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Optical deterioration of coated wrapping paper

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Abstract:

The aim of the research was to analyse the dependence of storage conditions on the optical deterioration of coated wrapping paper. Three methods of common storage conditions were applied for a period of three years: preservation in the dark and dry place, storage in the common office conditions, and keeping in room conditions that enabled stronger influence of natural light and atmosphere pollutants. In order to examine optical modifications due to accelerated ageing, the same sample of paper was exposed to UV/VIS lamp radiation. Visible and IR spectroscopy were used for the characterization and comparison of paper degradation with the emphasis on the colour alterations as the crucial quality component. This research provides a solid basis for further development of non-invasive methods for investigating and predicting shelf life of coated wrapping paper.

Keywords:

Accelerated Ageing; Colour Measurement; FTIR Spectroscopy; Natural Ageing; Wrapping Paper

1 Introduction

Many commercial applications of paper demand higher smoothness, resistance to dirt, moisture and wear, in one word they demand a high quality coating. A typical representative of this type is wrapping paper. Wrapping paper has a long shelf life and it is situated in various places within the stores. The storage conditions are critical as they determine the longevity of paper, so low temperature and low to moderate relative humidity are desirable, since they not only maintain the degradation rate due to chemical reactions to acceptable levels, but also keep the population of biological agents under control (moulds, fungi, bacteria) (Zervos, 2010). Moulds, with more than 200 varieties, are most represented biological agents. They produce enzymes that chemically attack paper fibers and simultaneously produce acidic wastes which considerably contribute to paper degradation. Another major component extremely important for the longevity of paper is exposure to atmospheric pollutants, primarily sulphates and nitrates, but its influence is more expressed in samples containing higher percentage of mechanical pulp (Williams and Grosjean, 1992). Paper sheets with higher content of mechanical pulp are more porous and have higher specific

surface area that increases sorption of atmospheric gases.

Even though there are numerous methods and techniques of predicting the long term ageing behaviour of paper none of them are reliable and precise. The main assumption of an accelerated ageing test is that it simply speeds up the chemical reactions which would normally come about under natural ageing conditions, unfortunately the changes that occur during the accelerated ageing strongly differ to the changes that occur during natural ageing, but nevertheless they can serve as a guiding principle for examining degradation of paper.

The increasing presence of various non destructive techniques, such as visible and FTIR spectroscopy, open new possibilities towards the development of more reliable and faster methods of sample testing capable for adequate substitution of currently established ones.

2 Material and Methods

In order to avoid underestimating the light stability of paper due to exposure of high concentration mechanical pulp (lignin containing fiber) to high intensity UV light (McGarry, et al., 2004), samples of matt wrapping paper with high content of chemical pulp were used.

Natural ageing of samples was carried out in the duration of three years, consisting of three kinds of storage: storage in the dark and dry place, storage in the common office conditions, and storage which enabled stronger influence of natural light and atmosphere conditions.

Accelerated ageing was achieved by exposure of samples to UV/VIS lamp for 70 hours. Spectrometric measurements of samples exposed to UV light were performed after every 30 minutes of exposure, taking into account the time required for stabilization of the sample after exposure to UV radiation.

Reflectance measurements in the visible region (370-750nm) were acquired using USB4000 Miniature Fiber Optic Spectrometar at a 45˚ angle. To minimize the errors in measurements, due to narrow time intervals and infinitesimal changes in reflectance values, each spectrum is the average of 30 individual scans. To determine the value of XYZ tristimulus values standard light source D65 and the standard 2° observer were simulated, from which lightness, hue and chroma were calculated. Colour difference was than obtained from Equation 1.

$$\Delta E_{00} = \sqrt{\left(\frac{\Delta L^*}{k_L S_L}\right)^2 + \left(\frac{\Delta C^*}{k_C S_C}\right)^2 + \left(\frac{\Delta H^*}{k_H S_H}\right)^2 + R_T \frac{\Delta C^*}{k_C S_C}\frac{\Delta H^*}{k_H S_H}} \qquad (1)$$

where ΔL*, ΔC* and ΔH* are the CIELAB metric lightness, chroma and hue differences respectively calculated between the standard and sample in a pair, while the fourth addend under the root is an interactive term between chroma and hue differences. The SL, SC and SH are the weighting functions for the lightness, chroma and hue components respectively, while the kL, kC and kH values are the parametric factors to be adjusted according to different viewing parameters such as textures, backgrounds, separations etc. for the lightness, chroma and hue components respectively (Luo et al.,2000).

