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The Progress of Ageing of Lignin-containing Paper Induced by Light and its Relation to Chemiluminescence – Temperature Runs

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Summary: Lignin-containing papers from different sources and of different age were irradiated by the visible light and the progress of the degradation reaction was followed by non-isothermal chemiluminescence method. Kinetic data obtained for papers degraded in oxygen were compared with double fold endurance test and carbonyl groups concentration. The effect of lignin on degradation of cellulose after deacidification treatment of the paper by methoxymagnesium methylcarbonate (MMMC) was ascertained and a mechanism of co-oxidation of lignin and cellulose in originally alkaline conditions was outlined.

Keywords: chemiluminescence; cellulose; deacidification; degradation; double folds; lignin

Introduction

Paper looses its mechanical properties and the remaining service life becomes considerably shorter when it is exposed to daylight. Light induced degradation of cellulose which is the main component of the paper occurs via free radical mechanism. Free radicals appear there due to initiation by various kinds of chromophores such as e.g. inherent groups (carbonyls) attached to the cellulose backbone or additives, fillers and sizing agents. The particular effect on degradation of cellulose may perform lignin introducing new reactive chromophores into the system. The light ageing of lignin containing papers is accompanied by colour changes from yellow to brown and a correlation between loss of brightness and the mechanical strength of paper has been depicted. Review articles[1,2] have shown that light-induced discolouration of paper coincides with a loss of its mechanical strength. Some recent papers, however, underlined that lignin-containing papers have excellent retention of mechanical properties upon accelerated ageing in the dark and that there is no correlation between discolouration of aged sample and mechanical strength[3–5]. The conclusion of the paper[6] that yellowing and loss of strength do not always coincide should be taken into account as well. The arguments of the authors is based on assumption that discoloration of lignin-containing paper is mainly due to oxidation of lignin which subsequently protects cellulose from a direct degradation initiated by oxygen. Radical scavenging effect of lignin and its antioxidant properties in free radical oxidation mechanism have been outlined in other papers[7,8]. Non-irradiated lignin proved to be an excellent trap for free radicals, an effect has been initially suppressed by irradiation, however, at longer irradiation times the radical trapping behaviour was restored [9].

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Deacidification of acid papers became a generally accepted methodology of the prolongation of their remaining service life. It eliminates the acid sites in the paper which are responsible for an acid mechanism of the main chain scissions. At the same time, an increased thermo-oxidation stability of the paper was attributed to the lower rate of formation of terminal semiacetal groups which are the sites of predominant attack of oxygen. Of interest, however, is whether the contribution of deacidification to an increased thermo-oxidation stability of papers may be also related with the better mechanical properties of the paper or not. Lignin in the presence of hydroxyl anions and oxygen reacts easily to give superoxo anion radicals. It seems then probable that the potential co-effect of lignin on groundwood paper degradation cannot be neglected, as well[10]. Oxidation of lignin with oxygen at temperatures from 20–170 °C in the samples which are initially alkaline is accompanied by the formation of singlet oxygen O_2^*. The conversion of singlet oxygen to the ground state is accompanied by a relatively bright chemiluminescence[11] which may be an indication of transformation of superoxoanions to hydrogen peroxyl radicals and their recombination as follows:

$$
\begin{aligned}
{}^{\cdot}O_2^- + H_2O &\rightarrow HO_2^{\cdot} + {}^-OH \\
HO_2^{\cdot} + HO_2^{\cdot} &\rightarrow H_2O + O_2*
\end{aligned}
$$

Several methodologies were used in the submitted paper for estimation the present state of various papers. It is non-isothermal chemiluminescence which has been shown[12] to be suitable for estimation of residual thermo-oxidation stability. The method was complemented by carbonyl groups determination of degraded samples. Then it is double fold test which is related to the residual mechanical properties. Regardless that it has a relatively large scatter throughout respective samples it is expected to give concomittant results with tests on residual thermo-oxidation stability.

In the present paper we have focused on following problems:

a) Does exist a possibility to correlate rate constants (half-lives) determined from non-isothermal runs of oxidation of lignin-containing papers of different origin and double fold endurance rating for both the original papers and papers deacidified by methanol solution of MMMC?
b) Why magnesium ions in alkaline papers increase the chemiluminescence intensity so significantly in both the oxygen and nitrogen atmosphere?

The sets of samples either reference or deacidified with MMMC were irradiated by the day-light and respective kinetic parameters from non-isothermal chemiluminescence measurements were determined. The average rate constant of sample oxidation at 90 °C was calculated from values of activation energy and pre-exponential factor.

Experimental

The following papers have been examined:

Paper A – newsprint paper from Větřní (produced in 1996), Czech Republic, 66% of bleached groundwood, 24% of unbleached sulphite, 7–8% of kaolin, no sizing, residuals of aluminium sulphate and polyethylene diamine, 48.8 g/m^2
Paper B – newsprint paper from Štětí (produced in 1996), Czech Republic, 50% of classic groundwood bleached by hydrogen sulfide, 15% of half-bleached sulfate pulp, 35% of recycled mixture newspaper/magazine (1:1), 48.8 g/m^2
Paper C – paper from 1956, newspaper Hlas našej dediny, Slovak Republic, 61.7 g/m^2
Paper D – paper from 1942, newspaper Neue Ordnung, Croatia, 68.8 g/m^2
Paper E – paper from 1881, newspaper Pesti Hírlap, 86.1 g/m^2.

The samples of the paper were blank sheets from the above newsprint papers. They were exposed to the day-light within an interval 0–150 days at room temperature.

Carbonyl content in respective samples has been determined by the hydrazine photocolorimetric method according to the procedure described elsewhere[13].

The rate constants and half-life of the papers at a given temperature (90 °C) for thermo-oxidative degradation in oxygen were estimated from non-isothermal chemiluminescence runs according to the procedure described below.

