THE EFFECT OF SEVERAL NON-OXIDIZING BIOCIDES ON FINE PAPER WET-END CHEMISTRY

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Biocide programs have become necessary in most fine paper manufacturing circuits, as drastic reduction of fresh water consumption in the industry enhances microbial development. Depending on their chemical nature, biocides may interfere with typical wet-end chemistry additives and furnish. A reference wet-end chemistry was set (including fixing aid, dry strength aid, sizing agent, and retention system), then biocides were added to the furnish (bleached virgin fibres + mineral filler) prior to handsheet making. Four of the tested biocides (organo-sulfur, dibromonitrilopropionamide, isothiazoline, and glutaraldehyde) were not found to interact with wet-end chemistry. On the other hand, the tested quaternary ammonium salt biocide showed very detrimental effects: it reduced filler retention in the sheet, decreased sheet strength, and destroyed sizing (sheet hydrophobicity).

Keywords: Biocides; Wet-end; Interaction; Sizing; Dry strength; Retention

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INTRODUCTION

In order to manufacture fine papers, several different chemicals are required, most of them added in the wet-end. These additives serve several functions: process additives (e.g. retention and drainage aids), functional additives (sizing agents, dyes, optical brightening agents, etc.), and curative additives (biocides, defoamers, dispersants, etc.). Biocides are routinely used to minimize the productivity losses due to microbiological growth. Microbiological development can hardly be avoided in papermachine circuits. Reduction of water consumption by the industry leads to closure of the water loops, which favors the build-up of organic material, serving as nutrients for micro-organisms. Low levels of retention on the wire amplify the phenomenon, as un-retained starch accumulates in the circuits.

The chemistry of papermaking is becoming more and more complex over the years, and the additives need to be applied in higher concentrations, because of stringent productivity and environmental pressures imposed on the process (Gratton and Pruszynski 2003). Sometimes, interactions between additives can be synergistic, but two chemicals may also unfortunately react with each other, reducing their efficiency. These uncontrolled interactions may not only reduce their effectiveness but may also result in severe quality and productivity issues (Gliese 2003; Gratton and Pruszynski 2003; King 2004).

Biocides are likely to be involved in different kind of interactions, depending on their chemical structure. Therefore, a better understanding of their potential impact on wet-end performance is essential.

Besides oxidizing agents (such as chlorine dioxide or hydrogen peroxide), which react with any organic material, a variety of organic molecules are employed to selectively inhibit or kill bacteria. The main classes of biocides used in the papermaking industry are (from Simpson 2002, Prichard 2003): halogenated hydantoin, isothiazolones, dibromonitrilopropionamide (DBNPA), methylene bisthiocyanate (MBT), quaternary ammonium compounds, tetrakyshydroxymethylphosphoniumsulfate (THPS), glutaraldehyde, and carbamates as fungicides. The most recent trend for the development of biocides has been towards stabilized halogens and weak oxidants. In this paper, we focus on non-oxidizing biocides.

Chervenak (2000) gives a very good review of their bio-active mechanisms, which is summarized hereafter, for the biocides tested in this study.

Quaternary ammonium salts are prominent biocides in the field of water treatment (non-drinking). They are also employed to a lesser extent in papermaking, to treat fresh water. They modify the permeability of bacterial cell walls (which are anionic), which causes internal osmotic changes, and leads to the death of the cell. Their action can be impaired by a high chloride concentration, or organic foulants. Over-dosage of quaternary ammonium salts has been reported to cause foaming problems. They are both cationic and surface active, and as such, are likely to be involved in interactions with wet-end additives. Novel formulations of quaternary ammonium salts can also limit corrosion (Huang et al. 2009).

Organo-sulfur compounds (thio-carbamates) act as metal chelants (free iron, copper, etc.), which affect cell metabolism. They have a slow kinetic of action, which is an advantage in tightly closed systems. They carry an anionic charge.

Isothiazolones are very broad spectrum biocides. Their N-S bond reacts with thiol groups in proteins, which inhibits protein activity. They are non-ionic and non-surface active, which should limit potential interactions with other wet-end chemicals.

Dibromonitrilopropionamide (DBNPA) rapidly degrades under alkaline conditions. It is sensitive to UV light and nucleophilic substances. It is uncharged and non-surface active; therefore it seems unlikely to interact with wet-end additives.

Glutaraldehyde is a protein cross-linking agent, which is used as a biocide. It is able to bridge amino-acids or H-bonds, thereby modifying the protein’s folding and stopping its activity. It is thus likely to react and be consumed by wet-end additives that carry an amine function. Glutaraldehyde is sometimes replaced or used in combination with ammonium bromide to destroy catalase.

