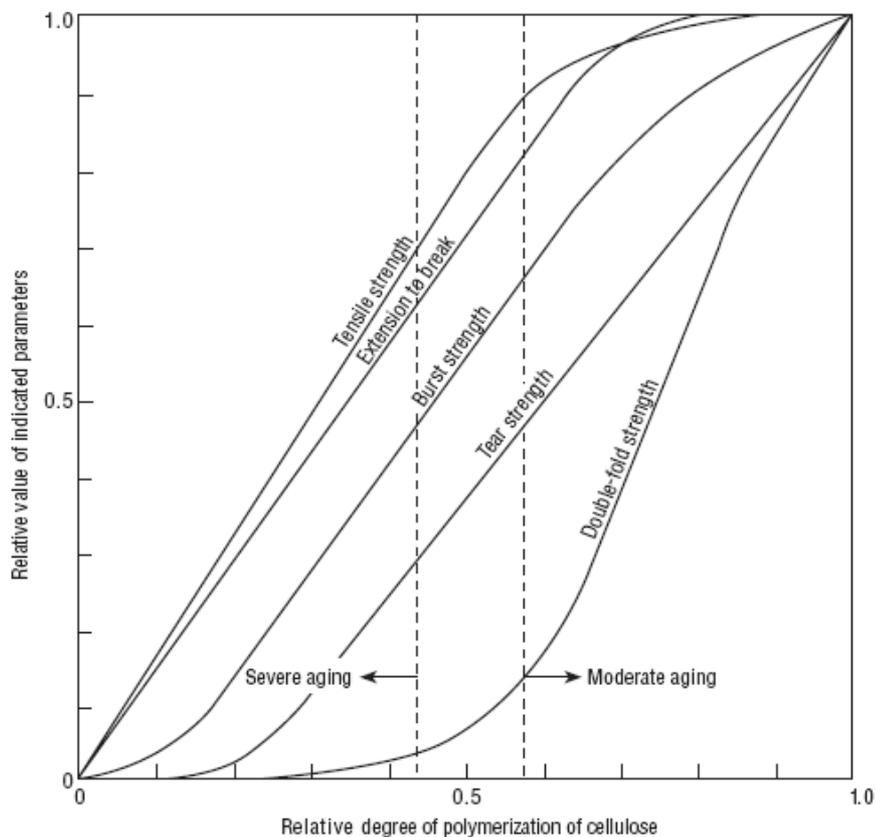
4. Using the equations listed above, the approximate lifetime of a fibrous raw material is:

$$\frac{(1/DP_t) - (1/DP_0)}{t_{Life}} = k = (A_{a0} + A_{a2} \cdot c(H_2O) + A_{a5} \cdot c(H_2O) \cdot c(H^+)) \cdot e^{-E_a/R \cdot T}$$

and therefore $t_{Life} = \frac{(1/DP_t) - (1/DP_0)}{A_{a0} + A_{a2} \cdot c(H_2O) + A_{a5} \cdot c(H_2O) \cdot c(H^+) \cdot e^{-E_a/R \cdot T}}$

Effects of cellulose degradation on strength properties

Cellulose degradation leads to varying degrees of strength losses. The diagram below shows the decrease in relative strength properties as a function of the DP of cellulose².



Aging has particularly drastic effects on folding strength and tearing strength, i. e. on the strength properties of single fibres.

² according to: Thermal aging of cellulose insulation. IEEE Transactions on Electrical Insulation, E1-12:61-66 (1977)

**Summary:
Influences on
cellulose degrada-
tion**

The diagram and publications on cellulose aging surveyed show clearly that cellulose degradation is influenced by the following parameters:

- DP of the initial pulp and tolerable DP after aging (usable DP range)
- temperature during aging (exponential influence)
- equilibrium moisture content and pH of paper during aging

Effects caused by manufacturing and converting processes (printing inks, adhesives etc.) are not covered by these influences. Assuming that modern papermaking processes avoid nearly all detrimental influences leading to acid pH levels and accelerated oxidation, the aging behaviour of cellulosic pulps is influenced by the parameters listed above.

Assuming as well that the calcium carbonate fillers contained in archival paper and paperboard provide for sufficiently high alkali reserves, the effect of varying pH levels on pulp aging is only marginal.

Because the usability of paper depends on its strength properties, we can also assume that there is a more or less identical final DP which no pulp should fall below. This final DP must be a value somewhere above the LODP (Level of DP – DP of crystallites), for example DP 200 for chemical pulps and DP 300 for cotton pulps.

This shows that the permanence of fibres in archival paperboards containing sufficiently high alkali reserves hinges upon the initial DP and aging temperature. There are practically no differences between cotton and chemical pulps as long as they have comparable ranges of usable DP's.

