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Stability of alkaline paper

Can chemiluminescence foretell the future?

While the studies of chemiluminescence (weak light emitted during a chemical reaction) have lead to a superior knowledge of oxidation mechanisms in many synthetic polymers during the past 30 years, the scientists almost completely overlooked cellulose and paper until very recently. Although still not numerous, the existing studies on cellulose revealed many interesting phenomena, interesting not only to a paper chemist, but also to a conservation chemist, as the applicability of chemiluminescence measurements can easily be extended to studies of cellulose and paper stabilisation and conservation. With a special emphasis on these fields, the technique is briefly introduced and the present state of knowledge of cellulose chemiluminescence phenomena during oxidation reviewed. Several such mechanisms have been identified or postulated: decomposition of macromolecular peroxides, superoxide annihilation, decomposition of charge-transfer complexes formed during irradiation with visible light, and transglycosylation. Although most data have so far been obtained at elevated temperatures, >100 °C, their relevance to the temperature region of interest to a paper conservation chemist, < 90 °C, is discussed. Since chemiluminescence measurements can easily be performed at temperatures lower than the typical accelerated ageing temperatures, the technique is well worth of an in-depth study. Namely, the relevance of data obtained at temperatures closer to the temperature of use, i.e. room temperature, is much higher due to the extrapolation errors inherent to the much used and sometimes controversial accelerated ageing tests.

Während in den letzten 30 Jahren Untersuchungen zur Chemiluminiszenz (Ausstrahlung eines schwachen Lichts während einer chemischen Reaktion) das Verständnis der Oxidationsmechanismen bei vielen synthetischen Polymeren grundlegend verbessern konnten, wurden Papier und Zellulose von der Wissenschaft bisher fast völlig vernachlässigt. Die wenigen in der Zwischenzeit entstandenen Arbeiten enthüllten viele Phänomene, die nicht nur für den Papierchemiker interessant sind, sondern auch für Chemiker im Bereich der Restaurierung, da die Chemiluminiszenz-Meßergebnisse gut auf den Bereich der Zellulose- und Papierstabilisierung übertragbar sind. Unter diesem Aspekt wird die Technik kurz erläutert und der aktuelle Wissenstand zum Thema Chemiluminiszenz-Phänomene bei der Oxidation von Zellulose erörtert. Verschiedene solcher Mechanismen wurden postuliert und identifiziert: die Zersetzung makromolekularer Peroxide, die Vernichtung von Superoxid, die Zersetzung von Charge-Transfer-Komplexen, die durch sichtbares Licht entstehen, sowie Transglycosierung. Obwohl die meisten Daten bei erhöhten Temperaturen, >100 °C, gewonnen wurden, wird ihre Relevanz für die Temperaturbereiche, die den Chemiker im Bereich Restaurierung interessieren, nämlich < 90 °C, diskutiert. Da Chemiluminiszenz-Messungen ohne Probleme in niedrigeren Temperaturbereichen stattfinden können als den für die beschleunigte Alterung typischen, verdient die Technik eine tiefergehende Untersuchung. Die Relevanz der Daten, die bei real existierenden Temperaturen (d.h. Raumtemperatur) gewonnen werden, ist auf Grund der inhärenten Extrapolationsfehler bei Tests mit beschleunigter Alterung sehr viel höher.

The application of accelerated ageing experiments at an elevated temperature for modelling the ageing behaviour of paper, especially alkaline paper, has long been questioned (Porck 2000). Although the ISO Standard 5630/3 prescribes the ageing conditions for paper (80 °C at 65% RH), the result of such an ageing experiment for alkaline cellulose impregnated with iron chelator diethylentriaminepentaacetic acid (DTPA) was shown to be in a contradiction with the expected behaviour of the sample at room temperature, as it was shown in a recent study (Strlič et al. 2000 a). Indeed, in a multi-reaction system like cellulose autoxidation it is difficult to expect that a single accelerated ageing experiment can provide a good estimation of the ageing behaviour at the temperature of use. A set of experiments has to be performed at various temperatures in order to be able to obtain an apparent activation energy E_a for the rate constant of material degradation k from the corresponding Arrhenius plot: $\ln(k) = -E_a/R \cdot T$. Once equipped with the apparent activation energy, it is possible to calculate the value of the measured material property at the temperature of use from the above equation, i.e. to predict the ageing behaviour of the particular paper. However, a typical ageing experiment at 50 °C may last up to a few months,

depending on the degree of stabilisation of a particular sample, and experiments at still lower temperatures are desirable in order to obtain better quality data. Since such studies may become extremely time-consuming, other solutions are intensively searched for.

