Alternatives to Conventional Biocides in the Pulp and Paper Industry

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ABSTRACT

176 tons of active ingredients of conventional biocides were used as slimicides in Swedish pulp and paper mills in 1998. Examples of biocide-free slime control and inhibitors of compounds produced by microorganisms are presented as alternatives. The concept of "green biocides" is also discussed.

Key words: Green biocides, Biocide-free slime control, Inhibitors of catalase, Reduction of Hydrogen sulfide.

INTRODUCTION

Swedish pulp and paper mills are under strict environmental regulations, and can today chose between a high degree of closure of the process waters or the use of biological waste water treatment plants. A trend is to re-use the effluent from the waste water treatment plants in the process. Another trend in the mills is to get closer to neutral pH. Together these trends favor the growth of microorganisms, and cause an increased need for efficient slime control. Traditionally, the paper maker has used biocides to control the growth and activity of microorganisms, but the opinion regarding environmental issues has in Sweden led to a strict microorganisms, and less of different biocides to chose between. In this context environmentally friendly biocide-free alternatives will be more and more attractive to the mills.

This paper describes alternatives to conventional biocides in three different areas, and also discusses the pros and cons of "green biocides".

"GREEN BIOCIDES"

There are some applications of biocides in pulp and paper mills that cannot yet be replaced by biocide-free alternatives, but where green biocides can help alone or in combination with conventional biocides. In the latter case less of the conventional biocide is required. A green biocide is degraded as it kills the microorganisms, and the resulting end products are harmless or causes little harm to the environment. Examples of green biocides are hydrogen peroxide peracetic acid and glutar aldehyde. Most green biocides are highly reactive, and may therefore be dangerous to man as they may cause corrosion or skin irritation or bursting of containers. However, these bad features are overcome with the correct handling of the chemicals. Green biocides are to prefer from an environmental point of view.

BIOCIDE-FREE SLIME CONTROL

The activity of microorganisms causes the so-called slime problems in paper mills. Biofilms containing mostly bacteria and sometimes fungi causes breaks and stops for cleaning corrosion, spots and odours in paper, tissue and board and decomposition of raw materials and additives.

Today the various biocide-free slime control products are based on dispersants, enzymes, paraffine,

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Table 1 "Green biocides"

Biocide	End products
Glutar aldehyde	Carbon dioxide and water
Hydrogen peroxide	Oxygen and water
Peracetic acid	Oxygen and water. Acetic acid, further degraded bacteria to carbon dioxide.

Fig. 1 a

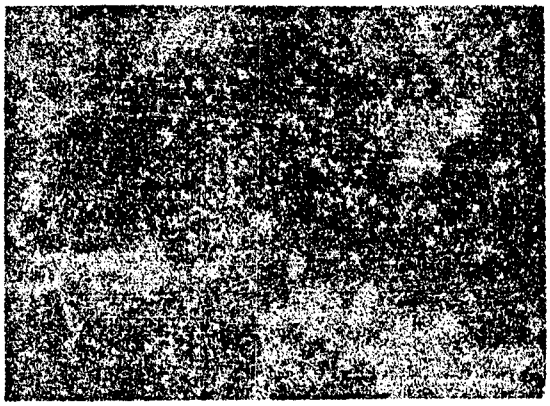
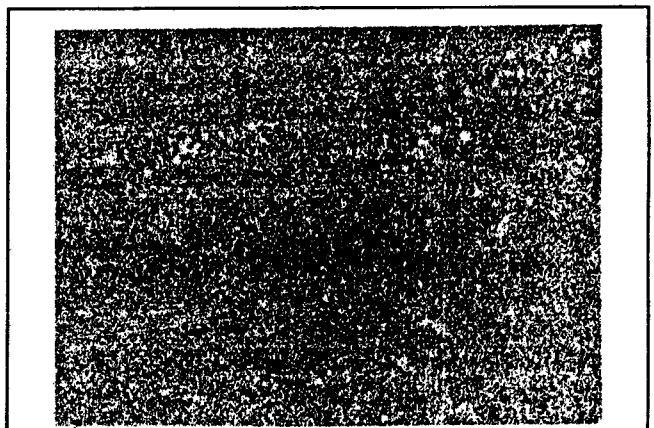


Fig. 1 b



Equal number of bacteria (staphylococcus warneri) was grown in process water from a paper mill for three weeks in the abscense (1a) or presence of 500 ppm Bimogard. The fluorescense stain indicates extracellular polysaccharides, or so-called slime.