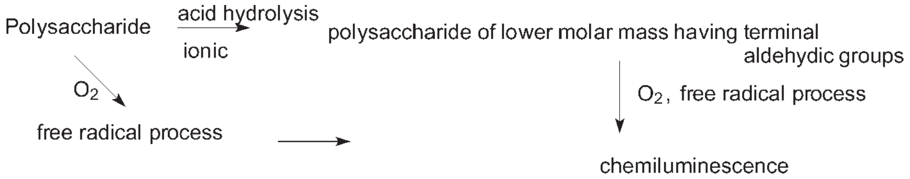
Double folds were measured according to Schopper[14]. Induced tension was 10 N for samples A and B and 2.5 N for samples C, D and E. An average of 10 runs has been taken as the resulting double folds rating.

Deacidification has been performed by neutralization of papers for 5 minutes in 4% methanol solution of MMMC[15]. Deacidification followed the washing of original samples out with methanol for 5 minutes.

The chemiluminescence measurements were carried out with Lumipol 3, photon counting luminometer produced at the Polymer Institute of Slovak Academy of Sciences, Bratislava. The instrument has very low dark counts at room temperature (2–4 counts/s). Experiments were performed in the overall oxygen flow 3.6 l/h at the rate of sample heating 2.5 °C/min.

On The Origin of Chemiluminescence From Oxidized Paper

Chemiluminescence accompanies the oxidation of all organic compounds, however, the intensity of the light emission may differ significantly throughout the series of compounds oxidized. In the case of paper, the main light emission comes from oxidation of cellulose. The heat which is released in exothermic free radical termination promotes some reaction species (carbonyl groups, oxygen) into an excited state. The conversion from excited state to a ground state may occur with the light emission, however, the yield of such a process is usually extremely low. Photons emitted may be registered due to a high sensitivity of photomultiplier and the method is stepwisely finding its place in description of kinetics of polymer oxidation.



The oxidizable sites on the cellulose molecules have the character of either terminal groups or they are distributed randomly along macromolecular chain. If the latter case predominates, the chemiluminescence intensity reflects the rate of reduction of average molar mass due to the main chain scissions while in the former case it simply expresses the rate of oxidation of chain end groups. As both processes may be mutually interrelated, the kinetic picture of oxidized paper samples is sometimes rather complex [16] (See the scheme above).

The chemiluminescence intensity I is determined by both the rate of the oxidation reaction w and proportionality constant Φ which depends on the presence of additives and physical quality of the paper, respectively.

$$I = \Phi w$$

Determination of Kinetic Parameters from Non-isothermal Chemiluminescence Test

Kinetic parameters from experimental runs of chemiluminescence intensity vs. temperature, which occur as a monotonous increase until 220 °C, may be found if a suitable model relating chemiluminescence intensity with the rate of oxidation reaction is used.

The kinetic model of the cellulose degradation which has been the subject of numerous papers was used first by Ekenstam[17] and developed by Emsley[18]. The degree of polymerization (DP) of cellulose is defined here as the ratio of concentration of monomer units (N) and polymer molecules (i) as follows:

$$DP = \frac{N}{i} \tag{1}$$

The concentration of polymer molecules increases in time with increasing extent of degradation reaction. The process of chain scissions is assumed to be of zero order $\left(\frac{di}{dt} = k\right)$ and the concentration i of macromolecules changes in time as a linear function of time.

$$i = i_0 + kt \tag{2}$$

Here k is the rate constant of main chain scissions and i_0 is initial concentration of macromolecules in the system, respectively. For DP we thus have:

$$DP = \frac{N}{i_0 + kt} \tag{3}$$

or $DP = \frac{DP_0}{1+\frac{k}{i_0}t}$, where $DP_0 = \frac{N}{i_0}$.

After transformation we receive:

$$\frac{1}{DP} - \frac{1}{DP_0} = \frac{k}{i_0 DP_0} t \tag{4}$$

$$\text{or } \frac{DP_0}{DP} = 1 + \frac{k}{i_0} t \tag{5}$$

The equation 4) is the Ekenstam equation[17] which may be found in literature. However, it is licit to work with equation 5 which gives the rate constant $\frac{k}{i_0}$ of the magnitude s^{-1}. This allows for a direct comparison between samples of different initial DP.

Provided that the chemiluminescence intensity I is proportional to the rate of change of polymerization degree in time we have:

$$I = \Phi\left[-\frac{dDP}{dt}\right] \tag{6}$$

Φ is proportionality constant involving quantum yield of chemiluminescence reaction.

The above case corresponds to the randomly oxidized sites on cellulose backbone

According to eq. 5) $-\frac{dDP}{dt} = \frac{k}{i_0 DP_0} DP^2$ and for non-isothermal conditions we obtain:

$$-\frac{dDP}{dT}\frac{dT}{dt} = \frac{A\exp(-E/RT)}{i_0 DP_0} DP^2 \tag{7}$$

Here T is temperature, A and E are pre-exponential factor and activation energy, respectively and $\frac{dT}{dt} = \beta$ is the linear rate of sample heating.

After integration of eq. 7) and back substitution into eq. 6), for non-isothermal conditions we receive:

$$I = \Phi\frac{A\exp(-E/RT)}{i_0} \times \frac{DP_0}{\left[1 + \frac{A}{\beta i_0}\int_{T_{room}}^{T} \exp(-E/RT)dT\right]^2} \tag{8}$$

Such mechanistic approach enables to simulate experimental curves of chemiluminescence intensity vs. temperature from several component runs corresponding to several independent initiating events. Provided that the process of light emission corresponds to three such events ($i = 3$) we have:

$$I = \sum_{i=1}^{3} \frac{P_i}{\left[1 + \frac{A_i}{\beta i_0}\int_{T_{room}}^{T} \exp(-E_i/RT)dT\right]^2} \tag{9}$$

Here P_i is the proportionality constant including the corresponding terms from eq. 8, A_i and E_i are pre-exponential factor and activation energy of respective component of the initiation reaction. An averaged value of rate constant of paper degradation may be calculated by means of respective Arrhenius parameters which allow to estimate the rate constant of each component of initiation event at any temperature.