However, these considerations make no allowance for strength properties like zero span breaking length, folding strength, tensile, burst and tearing strength, whose levels are different in cotton and wood pulps.

**Comparison of
compositions**

The table below shows a comparison between the properties of bleached papermaking pulps obtained from softwood (SW) and hardwood (HW) as well as cotton or cotton linters pulps.

Explanations for differences and effects:

There are only marginal differences between cotton and wood (bleached chemical) pulps. The following differences exist in the aging properties of the two pulp types:

- Cotton pulp has virtually no hemicelluloses and is free from acid carboxyl groups (low acid content = more durable).
 - Because of their higher crystallinity and LODP, cotton pulps are degraded less than wood pulps. Papers obtained from these pulps will therefore have different strength properties. This can also be a drawback (because of the stiff cotton fibres).
 - The lack of lignin and acid extractives is an advantage. However, compared to bleached wood pulps and pulps containing sufficiently high alkali reserves, the effect on paper properties is only marginal.
 - The initial DP of cotton pulps can vary greatly depending on how they are
-

produced. Preference should be given to pulp types with high initial DP.

- Softwood kraft pulps have advantages in terms of strength.
- When using hardwood kraft pulps, eucalyptus pulps should be preferred to birch and maple pulps because of their lower hemicellulose contents.

	Bleached HW papermaking pulp	Bleached SW papermaking pulp	Bleached cotton- / cotton linters pulp
Cellulose [%]	80 -90	85 -90	> 93
DP	500 - 900	600 – 1100	300 - 1500
LODP	approx. 100 -200		approx. 300
Crystallinity index	approx. 0,60		approx. 0,70
Hemicelluloses [%]	10 - 15	15 – 25	none
Residual lignin	Kappa < 1	Kappa < 1	no lignin
Extractives [%]	< 0,1	< 0,1	< 0,1
Ash [%]	0,2 – 0,3	0,1 – 0,2	<0,1

Examples of aging properties

Aging properties were predicted by means of the equations listed above, allowing for the following main influences: initial DP calculated from LVN according to IMMERMIGUT et al. Compared to other authors, this pulp life prediction is rather pessimistic.

Based on standard conditions, the initial LVN (or DP) and mean values of pH, equilibrium moisture content and aging temperature were varied. The effects of these influences on pulp lifetime up to a final DP of 200 and 300, respectively, are clearly visible. The final DP of 200 refers to wood pulps, DP 300 to cotton pulps.

The results show that the effects of exchanging cotton pulp for wood pulp would be rather small. Decisions must be based on the paperboard strength required in each case. Marginal differences can be utilised to choose the most cost-effective fibrous raw material.

The values show the trends of different influences on lifetime. Being an exponential influence, the aging temperature has significant effects.

1. Variation of LVN or initial DP

LVN initial [ml/g]	Standard	Variation of initial LVN (DP)				
		1200	1000	600	1000	800
DP initial	757	1152	954	562	954	757
DP(final)	200	200	200	200	300	300
pH	7,00	7,00	7,00	7,00	7,00	7,00
Paper moisture [%]	6,00	6,00	6,00	6,00	6,00	6,00
T(aging °C) [K]	25	25	25	25	25	25
Life [a]	751	834	801	667	467	417

2. Variation of pH

	Standard	pH variation of aqueous extract				
LVN initial [ml/g]	800	800	800	800	800	800
DP initial	757	757	757	757	757	757
DP(final)	200	200	200	200	300	300
pH	7,00	5,00	6,00	8,00	6,00	5,00
Paper moisture [%]	6,00	6,00	6,00	6,00	6,00	6,00
T(aging °C) [K]	25	25	25	25	25	25
Life [a]	751	563	729	753	405	313

3. Variation of equilibrium moisture content

	Standard	Variation of equilibrium moisture content				
LVN initial [ml/g]	800	800	800	800	800	800
DP initial	757	757	757	757	757	757
DP(final)	200	200	200	200	300	300
pH	7,00	7,00	7,00	7,00	7,00	7,00
Paper moisture [%]	6,00	10,00	8,00	4,00	6,00	4,00
T(aging °C) [K]	25	25	25	25	25	25
Life [a]	751	455	567	1112	417	618

4. Aging temperature

	Standard	Variation of mean aging temperature				
LVN initial [ml/g]	800	800	800	800	800	800
DP initial	757	757	757	757	757	757
DP(final)	200	200	200	200	300	300
pH	7,00	7,00	7,00	7,00	7,00	7,00
Paper moisture [%]	6,00	6,00	6,00	6,00	6,00	6,00
T(aging °C) [K]	25	15	20	30	20	30
Life [a]	751	3459	1591	363	884	202