It has long been known that emission of light, reffered to as chemiluminiscence (CL), accompanies some chemical reactions and studies of chemiluminescence accompanying degradation of polymers have been attracting the attention of chemists for almost four decades (Ashby 1961). However, for various reasons, the most obvious one being the complexity of data obtained, the technique has never been widely used. Even so, it contributed a vast amount of knowledge on the degradation mechanisms of artificial polymers (Zlatkevich 1989). Although not routinely in use, the lifetime predictions obtained by chemiluminescence studies have been shown to correlate with accelerated ageing studies for some artificial polymers (Billingham 1999). Since such experiments are not nearly as time-consuming as accelerated ageing and since due to the extreme sensibility of the present-day CL instruments the reaction temperature may be significantly lower than the ISO Standard 5630/3 temperature, we are faced with a possibility

to complement the existing accelerated ageing studies and obtain more reliable results more quickly. The temperature, at which the measurements (or accelerated ageing) are performed, is vital: the lower the temperature (or: the closer to the temperature of use) the more likely is the expected performance of material to correlate with performance at the conditions of use.

The elegance of the chemiluminescence technique is that we can follow the chemical changes in situ, i.e. while the very reactions take place, with the help of a photomultiplyer. Another advantage is its ability to provide valuable information on the initial stages of polymer degradation. For the reasons discussed, chemiluminescence measurements may provide some advantages over the conventional paper ageing techniques. In the area of conservation research, more refined analytical methods for comparative investigation of paper ageing are needed (Porck 2000; Pedersoli 1999), and we shall briefly review the general principles, the present state of knowledge, the future potentials of this technique and discuss the applicability of the method for a paper chemist and conservator.

Experimental

Cellulose samples of different origin (Whatman filter paper, MoDoCrown elementary chlorine free bleached sulphite softwood pulp, Imperial elementary chlorine free bleached sulphate softwood pulp) were prepared as disks of diameter 0.6 cm. Some samples were prepared by immersion in solutions of 0.01 mol L^{-1} Mg(HCO$_3$)$_2$, Ca(OH)$_2$, Sr(OH)$_2$, and Ba(OH)$_2$, which on drying yield the corresponding carbonates. Model substances, such as cellobiose, maltose, lactulose, glucose, levogluocosan were also examined.

The chemiluminescence experiments were performed with the photon counting instrument Lumipol-1 manufactured at the Polymer Institute of Slovak Academy of Sciences, Bratislava, Slovakia. Different atmospheres (O$_2$, N$_2$, air) were maintained by a gas flow through the sample cell of 3 L/h. A sample was placed on an aluminium pan on a calibrated heating plate (oven) in the sample compartment. The sample compartment is divided from the photomultiplyer tube (PMT) by a glass window and a mechanical shutter to prevent irradiation of the PMT during sample exchange. The PMT response reflects the number of incident photons emerging from the sample, and is processed by signal counting circuitry.

Isothermal experiments in a selected atmosphere are the most common. In some experiments, the gas is exchanged several times during an experiment thus providing atmospheric perturbations, similar to experiments in dynamic thermal conditions. Additionally, the samples may be pretreated by irradiation, plasma treatment, humidification etc., thus providing other types of chemical perturbation.

Thermal degradation of samples in nitrogen or oxygen was carried out outside the CL instrument in a glass reactor (flow of gas 3 L/h). It was placed into an oven thermostatted to the desired temperature (±1 °C). The degree of polymerisation (DP) was determined according to the standard method (SCAN-CM 15:88 1988), calculated from the intrinsic viscosity using the equation DP$^{0.85}$ = 1.1 [η] and thus denotes viscometric average degree of polymerisation throughout the text.

Iodometric determination of peroxide groups was done according to the method by Mair et al. (1964), which was slightly modified (isopropyl alcohol/NaI/CH$_3$COOH mixture was left overnight to react with the sample at room conditions in darkness). The mass of dry sample was 1 g, approximately.