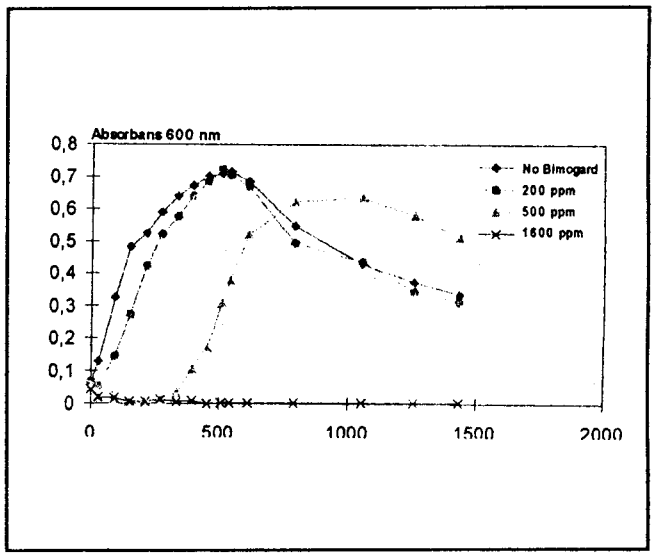
modified lignin polymers, surfactants (also called biodispersants) or combinations of these. The oldest and most tested products on the market are based on various lignin polymers. The Bimogard® system described below is based on chemically modified lignin polymers and surfactants. Bimogard does not kill microorganisms, is not toxic, and is biodegradeable and thus environmentally friendly.

Firstly, Bimogard has cleansing effects on the sufaces in the process (data not shown), and also fewer bacteria adhere to the walls in the process, as shown in figrure 1 a and b.

Secondly, Bimogard lowers the activity of microorganisms by i) decreasing the bacterial production of extracellular polysaccharides by some 80% (fig.1),ii) delaying the growth of bacteria (fig.2), and thereby delaying the spore formation (table 2).

The delay of spore formation is important in tissue mills, as most vegetative bacteria are killed in the drying section of the paper machine, but endospores are not. The delay lowers the amount of spores in the ready - made product by some 80% (data not shown).

Fig. 2 Bacillus subtilis



Bacillus subtilis were grown 24h in the absence or presence of Bimogard, as indicated. The growth was delayed in a dose-dependent manner.

The laboratory tests shown above have all been confirmed in mill cases. Also, the runability of the

Table 2 Endospore formation of Bacillus subtilis (CFU/ml)

Time (h)	No. Bimogard	500 ppm Bimogard
9	$1,6 \times 10^4$	-
13	$1,5 \times 10^5$	-
17	$1,6 \times 10^5$	$1,6 \times 10^6$
21	$3,4 \times 10^5$	$3,0 \times 10^6$
24	$5,3 \times 10^5$	$4,9 \times 10^6$

Bacillus subtilis were grown for 24h in the absence or presence of Bimogard. The endospore formation was delayed in the presence of Bimogard.

paper machines usually increases when the machine is converted from conventional biocides to the Bimogard system. So far, Bimogard has decreased the consumption of conventional biocides in paper mills in Sweden with between one-fifth and one fourth parts.

INHIBITORS OF HYDROGEN PEROXIDE DEGRADING ENZYMES OR "THE CATALASE PROBLEM"

The use of recycled fibers is a big step in the recycling of raw materials in the society. Recycled fibers from journals and newsprint need to be de-inked. The most common deinking chemical is hydrogen peroxide. Microorganisms produce hydrogen peroxide degrading enzymes (HPDE), of which the most wellknown is catalase, and so this is referred to as the catalase problem. Microorganisms thrive in the de-inking process due to comparative low temperatures and close to neutral pH.

The disadvantage of using biocides in the de-inking process is that dead and damaged bacteria release HPDE into the process waters, so a total kill of all bacteria before the de-inking is required. This is hardly possible for technical and economical reasons. Also, one catalase molecule can decompose one million molecules of hydrogen peroxide, so near sterile conditions are not sufficient.