Some biocides have been reported to have a detrimental impact on AKD and ASA sizing (Raymond et al 2001): poly(oxyalkenes), benzylammonium, bromonitrostyrene, and benzothiazoles. The three first biocides are cationic. The poly(oxyalkene) used in this study was also surface active. This may partly explain the observed detrimental effect on sizing (see Zeno et al. 2005 for a detailed account of interactions between surface active substances and sizing development). On the other hand, sulphones, carbamate, glutaraldehydes, and acetophenones were not found to interfere with either AKD or ASA sizing.

The objective of this study is to evaluate the potential interactions between selected non-oxidizing biocides and typical wet-end chemistry additives used for fine paper grades. A reference wet-end chemistry is set (including fixing aid, dry strength aid, sizing agent, and retention system), then model biocides (pure molecules of the main active substances in commercial formulations) were added to the furnish (bleached virgin fibres + mineral filler) to evaluate whether they would affect filler retention, sizing development, and sheet mechanical properties.

EXPERIMENTAL

Materials

Biocides

Commercial biocidal formulations are often mixtures of several classes of biocides, to ensure the widest spectrum of action on bacteria. Commercial biocides are known to be formulated with anionic dispersants that could interfere with cationic wet-end additives.

Five biocides type were selected to be representative of industry practice (namely quaternary ammonium salt (quat.), organo-sulfur (thiocarbamate), DBNPA, isothiazoline, and glutaraldehyde). Then, corresponding pure molecules of the main active substance of the commercial mix were obtained and used as model biocides, so that formulation additives would not interfere here (see Table 1).

Table 1. Selected Molecules as Model Biocides

type	molecule	CAS	reference
quaternary ammonium salt	benzyltetradecyldimethylammonium chloride	139-08-2	Sigma B5651
organo-sulfur	sodium dimethyldithiocarbamate	128-04-1	Sigma 71513
DBNPA	2,2-Dibromo-2-cyanoacetamide	10222-01-2	Sigma 540978
isothiazoline	5-chloro-2-methyl-thiazol-3-one	26172-55-4	Sigma 00344
glutaraldehyde	pentanedial	111-30-8	Sigma 340855

Other wet-end additives

The selected additives required by the reference wet-end chemistry are listed in Table 2. The fixing aid was polyaluminium chloride (PAC). The dry strength aid was a cationic potato starch. The sizing agent was alkenylsuccinic anhydride (ASA), emulsified with cationic starch (1:1 emulsion, 30 s mixing at 20000 rpm in a blender, STARO,

Table 2. Additives of the Reference Wet-End Chemistry

Function	Type
Fixing aid	PAC (Eka PAC18)
Dry strength aid	Cationic starch (Roquette Hi-Cat)
Sizing agent	ASA (Kemira Hydrores SA1000)
Sizing agent emulsifier	Cationic starch (Roquette Vector SC)
Retention polyelectrolye	CPAM (Kemira K3400R)
Retention microparticle	Bentonite (Kemira Altonit SF)

France). The emulsion was used within 3 hours, then a fresh one was prepared. The retention system consisted of a flocculant (cationic polyacrylamide, CPAM) and a microparticle (bentonite).

The Optical Brightening Agent (OBA, also called a “fluorescent whitener”) used in some experiments was a “di-sulfonated” type (di-amino-stilbene-di-sulfonated acid, pure molecule).

Pulp and filler

The furnish consisted of a virgin fibre mix (bleached kraft pulp) with 20% of added filler. The fibre mix consisted of 80% hardwood fibres refined at 34°SR (mixture of birch, beech, and eucalyptus in equal proportions) and 20% softwood fibres refined at 24°SR. The fine elements content of the fibre mix was 17% (defined as elements passing through a 200 mesh wire during hyperwashing with the dispersing agent sodium tetrapyrophosphate, TAPPI test method T261cm94). The fibres were reslushed in tap water at a temperature of 40°C and a concentration of 3 g/L. The filler was a slurry of precipitated calcium carbonate (PCC, Omya Syncarb F0474 MJ slurry).

Methods

Biocides characterization

Cationic demand was measured by colloidal titration using polyethyleneimine (PEI), and anionic demand using PVSK (potassium polyvinyl sulfate), both with a Mütek PCD03 streaming current detector.

Their effect on surface tension was measured with a Maximum Bubble Pressure tensiometer (Sita t60), with bubble life time = 15 s, at 22°C. Biocides were diluted in tap water only, at dosages corresponding to same liquid phase concentration as with the pulp.

Additives injection sequence and handsheet making

All experiments were performed with tap water ($[Ca^{2+}]$=70 mg/L) at a temperature of 40°C, unless otherwise specified. The furnish consisted of fibre suspension at 3 g/L with 20% added filler (i.e. 0.6 g/L).

Biocides were added to the furnish before all other additives (under gentle stirring in a beaker), with a minimum contact time of 10 min. Tests were performed within 3 hours.