Discussion

Polymer luminescence is light emission resulting from sample excitation, which can be a consequence of sample irradiation, heating, oxidation, physical stress (Zlatkevich 1989) etc. The term chemiluminescence (CL) is usually applied only to photon emission during relaxation of reaction products. This does not necessarily imply that the reaction should be exothermal, although this is usually the case. Several reaction pathways may yield excited molecules which emit light, and it is most often assumed, on the basis of luminescence spectral analysis, that the actual emitter is an excited carbonyl. The Russell mechanism (Russell 1957) is often discussed:
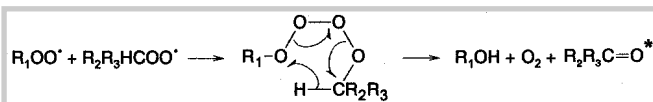
though it is not generally applicable and a variety of other mechanisms have been proposed. However, since most CL mechanisms involve macromolecular peroxides, and these are in turn important intermediates during oxidative degradation of polymers, the connection between cellulose ageing and CL is worth exploring.

Stationary and quasi-stationary experiments

The experimentally most straightforward are stationary experiments, in which the sample is subjected to isothermal heating in a chosen atmosphere. In oxygen the CL levels are often high enough to be measured at a few degrees above the room temperature (Fig. 1). Since it is usually assumed that the decomposition of peroxides is the most prominent chemiluminescent mechanism in the presence of oxygen, the levels of chemiluminescent signals may in some way correspond to the oxidisability of the material. The intensities of emitted light are proportional (in the logarithmic scale) to the applied temperature and can be analysed using the Arrhenius equation (Fig. 2) and the corresponding apparent activation energy can be obtained after a few short experiments. Since the lowest temperature used is close to room temperature, an extrapolation of the rate of the process to the temperature of use may be more reliable than results obtained through the classical accelerated ageing experiments.

However, despite the obvious potential of the method for evaluation of ageing properties of paper, the above derivation of E$_a$ is but a demonstration, since we know very little about the specific chemistry which leads to the chemiluminescence phenomenon. There are cases, though, where the present knowledge of cellulose degradation chemistry allows us to

draw conclusions on the kinetics of a particular degradation process. One such case is thermal degradation of cellulose in nitrogen atmosphere in the mid-temperature region (100–200 °C), which is not of primary importance to the conservator, but will provide some good examples.

It has been observed, that cellulose exhibits high CL levels upon heating in nitrogen (Strlič et al. 2000). Since oxygen is absent, the already discussed CL phenomena involving peroxide species can be excluded, and it was found (Strlič et al. 2000) that the integrated CL intensity (in time) is proportional to the decrease in DP of samples, isothermally heated in a flow of nitrogen for a prolonged time (up to 12 h). Therefore, the CL is in some way proportional to the chain-scission process, called transglycolisation (Shafizdaeh 1982). Its source may be radical recombination reactions provided that a suitable acceptor of the released reaction energy is present, e.g. a carbonyl group. Several sources of excited carbonyl groups are possible, either the transglycolisation reaction itself, or the subsequent elimination reactions. In any case, the CL experiments complement well the parallel DP determinations. Recently, it was shown that the addition of alkali-earth metal carbonates to cellulose influences the rate of transglycolisation and a correlation between the cation's electronegativity and the degradation rate indicates that a complex is formed between the earth-alkali metal cation and glycosidic

oxygen (Strlič et al. 2000 b). Similarly, the higher rate of degradation of cellulose impregnated with $MgCO_3$ is mirrored by the higher CL intensity (Fig. 3). It is important to note that this degradation is not influenced by sample pH, as after 10 min at 180 °C, the samples are thoroughly dry. It is possible to obtain the apparent activation energy for this process both from DP-determinations and from CL measurements. In analogy to the above example, a quasi-stationary experiment can be performed (Fig. 4). After a sample achieves some equilibrium (in Fig. 4 after an hour at 200 °C), the temperature is stepwise decreased and the corresponding CL intensities monitored. The obtained intensities can be plotted in Arrhenius' coordinates and the corresponding apparent activation energy for the chemiluminescent process can be obtained reliably (Fig. 4, smaller graph).