Averaged rate constant k_{av} for 3 components of initiation (i = 3) leading to the light emission is defined as:

$$k_{av} = \frac{P_1}{P_1 + P_2 + P_3}\frac{k_1}{i_0} + \frac{P_2}{P_1 + P_2 + P_3}\frac{k_2}{i_0} + \frac{P_3}{P_1 + P_2 + P_3}\frac{k_3}{i_0} \qquad (10)$$

k_1/i_0, k_2/i_0 and k_3/i_0 are rate constants at a given temperature of the respective initiating process. They have the magnitude of the first order reaction (s^{-1}). The first constant is related to faster process, the second and the third to two slower processes of cellulose degradation. Faster process is usually ionic degradation while the two slower may be attributed to free radical degradation which takes place on terminal groups and/or statistically on macromolecular chain.

In practical computation procedure we determine the corresponding parameters for any of the three initiating event by non-linear regression analysis taking into account the experimental runs normalized to unity value at the maximum temperature of the experiment 220 °C.

Results and Discussion

a) Chemiluminescence from papers degraded by light measured in oxygen

In the Fig. 1 there are examples of chemiluminescence – temperature course for original papers D exposed to the daylight from 0 to 156 days. One can see that each paper performs a particular run typical by a steady increase of chemiluminescence intensity with temperature. The maximum chemiluminescence intensity achieved at 220 °C (maximum temperature of the experiment) has the tendency to decrease with time of irradiation, however, some scatter may be observed probably due to the paper non- homogeneity (Table 1, Table 2).

A qualitative comparison of the stability of respective samples at lower temperatures is possible after normalization of the curves to the value 1 (Fig. 2) for 220 °C (the highest temperature of the experiment). In such a way we eliminate the variability in proportionality constants Φ from eq. 6 and may thus determine the approximate sequence of stability of respective samples. One can see that according to the time of irradiation, the remaining stability of

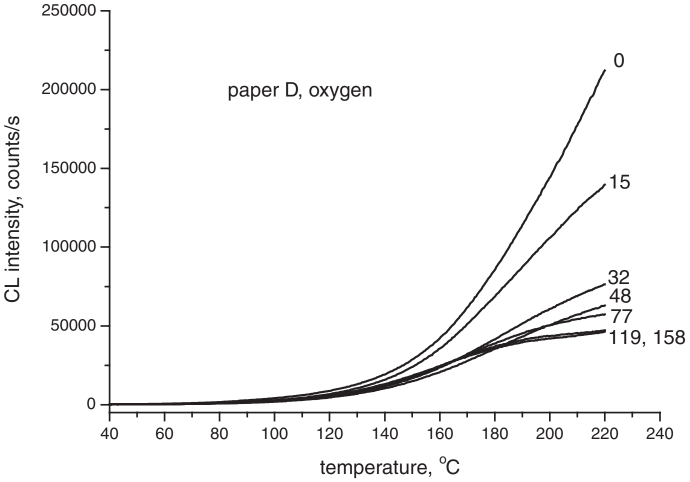


Figure 1.
Chemiluminescence intensity-temperature runs measured in oxygen at the rate of heating 2.5 °C/min for paper D irradiated 0–156 days (numbers at corresponding lines).

Table 1.
Rate constants of oxidation at 90 °C determined from non-isothermal chemiluminescence measurements and double folds ratings for samples of papers A,B,C,D and E

Paper	**Days of irradiation**	**Original paper**		**Deacidified paper**	
		$k_{average}{}^{*}10^{6}$ s^{-1} 90 °C	**Double folds,**	**$k_{average}{}^{*}10^{6}$ s^{-1} 90 °C**	**Double folds,**
A	0	2.94	1076	2.46	615
	15	4.72	939	1.01	514
	32	5.96	503	—	337
	48	6.70	164	1.61	142
	77	6.87	148	1.97	203
				2.27	
	119	7.41	73	3.05	140
	156	6.42	57	2.59	136
B	0	2.21	1653	0.59	1242
	15	2.89	1598	1.15	1041
	32	4.00	1500	1.57	929
	48	—	971	1.52	758
	77	6.41	825	—	684
	119	—	633	—	494
	156	6.37	665	2.19	524
C	0	—	1018*	—	540*
	15	5.87	891*	1.64	104*
		6.29		1.58	
	32	7.71	314*	1.92	39*
		8.29		1.87	
	48	8.04	317*	2.22	31*
		8.47		1.87	
	77	10.8	148*	2.77	18*
		10.2		2.86	
	119	—	97*	2.96	6*
	156	11.9	57*	2.25	10*
D	0	4.79	1751*	—	1176*
		6.21		—	
	15	6.33	1065*	2.55	398*
		5.84		2.29	
	32	8.65	1021*	2.14	399*
		7.26		2.38	
	48	7.70	747*	3.67	177*
		7.96		—	
	77	7.99	411*	2.16	178*
	119	10.2	305*	4.36	149*
				3.58	
	156	10.4	284*	4.00	133*
E	0	—	—	—	98*
	15	8.1	117*	1.59	19*
		7.2		1.50	
		6.8			
	32	8.25	88*	1.38	9*
	48	8.54	59*	2.07	8*
		7.42		1.49	
	77	8.04	24*	1.62	7*
	119	—	21*	1.67	8*
				2.02	
	156	9.65	20*	1.60	6*
Whatman	0	0.36	890	0.0028	1350
	15	—	600	0.0032	1360
	32	—	495	—	1400
	48	—	493	—	1230
	77	2.25	491	0.0049	1020
	119	—	503	—	1060
	156	1.27	504	0.0068	1100
		1.57			