Handsheets were made on the FRET device (Retention Handsheet Former, Techpap, Gières, France), which can form handsheets at near headbox consistency and shear level (here handsheet were formed without dilution at 3.6 g/L). This made it possible to evaluate all relevant wet-end performance properties on handsheets (and on the same furnish batch as well). The fixing aid and cationic starch were added to the furnish (under gentle stirring in a beaker) with the following kinetics:

- t=0 min : introduction of PAC solution to the furnish
- t=2 min : introduction of cationic starch solution
- t=5 min : start of FRET test ➔ furnish poured into the bowl of the FRET

Then the next additives were added in the FRET bowl under strong and constant stirring (1500 rpm) :

- t=5 min 0 s : introduction of ASA emulsion
- t=5 min 15 s : introduction of CPAM solution
- t=5 min 40 s: introduction of bentonite suspension
- t=5 min 50 s: filtration / sheet forming (The pulp sample was drained for 2 s with a vacuum of 400 mbar through a bronze single forming fabric (Martel Catala, Tricot 25/cm, newspaper grade)).

The handsheets were then dried on a Rapid Köthen device (7 min, at 93°C). The target grammage was 80g/m².

Sheet testing procedures

The sheet physical properties were assessed using the following standard methods: pre-conditioning (NF EN 20 187, 1993), basis weight (NF EN ISO 536, 1996), burst index (NF EN ISO 2758, 2004), and sizing degree (NF EN 20535, 1994, i.e. Cobb60 test, which is a measurement of water uptake by the sheet during 60 s, under a given water column height).

Contact angles of water droplets deposited on the handsheet were measured by image analysis, with an axi-symmetric drop shape tensiometer (Tracker device, ITC, France). If angle>90°, the water droplet does not wet the substrate, because the surface has a lower energy; this is representative of high hydrophobicity and therefore good sizing. In this case, the contact angle value is usually constant over time, and recording an initial angle value is enough. On the other hand, when angle<90°, the droplet tends to spread over the substrate; here the contact angle value decreases with time. This is representative of poor sizing. In the case of high contact angles (angle>90°), water penetration in the sheet was found to be negligible over a time scale of several minutes (measured by comparison with a plastic substrate). For lower contact angles, the drops were quickly absorbed in the sheet.

The filler retention in the sheet was evaluated by incineration of the handsheet, at 525°C for 4h (ISO 1762, 2001).

Furnish zeta potential study

In order to directly assess adsorption of (charged) additives on the furnish, their influence on zeta potential (ZP) was measured. Biocides were added to the furnish under gentle stirring (at 3.6 g/L, 40°C). Samples were taken over time, and the furnish zeta potential was measured with a Mutek SZP-04 (with which a pulp pad is formed against a wire under pressure, and the streaming potential is measured.).

OBA/biocides interaction study

A pure optical brightening agent solution was tested for possible interactions with biocides, using a spectroscopic method. A fresh solution of OBA was prepared each time in deionized water (at a concentration corresponding to 0.4% addition on pulp), and the reference UV/visible spectrum was measured (SpectroFlex 6600 WTW). The diluted OBA solution was protected with an aluminium foil cover to prevent degradation from UV light (the OBA degradation over a typical measurement cycle was measured to be less than 1% under these conditions). Then the biocide was mixed with the OBA solution, and the corresponding spectrum was measured, as a function of time. Possible formation of complexes was tested by turbidity measurement (Hach 2100P), particle size (Malvern Nanosizer ZS), and particle zeta potential (Malvern Nanosizer ZS).

RESULTS AND DISCUSSION

Contrary to most process additives, biocides are dosed based on the volume of the liquid phase, as they are intended to treat a given volume of water (and not a given mass flow of furnish solids). We have tried to estimate their concentration in the circuits, based on a typical fine paper mill daily consumption of non-oxidizing biocides, limited to the short circulation. The reported data show that the average biocide concentration in the wet-end loop is about 0.5-1 ppm for most biocides (quat., organo-sulfur, DBNPA, glutaraldehyde). However, non-oxidizing biocides are usually added in shock treatment for better efficiency (typically 4 to 6 shots of 10 to 30 min per day). The instant biocide concentration after the shock injection is thus actually 8 to 36 times higher (i.e. roughly 5 to 50 ppm). This should be taken into account, as this is the effective concentration of biocide that may interact with other wet-end additives. Moreover, their anticipated low retention in the sheet will further increase their instant concentration in the short circulation. That is why the following concentration range has been studied here: (1,10,100 ppm).

On the other hand, isothiazoline is a very efficient biocide, so that lower average dosages are required (about 0.01 ppm). This corresponds to an instant biocide concentration of 0.05 to 0.5 ppm. The chosen concentration range for the isothiazoline was extended to (0.1, 1, 10 ppm).