Dynamic experiments

In these experiments, some parameter, usually temperature, is changed continuously (or at least in very small steps). This makes them more difficult to evaluate, as the CL intensities also change continuously and the rate of heating must be taken into consideration when a mathematical treatment of experimental curves is attempted. Most interesting are experiments with cellulose samples pre-oxidised in a flow of oxygen, and after flushing with nitrogen the temperature is con-
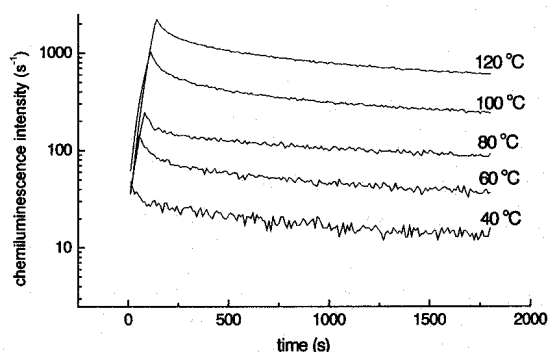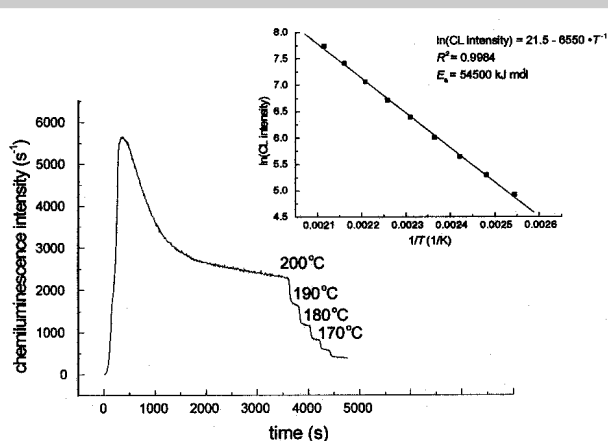

1   Isothermal CL experiments in oxygen atmosphere at the temperatures indicated. Sample: sulphite pulp.
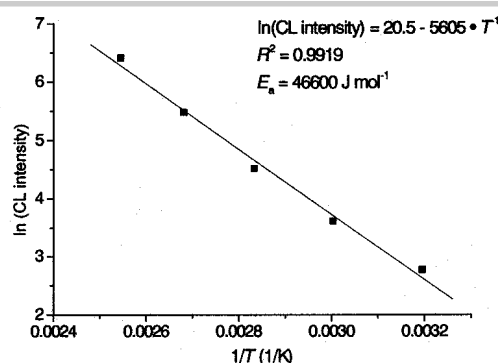
2   Arrhenius' plot of CL intensities after 1800 s of the same samples as in Fig. 1 and the corresponding calculation of the apparent activation energy of the process.
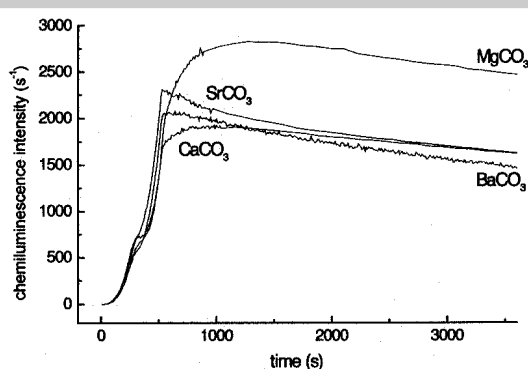
3   CL intensities of sulphite pulp samples, impregnated with earth-alkali metal carbonates in nitrogen atmosphere at 180 °C.

4   Quasi-isothermal chemiluminescence experiment with a sulphite pulp in nitrogen atmosphere. Smaller graph: the CL intensities plotted in Arrhenius' coordinates.

tinuously increased at a rate of 5 °C min^{-1} (Fig. 5). A peak in CL appears at approx. 140 °C which is absent if a second dynamic heating is performed (Fig. 5 a). If the sample is not oxidised first, the peak is hardly detectable (Fig. 5 b). This indicates the presence of a species which is introduced during oxidation and decomposes on heating in nitrogen.

In analogy with other polymers, mainly synthetic (Zlatkevich 1989), it can be shown that the height of this peak corresponds to the content of peroxide groups in the material, determined iodometrically (Strlič et al. 2000). In addition, the dynamic experimental curve B in Fig. 5, can be interpreted as two superimposed independent processes. Indeed, the steep rise in CL at temperatures approaching 200 °C was already discussed in the previous paragraph. If the curve A in Fig. 5 is fitted by non-linear regression (for mathematical treatments of such data see Zlatkevich 1989), the peak area can be obtained and from the curve parameters, the activation energy for peroxide decomposition can be calculated. The value obtained this way is $E_a = 75000$ J mol^{-1}. Since the most prominent chemiluminescent process in oxygen atmosphere is supposed to be decomposition of peroxides, the apparent activation energy for the decomposition can be obtained from a quasi-stationary experiment such as the one presented in Fig. 4. The value thus obtained is $E_a = 75000$ J mol^{-1}, which indirectly confirms the identification of the CL process.