*induced tension – 2.5 N (samples A, B and Whatman – 10 N)

Table 2.
Chemiluminescence intensity at 220 °C (I_{220}) in counts/s for circular cuts of paper D (diameter 9 mm) oxidized in oxygen under non-isothermal conditions from 40 to 220 at the heating rate 2.5 °C/min

Days of irradiation	Original paper	Deacidified paper
	I_{220}	I_{220}
0	207 161	—
	212 225	—
15	139 704	517 993
	118 115	564 566
32	76 352	484 559
	85 043	523 529
48	61 981	275 975
	62 825	
77	61 306	537 739
	57 306	
119	46 318	171 153
	50 792	296 450
156	47 229	260 177

respective papers in temperature region below 100 °C changes as follows:

$$0 > 15 > 32 > 48 > 77 > 119 \sim 156$$

This is well the sequence obtained by double folds endurance test for which a good correlation may by found with e.g. temperature of 20 % of chemiluminescence intensity corresponding to a maximum value at 220 °C (Fig. 2 and Fig. 3).

Provided that we perform the same comparison throughout all samples of papers of different origin and of different age (papers A-E) we receive the sequence of stability as follows (Fig. 4).

$$B > A > D > C > E$$

This corresponds again to the sequence of mechanical stability of respective papers determined according to double fold tests (Table 1).

$$1653(B) > 1076(A) - 1751(D) > 1018(C) > 207(E)$$

where the samples D, C and E were loaded by 2.5 N, only while those A and B by 10 N, respectively.

Provided that we estimate the thermo-oxidation stability of samples A, B, C, D and E from Fig. 1 according to the average rate constant k_{av} determined for 90 °C in oxygen we receive approximately the same sequence (Table 1):

$$2.89\ 10^{-6}(B) > 4.72\ 10^{-6}\ (A) > 6.08\ 10^{-6}\ (C, D) > 7.4\ 10^{-6}\ (E)\ s^{-1}$$

In the Table 1 we may notice several interesting features of thermal oxidation of groundwood papers as measured by non-isothermal chemiluminescence. Namely, it is a gradual increase of the rate constants of degradation determined for 90 °C with

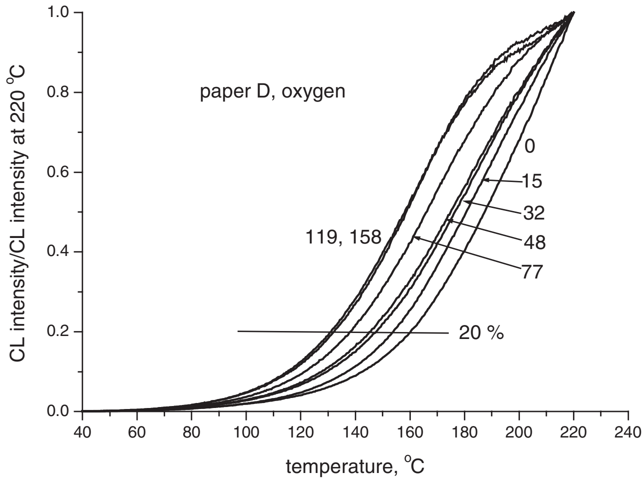


Figure 2.
The lines from Figure 1 transformed to the unity value of chemiluminescence intensity at 220 °C.

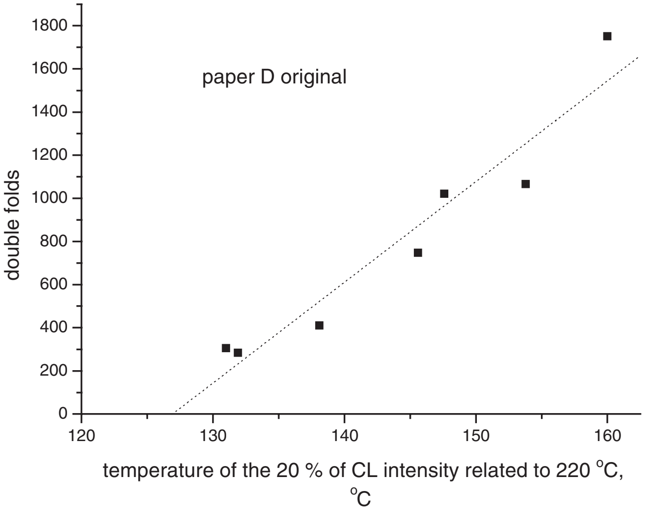


Figure 3.
Correlation of temperature at which 20% of chemiluminescence intensity at 220 °C is achieved during thermal oxidation of paper D under non-isothermal conditions (heating rate 2.5 °C/min, oxygen) with double folds. Paper D was exposed to the light from 0 – 156 days.

increasing time of paper irradiation. This is valid for both the groundwood papers as well as for Whatman paper. With prolonged time of irradiation the rate constants approach some critical value (around 1 10^{-5} s^{-1}). The most significant increase occurs during first 48 days of sample irradiation. One can assume that this increase is brought about by the accumulation of degradation products including low molar mass compounds and by their subsequent effect on further oxidation process.

Deacidified samples show significantly lower rate constants of degradation and

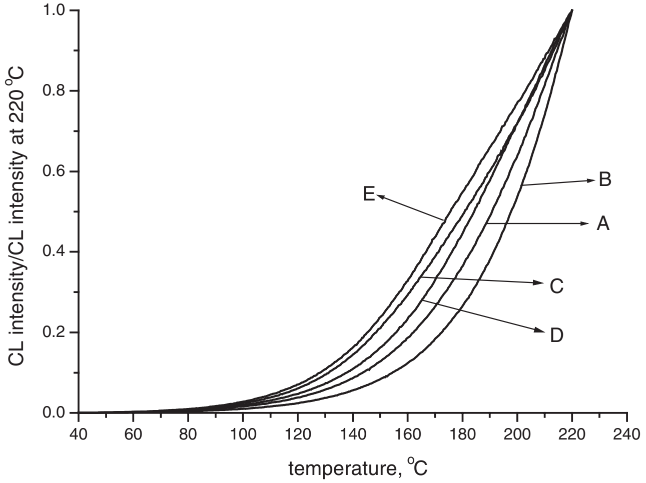


Figure 4.
The reduced chemiluminescence intensities courses for papers A – E oxidized in oxygen under non-isothermal conditions from 40 to 220 °C at the rate of heating 2.5 °C/min. Before chemiluminescence measurement papers were irradiated by the day-light for 15 days.