ATR spectroscopy is a powerful tool for analysing organic binder materials and in some respect the identification of pigments (Derrick et al., 1999; Mazzeo et al., 2007). Although

many inorganic pigments have characteristic absorption bands in the mid-IR region there are many that either do not absorb in that region at all or have absorptions that are at the low wave number end of the region and are not characteristic enough (Nyquist et al. 1997). The depth of penetration (dp) of the IR radiation into the sample depends on the (Eq 2.)

wavelength (λ) of the IR radiation, the angle of incidence of the radiation (θ), refractive index of the ATR crystal (nc) and the refractive index of the sample (ns).

$$dp=\lambda / 2\pi\, nc[\sin^2\theta - (ns / nc)^2]^{1/2} \quad (2)$$

It follows from Eq 2. that in order to observe any ATR effect, the refractive index of the sample must be lower than that of crystal. (Willis et al., 1987)

The FTIR spectra of natural and accelerated samples were recorded by FTIR IRAffinity-21

spectrometer in ATR mode for the investigations of paper and inks on paper. The Specac

Silver Gate Evolution is single reflection ATR sampling accessory with angle of incidence at

45° and a ZnSe flat crystal plate (index of refraction 2.4). A total of 15 cumulative scans were taken, for each sample, with the resolution of 4 cm-1, in the spectral range 500-4000 cm-1. From acquired spectra three types of information concerning cellulose degradation were obtained, and these are respectively ratio of crystallinity determined as the absorbance ratio from 1430 cm-1 and 893 cm-1 bands (Eq 2.) (Salmen, et al., 2005; Nelson, 1964),

$$Cr.R. = A_{1430}/A_{893} \quad (2)$$

followed by the energy of the hydrogen bonds (Eq 3.) which is influenced by the standard frequency that corresponds to free OH groups (ν0=3600cm-1), and the frequency of the bonded OH groups (ν) where 1/K is 2.625·102kJ (Ciolau et al., 2010)

$$E_H = (1/K) \cdot [(\nu_0 - \nu)/\nu_0] \quad (3)$$

and the asymmetric index (a/b) which is essentially the ratio between segment widths at half height of the OH adsorption band (Alcock, 1990).

Crystallinity of cellulose has been used for more than five decades to interpret changes in cellulose structure after physicochemical and biological treatments (Park, et al., 2010). It is important to note that chemical pulp in general has lower crystallinity ratio compered to mechanical pulp.

3 Results and Discussion

Figure 1 illustrates calculated colour differences after every 30 minute interval of accelerated ageing. It is evident that colour difference increases linearly from ΔE =1.5 until 66 hours of exposure to UV light, after which the slope significantly increases. Naturally aged samples are presented with dots numbered as follows, number one represents sample stored in the dark and dry place, two is sample stored in the common office conditions, and number three represents paper stored in a way that enabled stronger influence of natural light and atmosphere conditions. As expected, naturally aged paper stored in a dark and dry place shows the lowest ΔE=1.76, that is classified as very small noticeable difference for standard observer. Sample stored in the common office conditions has colour difference value of 6.2 which is defined as big noticeable difference in the colour for standard observer. It can be concluded that the same colour difference as the natural ageing by storing sample in the common office conditions can be achieved after 25.5 hours of exposure to UV light. Stronger influence of natural light and atmosphere pollutants led to pronouncedly high value of colour difference ΔE=13 which can be approximated by 66 hours of accelerated ageing. It is evident that approximations of the colour differences obtained by natural and accelerated ageing can help predict optical properties

