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Protective effects of synthetic and naturally occurring antioxidants in pulp products

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KEYWORDS: Antioxidants, Pulp, Hexanal, Brightness stabilization, Yellowing, Headspace GC, Organotellurium compounds, SEM-EDX.

SUMMARY: Various types of antioxidants (α -tocopherol, ethoxyquin, organotellurium compounds, flavonoids, cinnamic acid derivatives, avenanthramides) were added to handsheets of pulp (bleached thermomechanical pulp, mixtures of pulp, unbleached groundwood pulp) and headspace hexanal concentrations were recorded with respect to time in comparison with a control. α -Tocopherol and ethoxyquin were found to inhibit autoxidation in a dose dependent manner (up to 80 % inhibition). All of the antioxidants (at the 0.2 weight-% level), with varying efficacy, reduced hexanal formation. The most efficient protecting systems (α -tocopherol, organotellurium 12 together with sodium sulphite) caused a ca 90 % reduction in hexanal emission after 8 weeks as compared to the control. Significant reduction in hexanal formation was in some cases observed as long as eight months after addition to the pulp.

The antioxidants were also evaluated for their capacity to inhibit brightness reversion in pulp. After accelerated photo- and thermal aging, samples protected with some of the antioxidants (α -tocopherol, organotellurium 11) showed similar or slightly better yellowing characteristics as compared to the untreated control. However, the loss in brightness observed with many of the compounds seemed related to the colour of the antioxidants themselves. After this initial, post addition yellowing, further loss of brightness occurred much more slowly in the antioxidant-treated samples than in the control. Some of the additives (sinapinic acid, organotellurium 12) were almost as efficient inhibitors of this yellowing as Cibafast H and 4-hydroxy-TEMPO in the tested pulp systems.

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Paper is never completely odourless. There are several reasons for this. Microbial activity under anaerobic conditions is frequently a problem when recycled pulp is used. Also, paper additives and degradation of additives contribute to paper odours. However, auto- and photo-oxidation of wood extractives (linoleic acid, oleic acid, linolenic acid) is probably the main source of odour in many paper grades rich in wood extractives. Hexanal is a predominant oxidation product but a large variety of other aldehydes, ketones and alcohols are also formed. Several of these compounds have extremely low odour threshold levels (in or below the ppb region). One of the main purposes of food packaging is to protect and conserve the quality of the food. Contamination of the food with odorous compounds from paper packaging materials is therefore a big problem (Forsgren et al 1999;

Lindell 1991; Tice, Offen 1994). Also, consumers will disapprove of other paper products (for example catalogue paper) having intense or unexpected odours. Since autoxidation products (Gardner 1989) are the main reasons for the above problems, it would seem worthwhile to investigate the influence of added antioxidants to pulp and paper products. Some work along these lines has recently been reported. Thus, heat treatment under low oxygen pressure of paper made from TCF-bleached hardwood sulphite pulps and subsequent addition of surprisingly small amounts (less than 10 ppm) of various antioxidants (BHA, BHT, tert-butylhydroquinone, propyl gallate, sodium ascorbate and tocopherol) reduced the amount of volatiles (ca 25 %) in the paper headspace (Wiik et al 1998; Wiik 1999). For paper materials in general, it is also desirable to improve on brightness. At brightness levels comparable to what can be achieved with bleached chemo thermomechanical pulp (BCTMP), mechanical pulps could potentially be employed in high value paper products such as business forms, reprographical papers and writing papers. However, the rapid light-induced yellowing of these pulps restrict their use to short-life paper products. The yellowing phenomenon, also known as brightness reversion, occurs as a result of exposure to light and is partly attributable to photo-oxidation of lignin (Gellerstedt et al 1983). The processes responsible for photoyellowing are, as yet, incompletely understood (Leary 1994). However, there is little doubt that radicals are involved and yellow color is thought to arise due to oxidation of phenoxyl radicals to quinones.