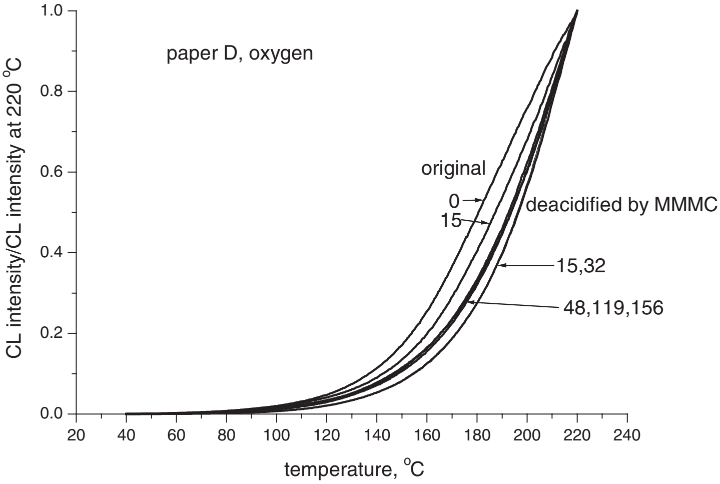


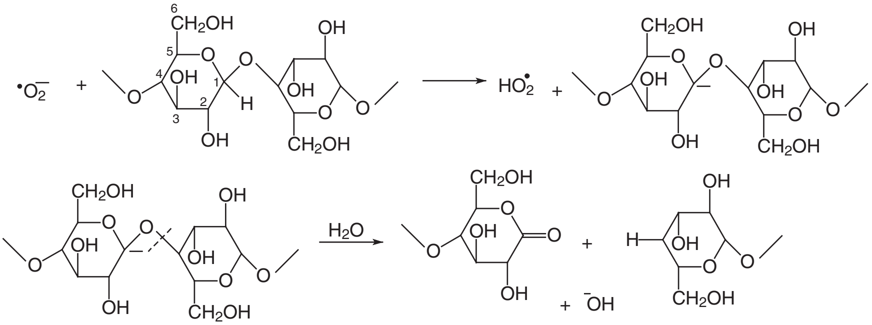
Figure 5.

The reduced chemiluminescence intensities runs for papers D (original and deacidified) oxidized in oxygen under non-isothermal conditions from 40 to 220 °C at the rate of heating 2.5 °C/min. Before chemiluminescence measurements papers were irradiated by the day-light for 0–156 days (numbers at respective line).

apparently they are more stable with respect to oxidation than the reference samples. As seen in Fig. 5 deacidified samples are more stable than original ones. Chemiluminescence – temperature runs are not so significantly shifted to a lower stability region as original samples when samples were irradiated from 0 to 156 days. This also corresponds to the fact that rate constants of oxidation also increase with time of irradiation, however, throughout the whole interval of irradiation (156 days) they do not achieve those of reference samples.

Contrary to all expectations, double fold endurance rating of non-irradiated groundwood paper is significantly reduced by deacidification with MMMC while that for Whatman paper it is higher. Double fold endurance rating continues to decrease with increasing time of paper irradiation for both the original and deacidified papers (Table 1).

While stabilization effect of deacidification against thermo-oxidation may be easily understood by significant suppression of cleavage of C–O–C bonds linking glucopyranosyl units and by a reduced formation of terminal semi-acetal groups which are prone to an easy oxidation, the reduction of double folds endurance for deacidified samples before irradiation is difficult to be understood. An idea that this may be due to an increased fragility of the paper caused by accumulated inorganic residue (MgO, $MgCO_3$) contradicts to observation with Whatman cellulose where opposite effect has been observed, i.e. double fold rating is better after treatment with MMMC (Table 1) than that for reference samples. The comparison of the effect of deacidification on double folds of Whatman paper which is almost pure cellulose and that of groundwood paper which contains lignin may lead to a conclusion, that it might be just lignin which is responsible for the above discrepancy. In alkaline environment lignin is obviously activated in a series of reactions which bring about an increase of free phenolic groups at one side[10] and their deactivation by formation of $O^- Mg^{2+-}O$ ionic bonds at the second side[19]. Phenoxyl anions are known by their capability to activate oxygen with formation of phenoxyl radicals and superoxide anionradicals (Scheme 1). While phenoxyl anions are fixed to lignin molecule and remain immobile which limits their antioxidant