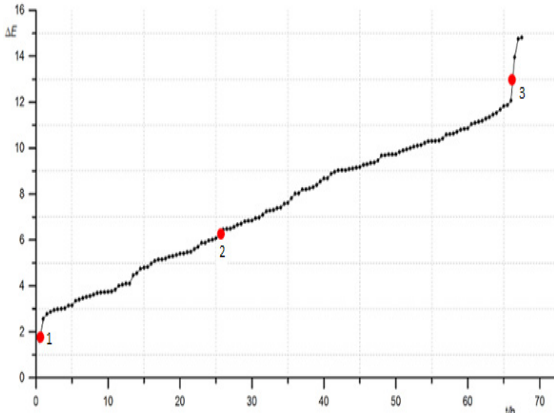

Figure 1. Colour difference in dependence to time of exposure to UV/VIS light

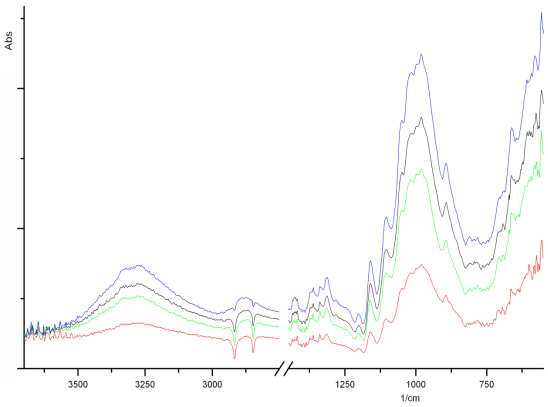

Figure 2. FTIR spectra of samples: exposed to stronger influence of natural light and atmosphere (blue), exposed to common office conditions (black), stored in the dark and dry place (green), exposed to UV light (red).

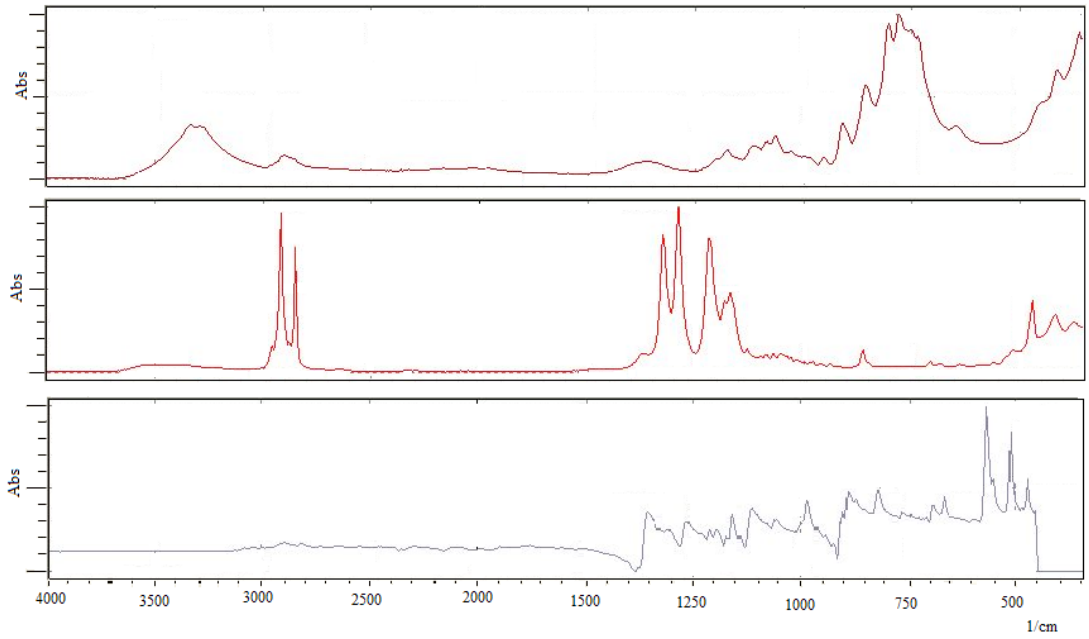

Figure 3. From top to bottom FTIR spectra of cellulose, calcium stearate and methyl yellow

of similar samples (papers constituted of same basic fibers, natural and synthetic sizing agents, coating additives and colorants) kept in similar conditions.