The goal of research into yellowing is to discover a way of inhibiting the process. The use of radical scavenging additives to retard brightness reversion of mechanical pulps has seen increasing attention. Ascorbic acid is a well-known radical scavenger reportedly capable of photostabilizing mechanical pulp to a certain extent (Ragauskas, 1994). Also, various thiols (Kutney 1986; Cole, Sarkanen 1987) were found to initially bleach existing chromophores and subsequently to retard yellowing. Since photoyellowing is brought about by such a multi-faceted mechanism, combinations of additives have been sought (Pan et al 1996; McGarry et al 1999).

In principle, antioxidants for pulp and paper products could be derived from any source and exert their anti-oxidative effect according to any of the established mechanisms for antioxidant protection (Scott 1988). Except for outstanding antioxidative capacity, certain criteria must be fulfilled for the applications indicated above, though. Thus, potentially useful compounds must show minimal toxicity, be colourless (or at least only weakly coloured), odourless, photochemically and thermally robust, nonvolatile and be available in large

quantities at a reasonable cost. In the present investigation, antioxidants obtained from natural sources (quercetin, catechin, α -tocopherol, cinnamic acid derivatives, avenanthramides) as well as some synthetic compounds (ethoxyquin, organotellurium compounds) were evaluated for their capacity to reduce emission of hexanal in pulp as assessed by headspace gas chromatography. The capacity of the antioxidants to inhibit brightness reversion was also studied.

Materials and methods

Antioxidants:

α -Tocopherol (1), ethoxyquin (2), quercetin (6), catechin (7), sinapinic acid (8), Cibafast H (Ciba Specialty Chemicals) and 4-hydroxy-TEMPO are commercially available. Organotellurium compounds 3 (Engman 1983), 4 (Kanda et al, 1999), 5 (Engman and Persson 1993), 11 (Shanks et al 2002) and 12 (Engman et al 2002), thiol 13 (Shanks et al 2002) as well as avenanthramides 9 and 10 (Bratt et al 2002) were prepared according to literature methods.

Pulp samples:

Handsheets were composed either of (A) bleached thermomechanical pulp (TMP), or (B) a mixture of TMP (55.9 %), groundwood pulp (GW) (16.1 %), bleached softwood kraft pulp (13.7 %) and recycled pulp (14.3 %) or (C) unbleached GW pulp.

Addition of antioxidants to handsheets:

Handsheets were produced according to a international method based on ISO 5269-2. Each handsheet weighted about 4.5 g with a basis weight of 150 g/m². Antioxidants were dissolved either in 15 ml water (14 ml plus 1 ml 1M NaOH in the case of compounds containing acidic groups) or 15 ml ethanol and sprayed or soaked onto the still wet handsheets to distribute them as evenly as possible over the material. After drying for 5 min at 96°C, the samples were stored under ambient conditions in tightly wrapped aluminum foil packages.

In order to test reproducibility of preparation and analyses, five sheets were treated with an antioxidant, and three GC headspace analyses per sheet were performed after one week. The analyses showed a standard deviations of up to 3 % for the triplicates (at a headspace hexanal concentration of about 25000 ng/g. The standard deviation for the mean values of the triplicates of the five samples was 14 %.

Headspace gas chromatography:

Each sample (1.0 or 1.5 g) was cut into strips (0.5 x 4 cm), placed into a 22 ml headspace vial sealed with a septum and introduced into a Perkin Elmer HS-40 XL Hewlett Packard 7694 auto headspace sampler. Each vial was then thermostatted at 90°C for 40 min and an aliquot of the headspace was directly introduced into the gas chromatograph (PE or HP). The volatile compounds were subsequently separated on a DB-1 column (length=30 m, inner diameter=0.53 mm, stationary phase=1.5 μ m) using a temperature program from 45°C to 230°C at 10°C/min, and detected with a flame ionization detector (FID).

The headspace hexanal concentrations from single extractions were determined using the following

procedure: calibration solutions were made by diluting a stock solution of hexanal in triacetin (Merck, Germany, >99 %) to suitable concentrations (0.3-0.4 μ g/ml). These calibration solutions were then added to the 22 ml headspace vials and analyzed in a randomized order using the conditions described above. A calibration curve (integrated area vs concentration) was used to calculate the headspace hexanal concentration of the samples.