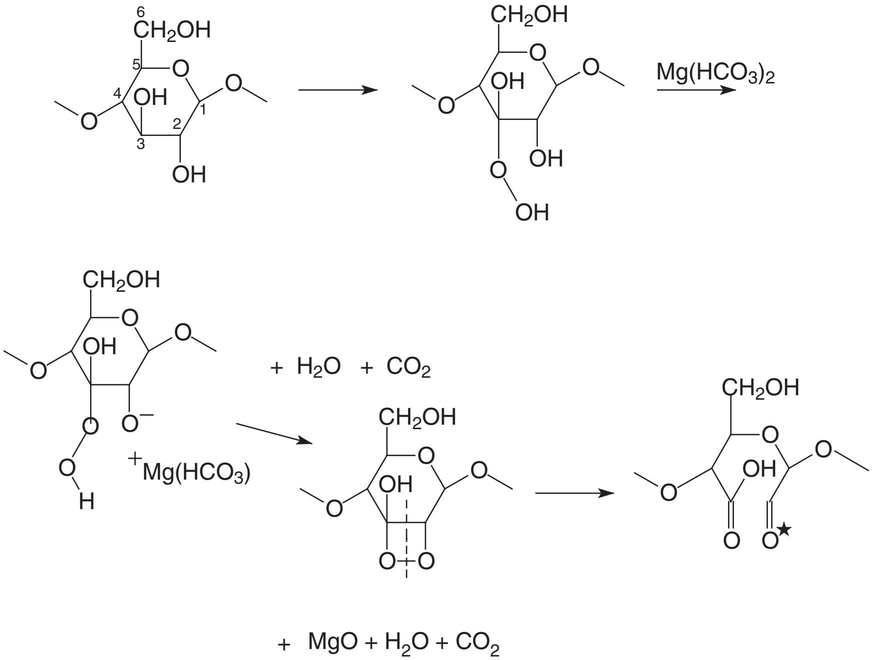
Scheme 1.

activity, superoxide anion radicals may penetrate easily into cellulose structure. They are capable of abstracting hydrogen from C_1 atom on glucopyranosyl unit and an anion may be formed in alkaline medium. Anion is subsequently cleaved by β-scission to corresponding products (Scheme 2) which is accompanied by a significant reduction of polymerization degree and thus by the reduction of mechanical properties.

Lignin increases the reactivity of papers in photo-oxidation reaction initiated by the day-light increasing the wavelengths at which the light is absorbed.

Of interest is also the correlation of average rate constant of paper degradation in oxygen at 90 °C and carbonyl content. For uniformly treated papers it is very good indeed (Fig. 6). A conclusion may be drawn that initially present carbonyl groups situated on both the lignin and cellulose macromolecules contribute to an easier course of oxidation reaction.

The samples of paper deacidified by MMMC give a significantly brighter light



Scheme 2.

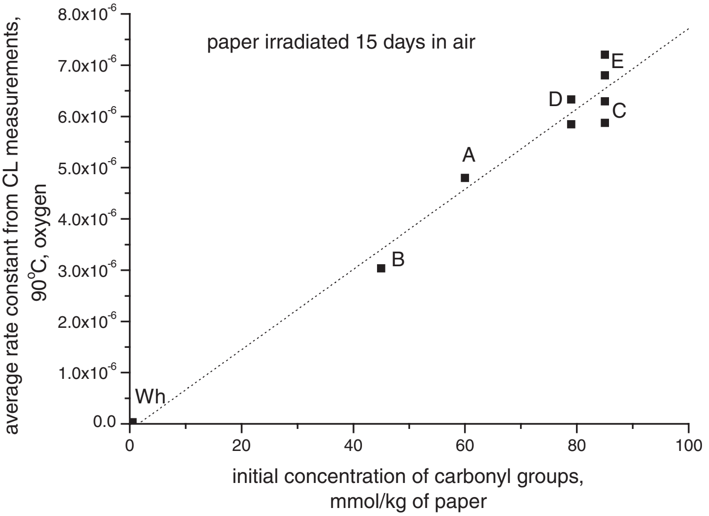


Figure 6.

Correlation between rate constants at 90 °C determined from non-isothermal chemiluminescence runs for papers after 15 days of irradiation and initial concentrations of carbonyls.

emission observed at increased temperatures than reference samples (Table 2 and Fig. 7). The phenomenon is due to magnesium ions from MMMC. The similar observation has been done with magnesium carbonates present in Whatman cellulose, while calcium carbonate practically did not change the intensity of light emission[20]. On the other hand, magnesium ions at pH <= 7 do not increase chemiluminescence intensity at higher temperatures of oxidized Whatman paper.

The Pauling's electronegativity of magnesium is 1.31 and calcium 1.00, respectively. It is of interest that a significant increase of chemiluminescence intensity above the values of reference samples was also observed when paper has been

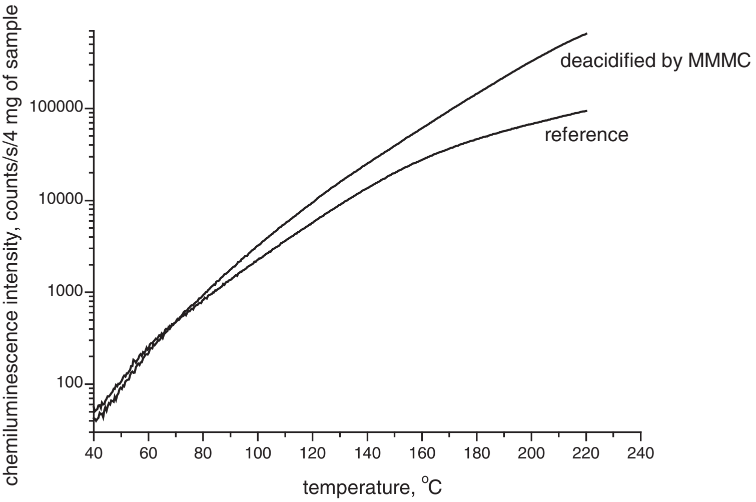


Figure 7.

