PERINI JOURNAL

N° 37 - SEPTEMBER 2011

TECHNICAL PAPER

Water is the connection

Oxidizing biocides are widely used in tissue making to guarantee machine cleanliness and runnability as they provide cost-effective performances. However, due to the large utilization of sodium hypochlorite, several paper machines have lately been experiencing severe corrosion issues.

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This article presents a novel non-halogen based oxidizing biocide program, which is based on Performic Acid (PFA) utilization. The PFA biocide program improves corrosion safety and sustainability while maintaining good cleanliness and end-product hygiene.
PFA is a reaction product of formic acid and hydrogen peroxide. Its efficacy is based on active oxygen, which means it is free of chlorine and bromine.
Kemira has developed and successfully evaluated PFA for microbiological control at tissue mills. These evaluations demonstrated the following benefits:

- no presence of any harmful irritating chemicals in the paper produced;
- quick decomposition of residual PFA in process water, yielding water and carbon dioxide; both byproducts are not harmful to mill personnel and the environment;
- the peroxide effect ensures the absence of anaerobic fermentations and high redox environment in the paper machine water loop without corrosion;
- continuous dosage permits a dramatic reduction of aerobic bacteria, yeast and mold counts, below < 500 CFU/ml, providing a safer working environment for paper machine personnel, who are normally exposed to vapor water in the vicinity of high and low
pressure showers;
- no reaction with other functional and process additives used in paper production;
- can be used in the Legionella control in cooling towers;
- eliminates foul odor and reduces colour in water;
- PiBa's (pigmented bacteria) count reduced to zero. This monitoring method is very important since many of the colonies growing on this specific media are primary-biofilm formers;
- zero contribution to AOX formation.

WHAT IS PFA TECHNOLOGY? Chemistry. Fennosan PFA is a peroxide derivative of formic acid that is capable of destroying microbiological cells. The optimal combination of formic acid and hydrogen peroxide gives a highly efficient disinfectant. It is well known that some paper grades are treated with hot hydrogen peroxide for disinfection. For example, liquid packaging board used for food contact purposes is recommended to be treated with hydrogen peroxide at high dosages.
This demonstrates the safety of peroxide technology for end-users of paper products.
PFA is produced in a catalytic reaction between formic acid and hydrogen peroxide:
The PFA molecule is very active and not stable enough for storage purposes. In order to overcome this, Kemira has developed a proprietary technology that allows production of PFA on site. The two precursors, formic acid and hydrogen peroxide, are significantly less hazardous and safer to be stored and handled than traditional biocides.

THE PFA EQUIPMENT HAS BEEN DESIGNED TO ACHIEVE EFFICIENT MIXING OF PRECURSORS, reliable temperature control and an overall safe operation to prevent thermal degradation of PFA. The equipment guarantees optimal reaction time and ideal temperature to reach the maximum PFA yield at the equilibrium solution. The reactor temperature is automatically controlled by a special cooling unit.
Safety in Kemira is of paramount importance. In the event of any unsafe situation, all the PFA components contained in the reactors are automatically sent to the sewer with plenty of water, while various warning alarms are activated. This

procedure is triggered, for instance, when temperature exceeds 40°C, even though the operation is safe up to 80°C. A dumper water tank guarantees the availability of water for flushing in all cases. In the event of a machine shut-down, PFA production stops. If the shutdown is longer than 6 hours, the equipment is flushed automatically.

APPLICATION, MONITORING & CONTROL. Studies demonstrate that PFA is highly effective against primary-biofilm forming bacteria. PFA is up to ten times more biocidal than peracetic acid on active ingredient basis. PFA is fully biodegradable and halogen-free and thus will not generate AOX compounds. This is a significant benefit over other biocide programs that can lead to formation and release of harmful AOX compounds into the environment. Smaller corrosion rates compared to active-halogen based oxidants have also been demonstrated for PFA.
A total solution approach is taken to applying PFA in tissue machines. This includes a new monitoring technique, the PiBa Assay. The PiBa assay allows the biocides program to be targeted more specifically at the most problematic microbes and thus optimize runnability and sustainability.
In the past, oxidizing biocide systems, especially the ones using hypochlorite, have been known to cause metal corrosion. Vapor phase corrosion tendency was tested with three oxidizing biocide systems: PFA, ammonium sulphate/hypochlorite [(NH4)2SO4+NaOCl] and ammonium bromide/hypochlorite [NH4Br+NaOCl]. White water from a paper machine was treated with these three oxidizers and corrosion of the newly polished steel samples was measured. The results clearly demonstrated no corrosion caused by PFA, unlike the halogen-based oxidizing technologies. For the monitoring of mill applications, Kemira has designed an on-line vapor phase corrosion sensor.

CASE HISTORY. A virgin fiber tissue mill wanted to improve machine cleanliness, safety in the workplace and differentiate their final product quality in terms of higher environmental sustainability. The machine had previously utilized several organic biocides and stabilized hypochlorite programs.
Looking at future paper trends, inhibition tests will be an issue bearing growing importance for those dealing with sustainability and green consumer products. In this test, a paper sample is placed in a growth media, inoculated with bacteria and yeast and the growth of these indicator organisms is checked. If these organisms did not grow, i.e., clear growth inhibition was recorded, the paper is suspected to contain biocide residuals on it with potential health and safety implications for end-users.
Kemira's PFA application achieved the following remarkable results:
- cleaner machine vs. the old biocide program (machine frames, white water tanks and showers are perfectly clean);
- no runnability problems at all;
- safety improvement for mill personnel: one worker was sensitive to one of the old biocides, and now can work without any problems;
- aerobic bacteria in process water was reduced from an average of 12,000 CFU/ml to less than 200 CFU/ml;
- anaerobic bacteria was completely eliminated;
- yeast and mold counts were reduced from an average of 200 UFC/ml to less than 3 CFU/ml;
- redox potential in white water increased from an average of 120 mV to 290 mV;
- no impact on the efficiency and performance of chemical additives including wet strength and Yankee coating;
- 25% cost savings compared to earlier biocide programs;
- safety improvement for mill personnel: no slippery floors, clean air;
- no foam detected, unlike during the use of some earlier organic biocides;
- passed all inhibition tests performed on the final paper products.

CONCLUSIONS. Performic Acid (PFA) is an effective non-halogen based oxidizing biocide. The efficacy of PFA is based on active oxygen with no potential for generating free chlorine or bromine, making it a much less corrosive alternative to halogen based biocides.
Overall, the following advantages are specific to the PFA biocide system:
- Performic Acid enables effective microbe control with no environmental concerns (no AOX compounds formed and released into the environment);
- corrosion safety of PFA reduces machine maintenance costs and improves the environmental footprint;
- technology for monitoring primary-biofilm formers enables accurate dosing based on true needs – no need for excess dosing just to be sure. This further increases sustainability;
- safer program for mill personnel;
- kills microbes within a very short contact time, then fully biodegrading to H2O and CO2;
- end-users of hygienic tissue grades could greatly appreciate green microbe control in tissue production, with no biocide residuals in finished products. •

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