The quaternary biocide is strongly cationic (specific anionic demand of 2955 μeq/g). The organo-sulfur biocide is weakly anionic (specific cationic demand of 15 μeq/g). The DBNPA, isothiozoline, and glutaraldehyde are neutral. The quaternary biocide is also a surface active molecule, which strongly lowers the surface tension of the liquid phase at concentrations used in the study, as reported in Fig. 1. Other biocides did not show significant effect on surface tension.

The reference wet-end chemistry was optimized (not detailed here), so that acceptable sheet properties were obtained (filler content, mechanical properties and sizing representative of fine paper characteristics, see Fig. 2). The filler content in the sheet was 12.6 %. The burst index was somewhat low; that is because the sheet was formed at a rather high consistency (compared to standard handsheet forming), so that formation was degraded. The required dosage of ASA to reach strong sizing was admittedly high compared to typical industrial usage, but in this case full sizing must be reached through wet-end addition only, whereas in the industry, sizing aids addition is usually split between the wet-end and the size-press (with starch contributing to sizing as well).

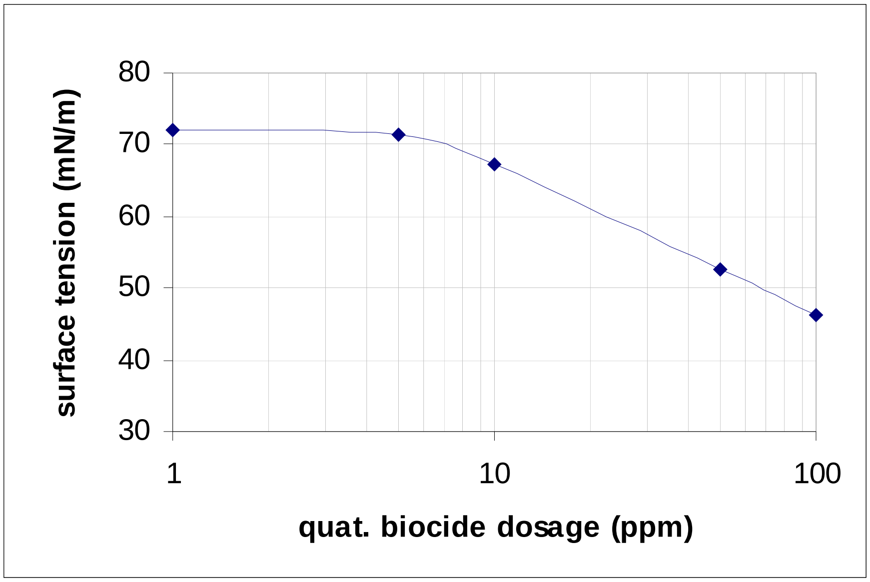

Fig. 1. Effect of added quat. biocide dosage on liquid phase surface tension (quat.=quaternary ammonium salts)

Additive	dosage (kg/T)
PAC	2.50
cationic starch	7.21
ASA	6.80
CPAM	0.66
bentonite	3.34

⇨

Property	
filler retention (%)	67.6
burst index (kPa.m²/g)	0.77
Cobb (g/m²)	17.5

Fig. 2. Reference chemistry additives dosages and corresponding sheet properties

Then, biocides were added to the furnish, prior to forming the handsheet (as detailed in the Experimental section), and their effect on wet-end performance was tested, in comparison to that reference situation.

The quaternary biocide was found to have a detrimental impact on filler retention (Fig. 3). It is strongly cationic; thus it competes with the retention polyelectrolyte for adsorption on anionic sites available on the furnish solids. This is clearly visible from the evolution of furnish zeta potential after quaternary biocide addition (see Fig. 4). The quaternary biocide alone caused a large increase of zeta potential. This is direct evidence that it is adsorbed on the furnish solids; that is not desirable, as it limits further adsorption of other cationic additives. Moreover, a biocide should remain in the liquid phase, to achieve the best biocide effect against micro-organisms growth.

Glutaraldehyde had a small beneficial effect on filler retention. This could be due to its ability to form hydrogen bonding at both ends of the molecule, and thus play the role of a bridging agent. Other biocides (organo-sulfur, DBNPA and isothiazoline) had no significant effect on filler retention.