Chemiluminescence intensity – temperature course for oxidation of reference and deacidified sample C, oxygen, the rate of heating 2.5 °C/min.

modified with zirconium carbonates. Electronegativity of zirconium (1.40) is close to that of magnesium. The another difference between magnesium and calcium ions consists in the fact that the former remain attached to one glucopyranosyl unit while the latter is capable of linking glucopyranosyl units of different cellulose chains[20]. Taking into consideration these facts one may propose the following mechanism of binding of magnesium carbonate which is formed from MMMC to glucopyranosyl unit. This mechanism may be also used for the explanation of increased intensities of light emission (Scheme 2). Hydroperoxides which were detected by chemiluminescence in nitrogen atmosphere and which are formed by oxidation of C_3 or C_2 atoms interact with magnesium carbonate with formation of intermediate dioxetanes which give in a subsequent decomposition bright light emission.

b) Chemiluminescence from papers aged in the light and measured in nitrogen

Samples of paper standing in air and subsequently heated in nitrogen show a course typical for decomposition of peroxidic compounds which are formed there by preceding oxidation. In the Fig. 8 there are shown chemiluminescence intensity – temperature courses in nitrogen for samples irradiated different times. Peroxidic peak has a maximum of chemiluminescence intensity at 160 °C. At the second heating which has been performed after several hours of sample standing in dark at room temperature no such peak can be observed that is an evidence that all accumulated peroxides were depleted by the first heating to 220 °C. The surface below this peak may be easily found by deconvolution of an experimental record fitted by 2 Gaussian lines using the procedure incorporated in the Origin program. For sample of paper E at 0 days of irradiation the deconvoluted line (Fig. 9) may be used for determination of activation energy and pre-exponential factor of decomposition of peroxides in cellulose and subsequently for calculation of the rate constant at a given temperature. The equation found for the rate constant of peroxide decomposition is:

$$\ln k = 10.12 - 59000/RT$$

and at 90, 100, 120 and 150 °C, the rate constant k is $9\ 10^{-5}$, $1.5\ 10^{-4}$, $4\ 10^{-4}$ and $1.4\ 10^{-3}\ s^{-1}$, respectively. The rate constant of fast decomposing hydroperoxides in polypropylene was reported to be $5.96\ 10^{-4}\ s^{-1}$ at 120 °C, however, activation energy was higher (around 100 kJ/mol)[21].

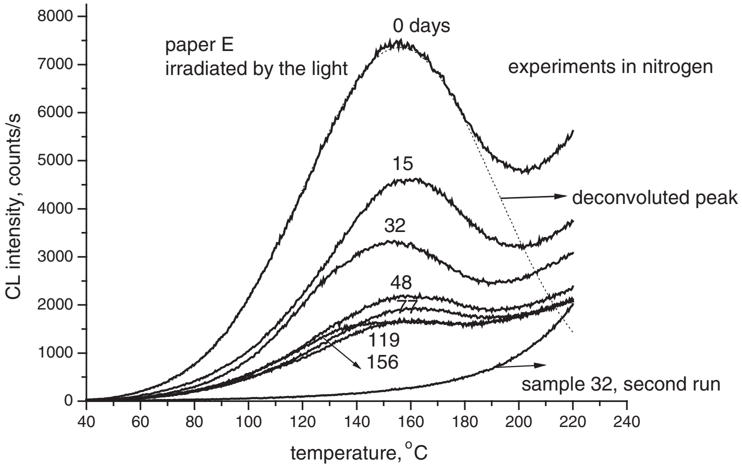


Figure 8.

Non-isothermal chemiluminescence runs for paper E in nitrogen (the rate of heating 2.5 °C/min) after paper irradiation by day-light (air). Numbers denote time of irradiation in days.

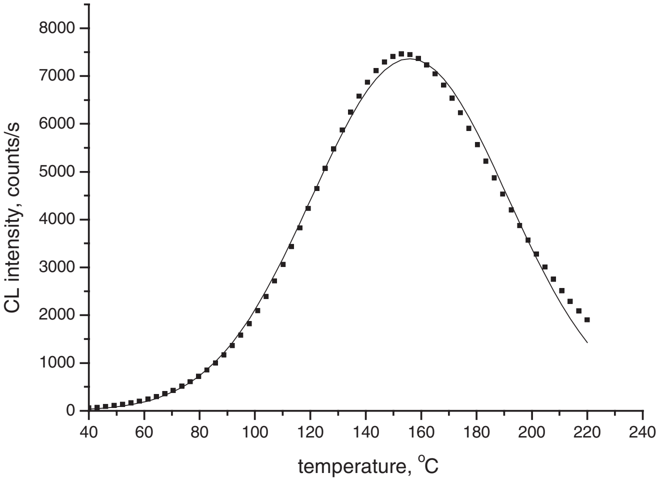


Figure 9.
Deconvoluted peak of peroxides for sample E, 0 days of irradiation, nitrogen, the rate of heating 2.5 °C/min. Points represent the fit by the first order process.

Long term irradiation of sample by day-light, reduces the intensity of this first peak (Fig. 8). The decay of hydroperoxidic peak is the most pronounced at the initial phases of irradiation and slows down at the latest stages (Fig. 8).

There exists the correlation between the surface below peroxidic peak and double folds (See papers D and E in Fig. 10), namely that the lower the surface of peroxidic peak, the lower double fold endurance. When plotting double folds vs. surface below the peroxidic peak we obtain straight lines which differ in slope depending on the quality of the reference paper and on the deacidification. Deacidification gives a lower slope.

It is of interest that even in nitrogen atmosphere the chemiluminescence intensity is more pronounced for samples

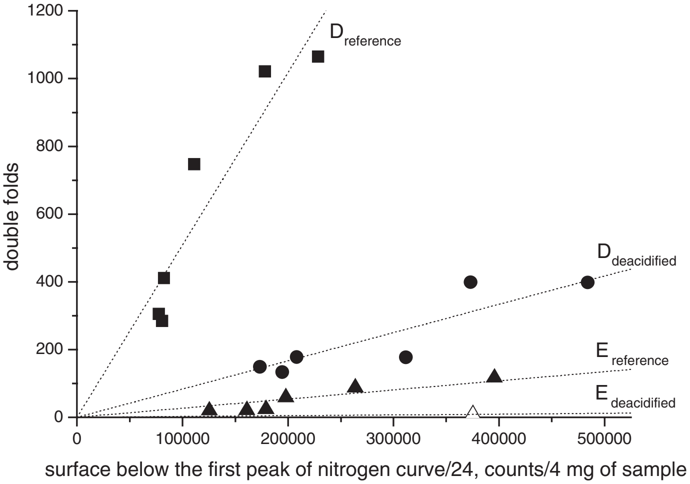


Figure 10.
Correlation of double folds and surface below peroxidic peak from chemiluminescence experiments in nitrogen for sample D and E irradiated by day-light from 0 – 156 days in air.