From the visual comparison of the measured FTIR spectra (Fig. 2.) and the spectra of cellulose (Fig 3.a) it can be deduced that no major degradation in the chemical and mechanical properties of cellulose occurred which will be further confirmed. The FTIR spectra of naturally aged and accelerated (after 66 hours of exposure) samples (Fig. 2.) show a strong broad band with the centre at 3300 cm-1, which is assigned to different O-H stretching modes and its characteristic of cellulose (Kondo, 1997), as well as two bands around 2920 and 2850 cm-1 which are mostly influenced by calcium stearate which can be seen from (Fig. 3.b). Calcium stearate ($C_{36}H_{70}CaO_4$) is used together with urea-formaldehyde and starch syrup as an additive in paper or paperboard coating formulations (Malloy, 1993). Calcium stearate acts as a lubricant to provide sufficient gloss, preventing dusting and fold cracking in paper and paperboard, urea-formaldehyde improves tear strength and starch provides additional strength to the paper web and improves moisture resistance.

All of the naturally aged samples show regularities in the spectra with minimal variations in the finger print region, furthermore naturally aged sample that shows the greatest colour difference has the highest absorbance, while the sample that has the same colour difference which was achieved true accelerated ageing has the lowest absorbance.

Table 1. Crystallinity index, energy of the hydrogen bond, asymmetric index of the samples studied

Storage	Cr.R./%	EH/kJ	a/b
Dark and dry place	38. 21	23.625	1.024
Common office conditions	34.93	23.697	1.043
Stronger influence of natural light and atmosphere	31.49	24.281	1.056
70 hours of exposure to UV light	39.56	22.385	1.028

Crystallinity index is correlated with the overall degree of order in the cellulose. The results (Table 1) obtained from naturally aged samples show decrease in CI with increasing environmental influences on the samples, contrary to that the highest CI was obtained for the sample exposed to UV light which may be due to a re-crystallization under applied conditions.

Analysis of the energy of hydrogen bond does not show large diversity in values. The lowest hydrogen bond was calculated for the sample exposed to UV light which indicates a decrease in the number of hydrogen bonds that is characteristic for the reduction of the tensile strength of the material. As for the asymmetric index, all of the calculated results indicate that all of the samples, regardless of their exposure to external conditions are evenly uniform.

Since extremely high colour differences were recorded, it is interesting to explore the changes that occur in the bands influenced by the methyl yellow which was characterized as the main colouring agent of the used samples. Methyl yellow (***, 2015), C14H15N3, has a refraction index of 1.567 which makes it applicable to ATR measurements. In comparing the spectra of measured samples (Fig. 2.) to spectra of methyl yellow (Fig. 3.c) one can observe broadening, lowering and even complete disappearing of bands around 1300, 800 and 600 cm-1.

4 Conclusions

Conducted research gave valuable information regarding the influence of various processes of natural and accelerated ageing on matte coated wrapping paper. Calculations of crystallinity index, energy of hydrogen bonds and asymmetric index showed that coated wrapping paper has high cellulose stability and uniformity and due to the use of calcium stearate can endure higher moisture environment without significant degradation in paper strength.

The proper selection of storage place can highly prolong shelf life of the wrapping paper, mainly its optical characteristics which will result in significant cost savings.

Even though accelerated ageing is not a reliable technique of predicting aging behaviour of paper it can provide fast and cost effective way to help the researchers foresight the optical appearance of samples depending on storage in the forthcoming years as long as the paper samples have similar material base. IR spectroscopy is a usable non-invasive tool for investigating paper strength without the necessity of mechanical testing, and a useful method of investigating the influence of various conditions on degradation in colour if the physical requirements for the ATR measurements are satisfied.

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