Compared with some synthetic polymers, e.g. polypropylene or polyethylene, the accumulation of peroxides in cellulose is relatively rapid (at 80 °C, the steady-state concentration is achieved in 60 min). Combined with their low concentration, i.e. ~1 mmol kg^{-1} (Strlič et al. 2000), we can assume a very short autoxidative radical chain length. This fact explains the small effect that radical scavengers, e.g. BHT (2,6-di-tert-butyl-4-methylphenol), exhibit in paper (Kolar et al. 1998).

Other dynamic techniques include temperature cycling experiments (Rychlý et al. 2000), which allow us to better differentiate the different degradation phases in thermal degradation of cellulose in nitrogen and oxygen.
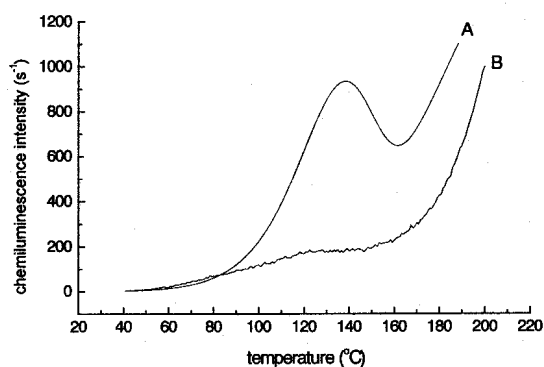
Irradiation experiments

The effect of cellulose irradiation can be studied by CL very conveniently. After a sample is irradiatied under a tungsten 60 W light source (in nitrogen, oxygen or air), it is quickly transferred to the oven and an elevated level of CL is usually observed in isothermal experiments, which quickly, in a matter of minutes, decreases to the level prior to irradiation (Fig. 6). This chemiluminescence can be numerically integrated and it was shown that the integrals depend on the composition of the surrounding atmosphere, more precisely on the square root of oxygen concentration. This leads to the conclusion that the phenomenon is not simple fluorescence, but that oxygen plays a role in the initiation process finally leading to CL. The existence of charge-transfer complexes between some atmospheric oxygen and some electron donor (carbonyl or glycosidic oxygen) in the cellulose macromolecular structure was postulated (Strlič et al. 2000). The phenomenon is not specific for cellulosic materials, but for all other model materials as well, including low-molecular weight models, e.g. glucose and cellobiose.

The decay of these complexes is slow, the half-lifetime being approximately 10 days at ambiental conditions. It was found that atmospheric humidity accelerates the decay. Presently, it is difficult to explain the role of oxygen/cellulose charge-transfer complexes, and the thought that they may lead to initiation of the autoxidation chain reaction is well worth of a more in-depth pursuit. Just how important this topic is for the conservation field was recently demonstrated (Havermanns, Dufour 1997).

The presence of a lively radical activity was detectable also in cold plasma-treated cellulose samples (air, 2000 V, 30 mA, 0.1 torr). The studies of reductive cold plasma treatment and of laser cleaning of cellulosic surfaces is thus another potentially rewarding research area.

Moisture: the evasive variable

Not many polymer chemiluminescence studies took atmospheric moisture into consideration, although it was early recognised that CL of cellulose and paper strongly depends on

5   Dynamic (ramp) chemiluminescence experiment of a pre-oxidised sulphite pulp (80 °C, 30 min, oxygen) in nitrogen atmosphere (curve **A**); sulphite pulp sample without a pre-oxidation step (curve **B**).
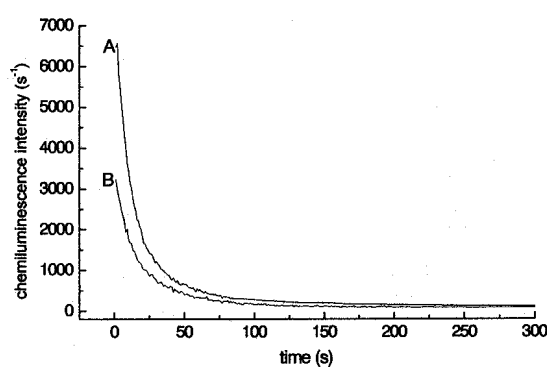
6   CL experiments performed with irradiated samples in air (sulphate pulp). Sample **A:** irradiated for 30 min; sample **B:** irradiated for 5 min.