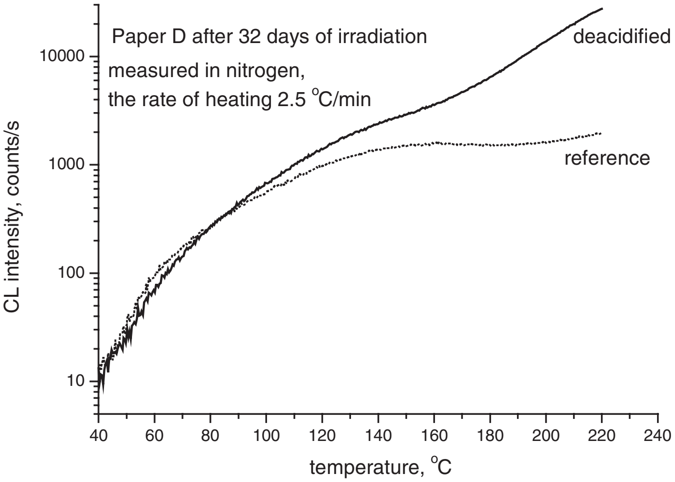


Figure 11.
Chemiluminescence intensity – temperature course for reference and deacidified sample of paper D after 32 days of irradiation by day-light, measured in nitrogen, the rate of heating 2.5 °C/min.

containing magnesium ions at pH > 7 (Fig. 11). This supports an idea that alkaline magnesium compounds are bound to some oxygenated structures (hydroperoxides), which at increased temperatures may lead to the sequence of reactions depicted by the Scheme 2.

Conclusions

Non-isothermal chemiluminescence experiments in oxygen may be used for estimation of remaining service life of groundwood papers containing lignin as well as of pure cellulose paper. There exists an unambiguous correlation between rate constants estimated form non-isothermal chemiluminescence runs and double fold endurance tests as it was demonstrated on different samples of groundwood papers aged by irradiation. Deacidified papers, however, show reduced mechanical properties measured by double fold method and correlations differ each from the other. This may be probably brought about by the degradation reaction of cellulose induced by lignin. However, the role of lignin in degradation of deacidified groundwood papers is far from being understood. A quite good correlation exists between the rate constant of thermo-oxidation degradation determined from chemiluminescence measurements and carbonyl content for paper sample treated in an uniform way which corresponds to already assumed mechanism of the light emission involving carbonyl groups as light emitters.

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[1] G. O. Phillips, J.C. Arthur, Cellulose Chemistry and its Applications (Editors T.P. Nevell, S. Zeronian, S. Haig), E. Horwood Publishing House, Chicester **1985**, p. 290
[2] P.J. Baugh, Developments in Polymer Photochemistry, Vol. 2, (editor N.S. Allen), Applied Sci. Publishers, London **1981**, p. 165
[3] X. Zou, N. Gurnagul, T. Uesaka, *J. Pulp Paper Sci.* **1993**, *19*, J235
[4] J. Stanley, D. J. Priest, *Paper Technol.* **1994**, *35*, 30
[5] G.J. Leary, X. Zou, Proceedings of the workshop on the effects of ageing on printing and writing papers, ASTM Institute for Standards Research, Philadelphia, PA, USA, **1994**, p. 86
[6] J.A. Schmidt, C. S. Rye, N. Gurnagul, *Polym. Degrad. Stab.* **1995**, *49*, 291
[7] T. Dizhbite, G. Telysheva, V. Jurkjane, U. Viesturs, *Bioresource Technology*, **2004**, *95*, 309

[8] T. Kasprzycka-Gutman, D. Odzeniak, *Thermochimica Acta*, **1994**, *231*, 161
[9] N. Duran, H. Mansilla, *J. Macromol. Sci. Chem.*, 1984, *A21*, 1467
[10] V. Bukovský, Degradation reactions of cellulose and lignin during natural and accelerated ageing of paper (in Slovak), Slovak National Library, Martin **2004**, p. 50
[11] A.D. Sergeev, E.I. Tschupka, Chemistry of cellulose (Khimiya Drevesiny) (in Russian), **1983**, *No. 1*, 90
[12] J. Rychlý, M. Strlič, L. Matisová-Rychlá, J. Kolar, *Polym. Degrad. Stab.*, **2002**, *78*, 357
[13] U. Albertsson, O. Samuelson, *Anal. Chim. Acta*, **1962**, *27*, 434
[14] ČSN 50 0345, Folding endurance of paper by the Schopper tester
[15] V. Bukovský, *Restaurator*, **2000**, *21*, 55
[16] M. Strlič, J. Rychlý, O. Haillant, D. Kočar, J. Kolar, Chemiluminescence of cellulose and paper. In: *Ageing and stabilization of paper*, Editors: M. Strlič and J. Kolar, National and University Library Ljubljana, ISBN 961-6551-03-5, **2005**, p. 133
[17] A. Ekenstam, Berrichte der Deutschen Chemischen Gesselschaft, **1936**, *69*, 553
[18] A. M. Emsley, R.J. Horwood, C.M.M. Ali, C.M. Eley, *Cellulose*, **1997**, *4*, 1
[19] G.J. Leary, *J. Pulp Paper Sci.*, **1994**, *20*, J154
[20] J. Rychlý, L. Matisová-Rychlá, M. Lazár, K. Slovák, M. Strlič, D. Kočar, J. Kolar, *Carbohydrate Polymers*, **2004**, *58*, 301
[21] J.C.W. Chien, H. Jabloner, *J. Polym. Sci.*, **1968**, *Part A-1, 6*, 393