Accelerated aging:

Accelerated photo aging and thermal aging of the samples were performed according to DIN 54 004 and ISO 5630 specifications, respectively.

Measurement of brightness:

Measurement of brightness of photo- and thermally aged samples were performed according to ISO 2470 specifications.

Distribution of antioxidant 11 in paper by EDX-analysis:

A ca 1 cm² piece was cut from a dried (1 h at 70°C) handsheet which had been sprayed from one side with an ethanolic solution of antioxidant 11 (2 % by weight). The piece was put between Teflon plates, cooled with liquid nitrogen and a clean cut made orthogonal to the surface with a scalpel. To increase the conductivity of the sample, the surface of the cut was covered with carbon vapour using a Balzers-Sputter-Coater. A Quanta 200 scanning electron microscope (FEI) was used for the investigation which involved linescan with EDX-mapping in 128 points between the two surfaces of the paper. For each point, the concentration of tellurium was determined. Since the signal to noise ratio was only 2/1, 20 linescans were run and the mean values used. Shown in Fig. 2 are the values obtained after subtraction of the background.

Results and discussion

When evaluating antioxidant studies in paper and pulp products, one must realize that the results should be interpreted with some caution. A breakthrough in the protection of one type of pulp with a certain antioxidant does not necessarily fully translate to other pulp and paper products. In fact, due to continuous changes in the quality of the raw-material or in the manufacturing process, it may even prove difficult to reproduce an observed antioxidant effect in a similar type of pulp. Also, differences in handling and storage of the materials could have a dramatic effect on the aging process. In order to make a comparison between different samples of pulp, we have therefore always included a well-established antioxidant in our studies to which the results could be related.

Hexanal is commonly used as an "indicator" as to the extent of autoxidation and/or photooxidation in various paper and pulp products containing unsaturated fatty acids (Forsgren et al 1999; Forsgren et al 2002; Frisell 2002). Its formation is known to involve many steps. Initially, linoleic or linolenic acid are transformed into the corresponding hydroperoxides via a radical reaction with molecular oxygen. These species then undergo degradation via various pathways to give hexanal as one of a multitude of decomposition products (Hancock, Leeves 1989; Przybylki, Eskin 1995).

Table 1. Emission of hexanal (in % of control) from handsheets of pulp A treated with various amounts of α -tocopherol (1) and ethoxyquin (2).

additive	amount added (weight-%)	hexanal after 9 days (in % of control)	hexanal after 3 weeks (in % of control)
control	0	100	100
α -tocopherol(1)	0.2	79	100
α -tocopherol(1)	0.5	30	67
α -tocopherol(1)	1.0	26	53
α -tocopherol(1)	5.0	13	20
ethoxyquin(2)	0.2	45	67
ethoxyquin(2)	0.5	40	70
ethoxyquin(2)	1.0	34	60
ethoxyquin(2)	5.0	21	53

Initially, we investigated the capacity of two well-known chain-breaking donating antioxidants, α -tocopherol (1) and ethoxyquin (2) (*Scheme 1*), to reduce emission of hexanal from pulp A. Concentrations ranging from 0.2 weight-% (2 kg/ton) to 5 weight-% (50 kg/ton) were used (calculated on “dry pulp”, which typically contains about 5-10 % water). As shown in *Table 1*, the antioxidants reduced hexanal emission in a dose dependent manner as compared with the untreated reference sample as analyzed after 9 days and three weeks. However, even in the highest concentrations it was not possible to completely inhibit hexanal formation. At the lowest concentration (0.2 weight-%), ethoxyquin seemed to be the best inhibitor after 9 days. However, as analyzed after three weeks, α -tocopherol turned out to be the most efficient protectant in essentially all concentrations used. In another series of experiments, samples containing 1 weight % α -tocopherol were stored tightly wrapped into packages of aluminum foil at room temperature and analyzed after 2,

4 and 8 months. The concentrations of hexanal in the headspace of these samples were 11, 16 and 26 %, respectively, of that found in the corresponding controls. Thus, provided the exposure of samples to light and air is kept to a minimum, the effect of added antioxidant could be maintained for a considerable period of time.