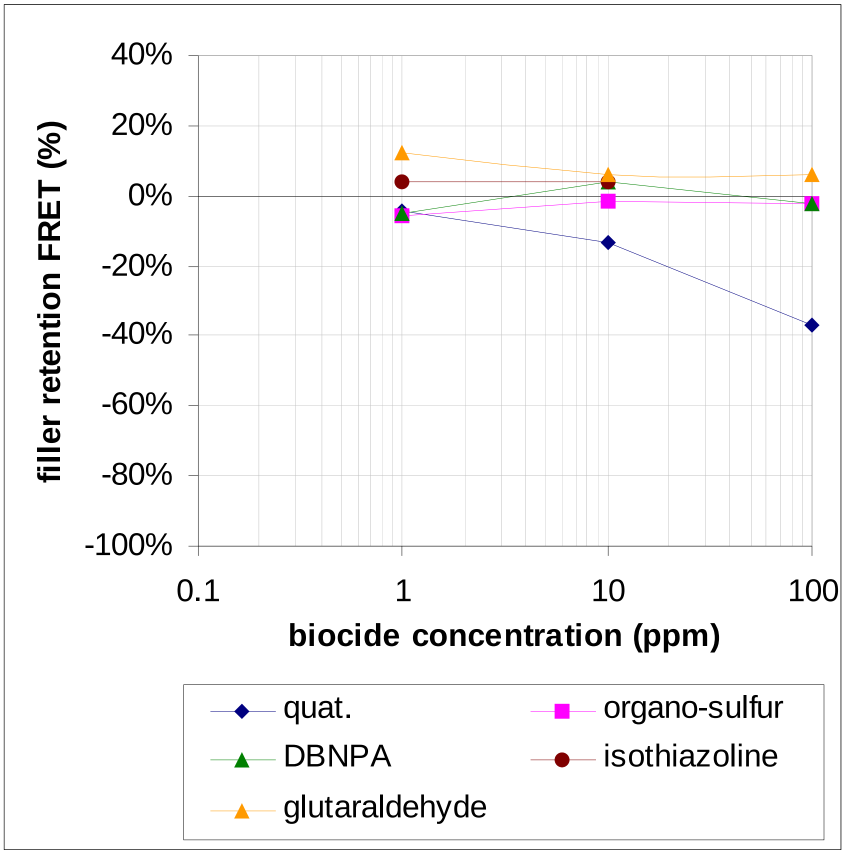

Fig. 3. Impact of biocides on sheet filler retention (relative variation around the reference chemistry value) (quat.=quaternary ammonium salts, DBNPA= Dibromonitrilopropionamide)

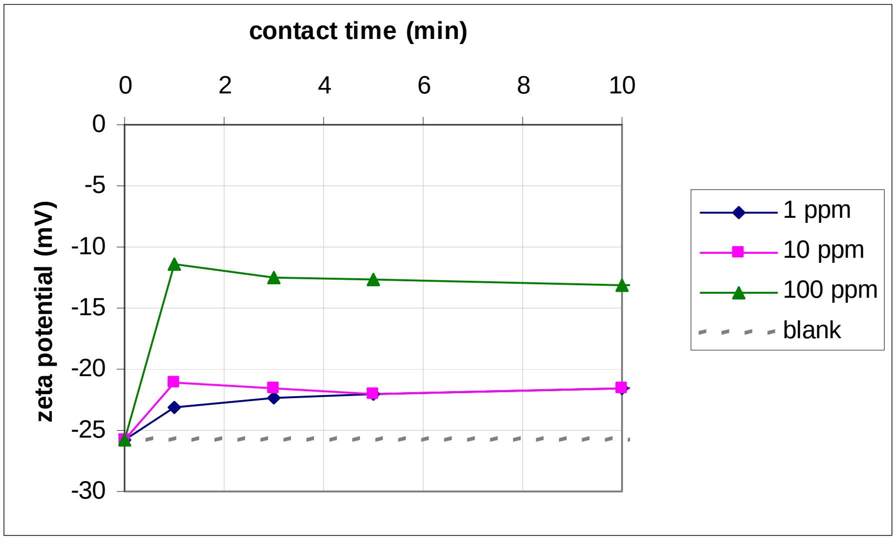

Fig. 4. Effect of quaternary biocide on furnish zeta potential ("blank" corresponds to furnish only, i.e. fibres+filler)

Four of the tested biocides (organo-sulfur, DBNPA, isothiazoline, and glutaraldehyde) were not found to have a significant effect on the sheet burst index, while the quaternary biocide showed a clear detrimental effect on sheet mechanical properties (Fig. 5). Considering the fact that it lowered filler content in the sheet at the same time, this suggests that the quaternary biocide adsorbed on the fibre fraction directly impaired inter-fibre bonding. This is consistent with the fact that the quaternary biocide has a very similar chemical structure to the main active compound of some de-bonder additives typically used in tissue paper grades; the quaternary biocide is a benzalkonium salt C14 alkyl chain, while the de-bonders in tissue grades are usually fatty alkyl (C16-C18) quaternary ammoniums (Poffenberger and Jenny 1996, Liu and Hsieh 2000). These de-bonder additives are used to control tissue softness by lowering sheet rigidity, through the following mechanism: the de-bonder adsorbs on fibres thanks to its cationic group, then the protruding alkyl chain prevents hydrogen bonding between fibres, thus lowering sheet strength. The quaternary biocide in this study may act through a similar de-bonding mechanism (although not directly proven).