it. Indeed, the first CL study on cellulosic materials was carried out in order to evaluate paper permanence in cooperation with The Library of Congress research department already in late 1970's (Kelly et al. 1979). The authors found out that the steady-state CL level of cellulose in moist atmosphere was lower than in dry atmosphere. Sadly, this remained the only publication on CL of cellulose or paper for a long time.

However, our studies showed different results. Although under non-stationary conditions with regard to moisture, the chemiluminescence intensity was invariably higher in the case of moist samples. Water might have various effects: by absorbing the surplus reaction energy and by increasing the mobility of cellulose molecules it could act as a CL quencher; or it could participate in a chemical reaction and promote oxidation. In the latter case, it could promote dissociation of ionic species (thereby increase the influence of pH) or it could take part in some hydrolytic reaction. The isothermal CL of a moist sample is higher both in nitrogen and in oxygen atmosphere (Fig. 7: an atmosphere exchange experiment). However, during drying of moist cellulose in nitrogen there is no detectable degradation (with viscometry), and another source of CL can be postulated under such conditions, namely singlet oxygen CL (Strlič et al. 2000 b).

The effect of moisture should certainly be evaluated under stationary conditions, i.e. in a CL instrument which allows the surrounding humidity to be controlled.
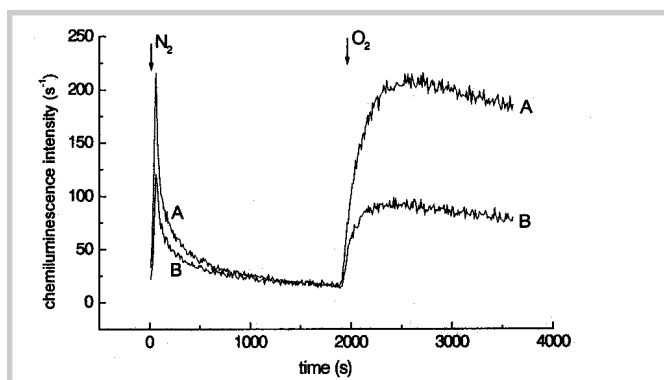
The practical value of CL measurements

At first sight (and at the present state of knowledge we are not far from the beginning), there are but a few practical consequences. Lately, the interest of researchers has turned to increasing the stability of neutral to moderately alkaline papers. It is well recognised by the conservation community that "treatment strategies must be targeted to retard specific scission chemistries" (Whitmore, Bogaard 1994). The stability of alkaline papers is largely impaired by autoxidation (Kolar 1997; Kolar et al. 2000) and it is exactly this mechanism (or the multiple successive and parallel mechanisms) that can be most conveniently studied by CL. Faced with a real sample,

however, one has to take into account its composition – the content of fillers, resins, lignin, colourants, etc. as they all influence the optical, physical and chemical properties of the material under investigation and in turn its chemiluminescence. Still, there is a possibility that chemiluminescence will enable us to evaluate the rate of degradation of cellulose and paper at room temperature at least as reliably as with oven ageing, but certainly much faster, offering the possibility of standardisation and validation of conservation procedures.

We have demonstrated the complexity of data that are usually obtained and in order to understand the underlying phenomena, one has to complement the technique with other analytical techniques. In the case of peroxides, we also demonstrated that CL measurements offer a possibility for comparative evaluation of peroxide content. The experimental techniques which allow us to obtain apparent activation energies, e.g. for peroxide decomposition or for transglycolisation, were shown to be straightforward and reliable. If, however, there is a correlation between natural or accelerated ageing and chemiluminescence in an oxidative atmosphere, remains to be seen. If so, the answer to the title question is: yes! The research to support this answer is currently undertaken in our laboratories.

7 Chemiluminescence (80 °C) of sulphate pulp samples: **A** = equilibrated in 100 % RH air, **B** = equilibrated at room conditions. Initial atmosphere: nitrogen, after 30 min exchanged with oxygen.

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