Organotellurium compounds show interesting antioxidative capacity. They are known to catalyze decomposition of hydroperoxides (Vessman et al 1995). Also, they could act as chain-breaking donating antioxidants (Malmström et al 2001). Addition of 0.2

weight-% of organotellurides 3 and 4 to handsheets of pulp A caused a reduction in the emission of hexanal by 46 and 40 %, respectively, as compared with a control after three weeks. Organotellurium compound 5 when added in low quantities (0.1 weight-%) to pulp B caused a 55 and 30 % reduction in hexanal emission after 2 and 9 weeks, respectively, as compared with a control. Shown in *Fig. 1* are representative chromatograms (intensity vs retention time in min) of the headspace of the reference and protected samples recorded after two weeks. Thus, compounds of this type could be as efficient as α -tocopherol or ethoxyquin in reducing hexanal emissions.

The study was then extended to include some other types of antioxidants. Flavonoids are an important class of dietary antioxidants largely distributed in plants. They can be considered as multi functional in the sense that they could act both as hydrogen atom donors and as metal chelators (Dangles et al 2000). This is also true for many naturally occurring cinnamic acids and derivatives

Fig. 1. Gas chromatograms of the headspace from a reference handsheet and the corresponding sample containing 0.1 weight-% of antioxidant 5 (intensity on y-axis vs retention time in min on x-axis). Chromatograms were recorded two weeks after preparation of the sample.

Table 2. Emission of hexanal (in % of control) from handsheets of a mixture of pulp B treated with various antioxidants.

additive	amount added (weight-%)	hexanal after 1 week (in % of control ^a)	hexanal after 4 weeks in & of control ^b)	hexanal after 8 weeks (in % of control ^c)
control	0	100	100	100
α -tocopherol (1)	0.2	29	25	42
quercetin (6)	0.2	18	20	49
catechin (7)	0.2	41	67	90
sinapinic acid (8)	0.2	16	17	40
avenanthramide 9	0.2	15	16	32
organotellurium 11	0.2	37	46	61
organotellurium 12	0.2	8	9	18
sodium sulphite	1.0	11	7	16
sodium sulphite plus organotellurium 12	1.0,0.2	7	5	11

^a 18000 ng/g ^b 56600 ng/g ^c 44800 ng/g

Table 3. Emission of hexanal (in % of control) from handsheets of pulp C treated with various antioxidants.

additive	amount added	hexanal after 1 week (in % of control ^a)	hexanal after 4 weeks (in % of control ^b)	hexanal after 8 weeks (in % of control ^c)
control	0	100	100	100
α -tocopherol (1)	d	55	11	7
avenanthramide 9	d	70	31	57
avenanthramide 10	d	43	37	50
organotellurium 11	d	14	50	59
organotellurium 12	d	18	35	30
sodium sulphite	d	114	432	186
thiol 13	d	17	3	8
thiol 13 plus organotellurium 11		13	7	42
sodium sulphite plus organotellurium 12	d,d	13	6	35

^a 1393 ng/g ^b 1160 ng/g ^c 13500 ng/g ^d 3×10^{-5} mol/4.5 g handsheet

Scheme 1. Structures of antioxidants studied in this work

thereof. The protective effects of quercetin (**6**), catechin (**7**), sinapinic acid (**8**) as well as avenanthramide **9** were therefore studied. Organotellurium compounds **11** and **12**, respectively, were included representing a lipophilic and a hydrophilic derivative, respectively. In order for the organotellurium compound to act in a catalytic fashion, a stoichiometric reducing agent has to be present. Sodium sulphite was therefore included in the study. This time, handsheets were composed of a mixture of pulps (TMP, GW, bleached softwood kraft pulp and recycled pulp; pulp B). Headspace hexanal concentrations in comparison with a control are shown in Table 2. 0.2 Weight -% of the antioxidants were sprayed on to the pulp. As shown in Table 2, all compounds showed a protective effect throughout the 8 weeks of the experiment.

However, the protection offered by catechin (**7**) was only very moderate (10 % reduction of hexanal after 8 weeks).