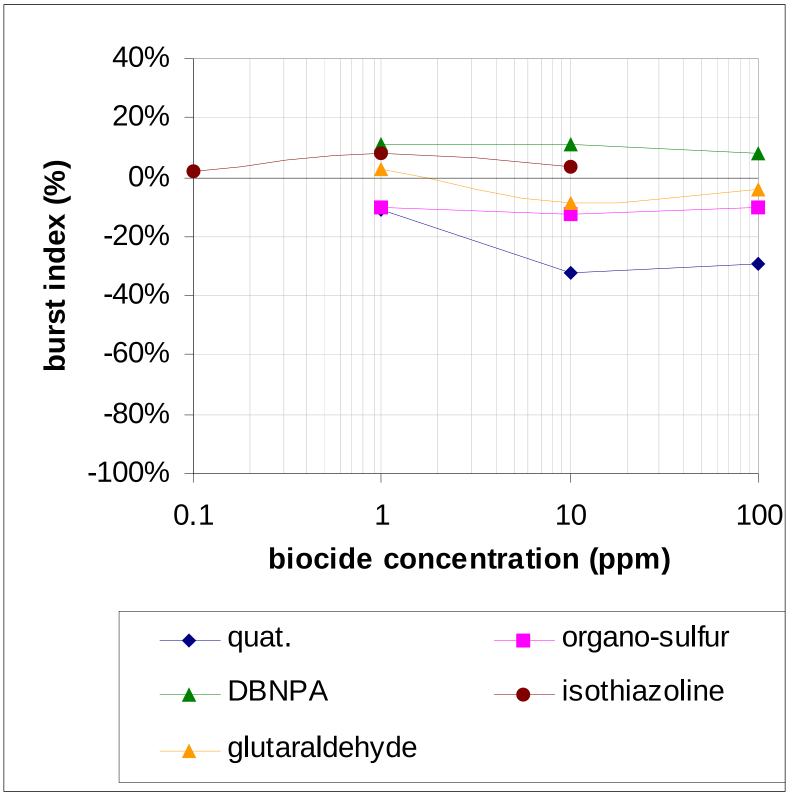

Fig. 5. Impact of biocides on sheet burst index (relative variation around the reference chemistry value) (quat.=quaternary ammonium salts, DBNPA= dibromonitrilopropionamide)

Four of the tested biocides (organo-sulfur, DBNPA, isothiazoline, and glutaraldehyde) had no significant effect on sizing, while the quaternary biocide destroyed sizing at concentrations higher than 10 ppm (see Fig. 6 for Cobb test results). This is unacceptable over the biocide instant concentration range, and might even be detrimental at equilibrium concentrations between 1 and 10 ppm. The Cobb test is very convenient, as it characterizes sheet hydrophobicity by a single index. However, it only gives information about water penetration after a given time, thus it is not possible to determine the kinetics of sheet wetting. Also, when water has pierced through the handsheet it is not possible to distinguish between average sizing and poor sizing.

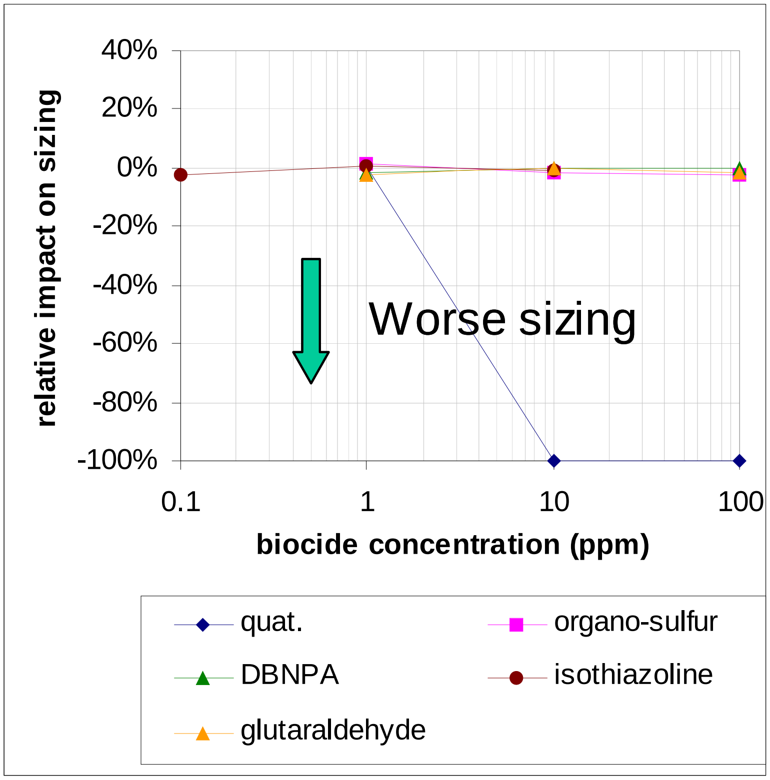

Fig. 6. Impact of biocides on sheet sizing (relative variation of Cobb value around the reference chemistry value, where no sizing is set to Cobb=100 g/m²) (quat.=quaternary ammonium salts, DBNPA= dibromonitrilopropionamide)