Fig. 3 Inhibition of catalase activity in a de-inking mill

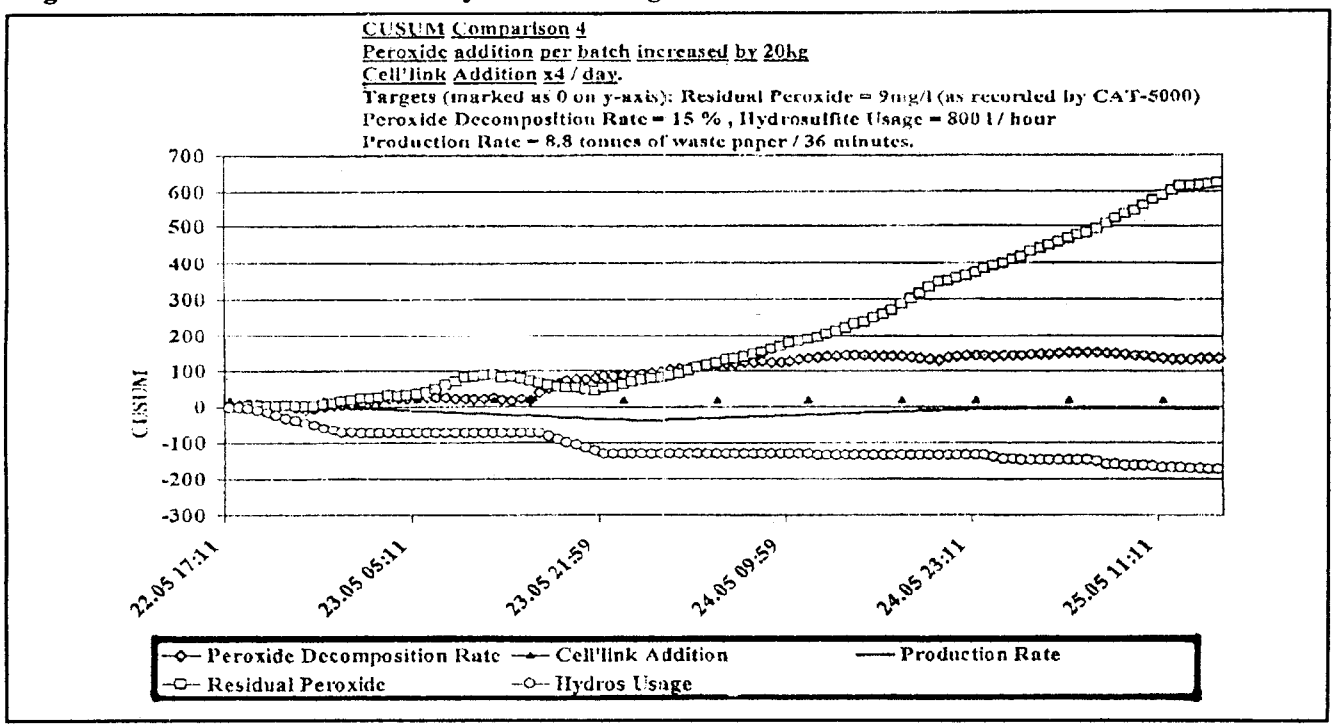
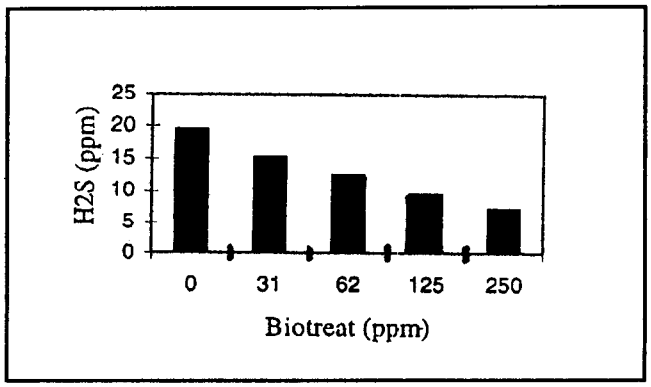


Fig. 4 Biotreat reduces hydrogen sulfide production.



Biotreat was added to process water on three consecutive days, and the amount of hydrogen sulfide was measured on day three using calibrated silver sulfate glass tubes.

The alternatives to biocides are inhibitors of HPDE. Some known inhibitors are hydroxylamine and its salts, sodium thiocyanate and aldehyde chemistry. Cell link is based on the latter, is environmentally friendly and exemplified in a three - day mill trial in figure 3.

The figure 3 shows a decrease in the consumption of hydrogen peroxide. and an increase in residual hydrogen peroxide after the de-inking step. The measurements were done on line with CAT 5000 from BTG, Sweden.

INHIBITION OF HYDROGEN SULFIDE

Hydrogen sulfide is produced by sulfur reducing bacteria, and a common problem in industrial wastewaters. Hydrogen sulfide is corrosive, toxic and has a bad odour, and is most often produced in anaerobic conditions with a low pH. The reactivity of the sulfide ion and the low pH degrades most biocides and lowers their efficiency. Alternatives to biocides are chelating molecules, which scavenges the sulfide ion, the "green biocides" hydrogen peroxide and peracetic acid, oxygen, nitrate, and other microorganisms, which colonise the habitat or affect the population dynamics. Biotreat is an example of a non-reproducing microorganism, which alters the population dynamics by increasing the number of sulfur oxidising bacteria and the number or activity of methanogens. The end result is decreased production of hydrogen sulfide (fig.4). Biotreat is still under development.

CONCLUSIONS

There are good or even better alternatives to conventional biocides today in several areas in the pulp and paper industry.