α -Tocopherol (**1**), quercetin (**6**), sinapinic acid (**8**) and the lipid soluble organotellurium compound **11** offered intermediate protection (39 – 60 % reduction after 8 weeks) whereas avenanthramide **9**, water soluble organotellurium compound **12**, and the mixture of compound **12** with sodium sulphite gave the best results (68 – 89 % reduction of hexanal after 8 weeks; Table 2). Since sodium sulphite efficiently suppressed hexanal formation by itself (84 % reduction after 8 weeks), it is not clear whether or not the organotellurium compound is acting in a catalytic fashion when co-administered with sulphite. The 8-weeks ordering of antioxidants was largely reflected also in the 4 weeks results. However, quercetin seemed to perform relatively better during the first four weeks of the study. As judged from the 8 weeks results, organotellurium **12** was the best protectant for this kind of pulp.

Some of the antioxidants were also added to pulp C and hexanal emission was monitored after 1, 4 and 8 weeks. In contrast to previous studies, the addition of antioxidants were made on a molar rather than weight basis. 3×10^{-5} Mol of antioxidant was added per 4.5 g of handsheet (this corresponds to 0.2 weight-% of a compound with a molecular weight of 300). Another avenanthramide **10** was included in the study and organo-

tellurium compounds **11** and **12** were also tested in the presence of equimolar amounts of a thiol reducing agent **13** and sodium sulphite, respectively. The results are shown in *Table 3*. Avenanthramides **9** and **10** and the lipid soluble organotellurium compound **11** offered some protection (41 – 50 % reduction after 8 weeks). The water soluble organotellurium compound **12**, with or without sulphite, and the lipid soluble organotellurium **11** with thiol offered intermediate protection (58-70 % reduction after 8 weeks) whereas α -tocopherol gave the best results (93 % reduction of hexanal after 8 weeks). Thiol **13** turned out to be a surprisingly efficient inhibitor by itself (92 % reduction of hexanal after 8 weeks). Much to our surprise, sodium sulphite acted as a prooxidant when present in such a low amount (the amount used corresponds to less than 0.1 weight-%). The results after 1 and 4 weeks (but not 8 weeks) with organotellurium **12** (with or without sodium sulphite) seem to indicate some regeneration of the organotellurium compound. Thiol **13** showed such efficient inhibition of hexanal emission by itself (92 % after 8 weeks) that its regenerating capacity could not be assessed. The 4-weeks ranking of antioxidants was slightly different from the 8 weeks results. Both organotellurium compounds, when added together with reducing agents, offered a much better protection during the first 4 four weeks of the study than after 8 weeks. In this type of pulp, α -tocopherol offered the best protection against autoxidation.

Antioxidant-treated handsheets prepared from pulp B were also subjected to accelerated photo aging (*Table 4*) and thermal aging at 105°C (*Table 5*) and their brightness assessed in comparison with an untreated control and handsheets containing Cibafast H (a UV absorber) and 4-hydroxy-TEMPO (which has been reported to efficiently inhibit yellowing) (McGarry, Yuan et al, 2000). Out of the antioxidants tested, only α -tocopherol (**1**) and lipid soluble organotellurium compound **11** caused a slight gain in brightness as compared with the untreated control after irradiation for 240 min or heating for 72 h (Tables 4 and 5). All other compounds caused a significant loss in brightness as seen already in the post addition values. This is probably because the compounds are colored by themselves. In order to compare the effects of the antioxidants after this initial yellowing, the brightness loss (BL) was calculated according to equation 1:

$$\text{Brightness loss (BL)} = \frac{\text{post addition brightness of sample} - 240 \text{ min (72 h) brightness of sample}}{\text{initial brightness of sample}} \quad [1]$$

Most of the antioxidants tested caused a larger or similar loss in brightness than observed for the control (α -tocopherol, quercetin, catechin, avenanthramide **9**, organo-

Table 4. Brightness (ISO 2470) of antioxidant-treated handsheets of pulp B before and after accelerated photo aging (DIN 54 004).