Then the effect of quaternary biocide on sheet hydrophobicity was investigated through dynamic contact angle measurements (Fig. 7). There was a clear influence of quaternary biocide on wetting with increasing dosage. Thanks to contact angle measurement, it was possible to distinguish between poor sizing (at 10ppm of added quaternary biocide) dosage and very poor sizing (at 100ppm of added quaternary biocide). In the case of the 10ppm dosage, the initial contact angle was still higher than 90°, then it slowly decreased with time; the deposited water droplet clearly spread at the surface of the sheet and started penetrating the structure after 40 s. This means that although the Cobb value was not measurable, the critical dosage of quaternary biocide that destroys sizing was close to 10ppm. At the higher dosage of 100 ppm, the deposited drop was quickly absorbed in the sheet, and it became difficult to record the kinetics of drop spreading; the sizing was totally destroyed.

The quaternary biocide is surface active, so that it may destabilise the ASA emulsion, thereby reducing sizing efficiency (impairing effect on sizing has already been observed for various surface active contaminants, Zeno et al. 2005). Also, as it is cationic, and adsorbs on fibres, it may reduce ASA retention by occupying the anionic sites on fibres.

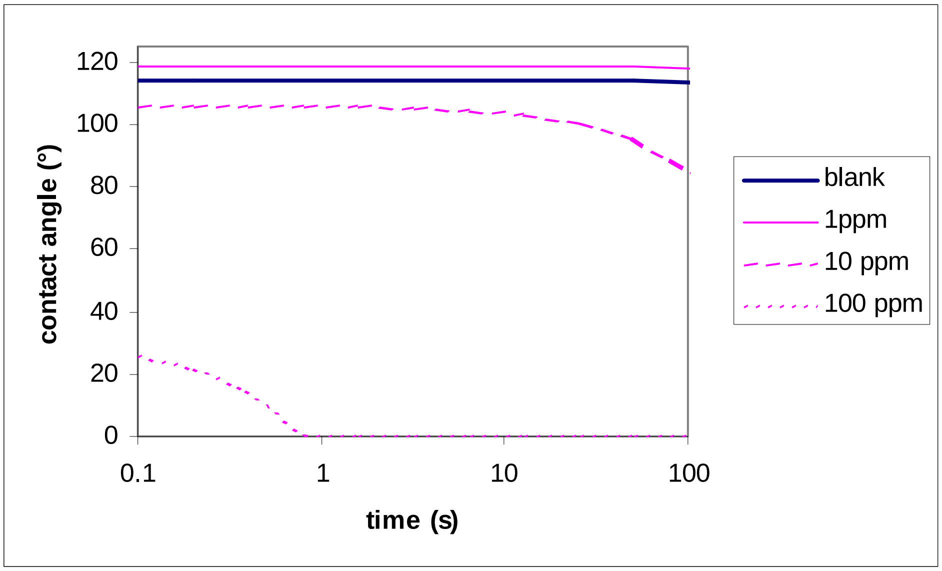

Fig. 7. Effect of quaternary biocide on dynamic contact angle (Blank = optimised minimum chemistry)

In summary, four of the five tested biocides (organo-sulfur, DBNPA, isothiazoline, and glutaraldehyde) had limited or no impact on the reference wet-end chemistry in general, while the quaternary ammonium class biocide was detrimental to filler retention, sheet strength, and sizing. (It may be useful to keep in mind that ammonium bromide (another popular biocide in papermaking) is not a quaternary ammonium compound, so that the conclusions of this study do not apply in that case).

Besides, OBAs are sometimes required in fine paper manufacturing to enhance brightness. They are substantive (capable of hydrogen bonding) and thus can bind to cellulosic fibres without assistance from cationic additives, although they carry an anionic charge. Because of their anionic charge, OBAs are involved in interactions of their own with wet-end chemistry additives and furnish.

Due to the growing complexity of the studied system, it was decided to study possible interactions among OBA and biocides separately. So, pure OBA solutions were prepared, then biocides were added, and possible interactions with OBA were studied through UV/visible spectroscopy. Only the quaternary biocide showed significant interaction with OBA. Here only 1 dosage of quaternary biocide was considered (intermediate dosage of 10 ppm), then spectra were recorded as a function of time (Fig. 8). It can be seen that the absorption peak was shifted to the right, attenuated, and it became very broad. Also the baseline increased greatly. This is characteristic of a turbidity increase (even absorption across the whole spectrum). The formation of a turbid solution was visible to the naked eye after 1 hour, and confirmed by turbidity measurement (Fig. 9). The complexation of OBA by quaternary biocide was so severe that charged colloids were formed, as shown by particle size and particle zeta potential measurements (Fig. 9). Such agglomeration may even lead to deposits problems during paper manufacturing. The observed changes in UV/visible spectrum may indicate changes in OBA effectiveness during sheet formation, but this would need to be determined experimentally.

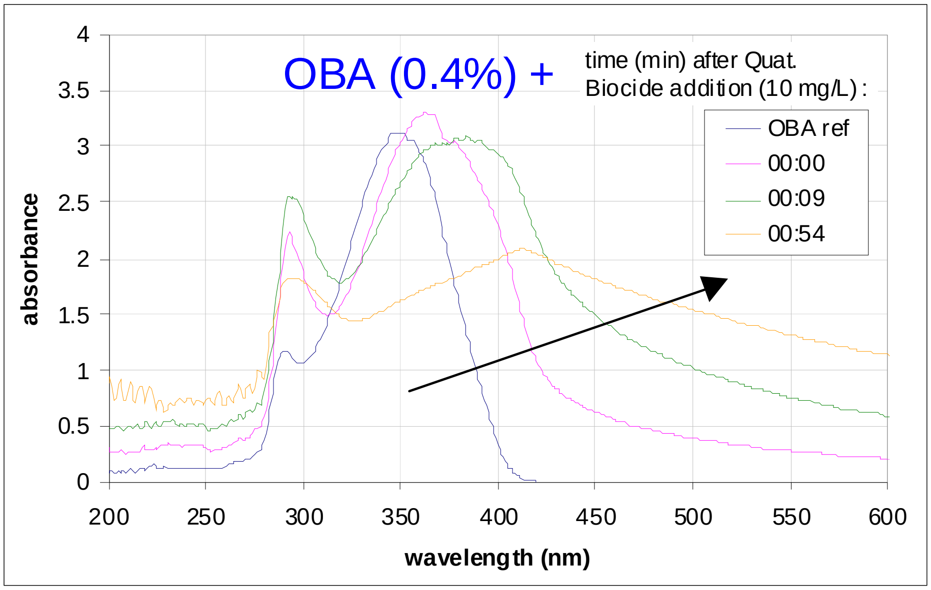

Fig. 8. Time evolution of OBA absorption spectrum after quat. biocide addition (10 ppm) (quat.=quaternary ammonium salts)

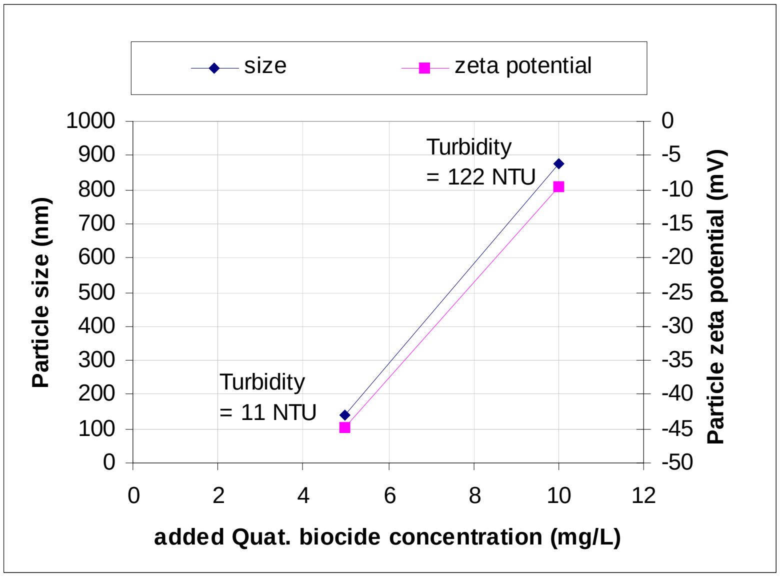

Fig. 9. Characterization of OBA/quaternary biocide complexes (measured after 1 hour of contact time)

CONCLUSIONS

1. A quaternary ammonium salt biocide (benzyltetradecyldimethylammonium chloride) caused detrimental interactions with a typical fine paper grade furnish (bleached kraft fibre mix and precipitated calcium carbonate as filler) and wet-end chemistry (including polyaluminium chloride as fixing aid, cationic potato starch as dry strength aid, alkenylsucccinic anhydride as sizing agent, together with a retention system involving a cationic polyacrylamide flocculant and a bentonite microparticle); it reduced filler retention, reduced sheet strength, and destroyed sizing. It also complexed di-sulfonated Optical Brightening Agents (di-amino-stilbene-di-sulfonated acid).
2. Organo-sulfur (sodium dimethyldithiocarbamate), DBNPA (2,2-dibromo-2-cyanoacet-amide), isothiazoline (5-chloro-2-methyl-thiazol-3-one), and glutaral-dehyde (pentanedial) biocides did not affect filler retention during sheet formation, and did not interfere with the development of sheet strength and sizing, with the tested furnish and wet-end chemistry.

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