additive	amount added (weight-%)	initial	post addition	30 min	60 min	240 min	BL ^a
control	0	70.4	69.4	67.5	67.3	66.4	3.0
α -tocopherol (1)	0.2	70.4	70.5	68.4	68.0	66.8	3.7
quercetin (6)	0.2	69.7	67.5	60.0	61.4	64.0	3.5
catechin (7)	0.2	70.2	68.7	66.3	65.8	64.3	4.4
sinapinic acid (8)	0.2	70.2	64.0	61.2	61.4	61.5	2.5
avenanthramide 9	0.2	70.4	65.6	62.8	62.7	62.6	3.0
organotellurium 11	0.2	70.6	70.7	68.1	67.9	66.8	3.9
organotellurium 12	0.2	70.6	64.4	62.8	62.8	62.5	1.9
Cibafast H	0.2	70.5	64.3	62.3	62.1	62.2	2.1
4-Hydroxy-TEMPO	0.2	70.2	64.2	62.7	62.5	62.9	1.3

^aaccording to eq 1

Table 5. Brightness (ISO 2470) of antioxidant-treated handsheets of pulp B before and after accelerated thermal aging (ISO 5630).

additive	amount added (weight-%)	initial	post	24 h	48 h	72 h	BL ^a
control	0	70.4	69.4	67.9	67.1	66.3	3.1
α -tocopherol (1)	0.2	70.4	70.5	68.3	67.3	66.8	3.7
quercetin (6)	0.2	69.7	67.5	63.6	63.5	63.2	4.3
catechin (7)	0.2	70.2	68.7	65.4	63.9	62.3	6.4
sinapinic acid (8)	0.2	70.2	64.0	62.4	62.1	61.7	2.3
avenanthramide	0.2	70.4	65.6	63.8	63.4	63.0	2.6
organotellurium 11	0.2	70.6	70.7	68.3	67.8	67.0	3.7
organotellurium 12	0.2	70.6	64.4	63.6	63.2	62.8	1.6
Cibafast H	0.2	70.5	64.3	63.8	63.4	62.9	1.4
4-Hydroxy-TEMPO	0.2	70.2	64.2	62.6	62.0	61.4	2.8

^aaccording to eq 1

tellurium **11**), whereas some additives markedly slowed down yellowing (sinapinic acid, organotellurium **12**). In fact, the protective effect of organotellurium **12** could match those seen with Cibafast H and 4-hydroxy-TEMPO. For the future, less colored antioxidants must be sought. Alternatively, the active protectants found could be tested together with additives which are known to cause an initial gain in brightness.

The organotellurium compounds studied in this work carry an atom which can be monitored by EDX (energy dispersive X-ray) analysis. Thus, these compounds offer a unique possibility to study penetration of the antioxidant into the paper material by SEM (scanning electron microscope) with linescan analysis. Antioxidant **11** (2 % by weight in ethanol) was therefore sprayed from one side onto a handsheet of paper (pulp C) and, after drying, the cross section analyzed in a direction orthogonal to the surface. *Fig 2* shows linescan of tellurium (with the proper correction for background) as a function of the distance from the surface. The figure indicates only a 97 μ m penetration of compound **11** into the paper. Thus, the antioxidant seems to interact strongly with the polar groups of the material. Due to exposure to light and air oxygen, the very surface of the paper material is likely to be most susceptible to autoxidation and yellowing. Enrichment of the antioxidant in the surface layer could therefore be desirable. However, for obtaining a better and longer-lasting antioxidant protection of the material, one could consider other ways of addition which cause a more even distribution of the antioxidant throughout the paper material.

Fig. 2 EDX-analysis. Concentration of tellurium (y-axis) in the cross section as a function of the distance from the surface (x-axis; 0-300 μm). The maximum penetration of the organotellurium compound 11 is ca 97 μm.

Conclusions

We have shown that various types of natural and synthetic antioxidants when added to handsheets of pulp in low concentrations (0.2 % weight-%) could significantly reduce the emission of hexanal. The most efficient compounds caused a 90 % reduction after eight weeks but significant reduction could be observed as long as eight months after addition. Because the antioxidants are coloured, their capacity to inhibit brightness reversion was limited (post addition yellowing). However, further loss of brightness occurred much more slowly in the antioxidant treated samples than in the control.

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