A LOW RESIDUAL TOXICITY MICROBIOLOGICAL CONTROL PROGRAM

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AN ON LINE DEPOSIT MONITOR HELPED TO DETERMINE THE EFFECTIVENESS OF AN ALTERNATIVE APPROACH TO CONTROLLING MICROBIAL SLIME BUILDUP.

THE PAPER INDUSTRY HAS BEEN SLOWLY AWAKENED to environmental pressures over the past 20 years in all areas of pulp and paper production. Microbiological control has become a necessary part of continuous paper and board production to ensure trouble-free running without slime-induced paper breaks and the resultant lost production. By its very nature, microbial control prevents organic growth and has, therefore, been seen as potentially detrimental to the environment.

Microbiological control techniques at the beginning of the century used chlorophenols, some of which were subsequently found to be mutagenic or carcinogenic. During the 1950s and 1960s, mercury-based compounds were widely used throughout the industry, but these chemicals were found to have a serious environmental impact due to high levels of residual toxicity and have been prohibited from use. Chlorine and other halogen compounds re-emerged, along with other biocides such as aldehydes and cyano-compounds, becoming the standard chemicals for microbiological control. Some of these are still in use, but new molecules continue to be developed that offer more environmentally acceptable solutions to this problem.

However, many of these new molecules contain halogens and/or sulfur species, and many are formulated in organic solvents that can give rise to associated problems. Also, the use of a single nonoxidizing biocide in a paper machine system can result in certain troublesome microbiological species developing resistance to attack. To counter this, more biocide is required, either by increasing the addition rate or by supplementing with other molecules. The net result is higher levels of nonoxidizing biocides, with increasing levels of residual toxicity from the mill.

Although these new microbiological control products are more environmentally acceptable at present, future legislation can only become more restrictive, and true environmentally friendly control methods need to be developed. In addition, there is a need for greatly improved monitoring of such programs to ensure that the minimum possible amount of biocide is used to the greatest possible effect, with minimal impact on the wider environment.

UK PAPER

UK Paper New Thames Mill, based in Kent, England, is one of the most dynamic and advanced mills in the United Kingdom. The mill has always been at the forefront of technology and is highly equipped with modern monitoring and measuring devices to detect process changes as they happen.

The mill has only one paper machine manufacturing a range of copier and uncoated offset grades. The paper machine is a fourdrinier machine having a bel-bond top former and a film metering size press.

Paper machine statistics are as follows:

Width: 6.8 m (22.1 ft) trimmed deckle
Speed: 950 m/min (3100 ft/min)
Capacity: 200,000 metric tons/year saleable paper
Grammage: 60 to 135 g/m^2

Over the past few years, management has concentrated its efforts to improve the mill's position on environmental issues. Developments on site during 1995 included the commissioning of a new combined heat and power plant and a recycled fibers plant, promoting efficiency improvements. This environmentally responsible approach also resulted in certification under BS 7750/ISO 14001 for all sites in 1995.

In line with the company's mission statement to reduce the impact that the papermaking operation has on the environment as a whole, management expressed a desire to reduce the mill's dependence on conventional, nonoxidizing, microbiological control methods. This was to be achieved without compromising the efficacy of the current control program. Indeed, mill operations staff also wished to move to a planned shut regime every four weeks from a pattern of every three weeks, but they were concerned about the increased probability of slime breaks and associated production losses, unless improvements could be made to their current microbiological control program.

Other goals the mill wanted to achieve were reductions in the residual toxicity loading of the effluent discharge and better control of all substances in use at the plant that were deemed to be hazardous in nature.

NEW TECHNOLOGY APPLICATIONS

Chemistry

New microbiological control agents are being developed, and research is going on all the time to find the ideal eco-friendly microbial deposit control program. One option being investigated is an equilibrium blend of peroxyacetic acid and hydrogen peroxide as part of an integrated microbial control package. This approach can provide a solution to the problem of residual toxicity associated with conventional programs, and synergy has been demonstrated when using the combination approach.

Hydrogen peroxide is not a powerful biocide at low temperatures or low concentrations, but it does exhibit a strong biostatic effect, inhibiting growth of many microbiological species. The biocidal properties increase with both temperature and concentration. It has been used as a sterilant for aseptic packaging for milk and fruit juice containers. It has also been used to control anaerobic bacteria in the paper industry.

Hydrogen peroxide is often used in conjunction with peroxyacetic acid, existing in an equilibrium mixture engineered to specific formulations to achieve the greatest effectiveness for paper industry applications. Peroxyacetic acid is an extremely powerful, fast-acting biocide having a broad spectrum of activity over a wide temperature range (below 0°C to above 100°C). Although classed as an oxidizing biocide, the mode of activity is not simply oxidation, as the molecule penetrates the cell wall to give a greater effect than pure oxidate. There is also no known immunity to peroxyacetic acid, provided sufficiently high active levels are maintained.

Peroxyacetic acid has long been used in sewage treatment and in the sugar, dairy, and brewing industries, as well as for medical sterilization for renal dialysis machines. Once reacted, it breaks down to nontoxic end products-water, oxygen, and acetic acid-which itself breaks down to carbon dioxide and water. It is nonfoaming, nontainting, and can reduce chemical and biological oxygen demands in effluent. The active ingredients can be easily monitored using proprietary electro-optical measuring equipment, giving parts per million concentrations within seconds.

The chemistry does have some limitations. It is less successful against organisms with thicker cell walls, such as filamentous bacteria and molds. Certain system chemistries—for example, high levels of carbonate filler—can mean that higher dosage rates are required to effect control.

Optical Fouling Monitor and biomanagement

Nalco Chemical Company has designed and developed two monitoring tools, the Optical Fouling Monitor (OFM) and a portable diagnostic unit called TRA-CIDE®. The OFM is intended for use in paper machine and process water streams. It allows on-line, real-time measurement of microbiological deposition rates. It uses a clear plastic disc suspended in a flooded sample trough, onto which microbiological organisms can deposit gelatinous slimes. The disc has an off-center axis, so a large area of the disc remains submersed in the stock-filled trough.

An onboard computer is programmed with date and time information prior to the start of a survey, using a serial cable and software for communication and control using a notebook computer. This enables accurate monitoring of changes in deposition rates, which can then be related to operational changes within the machine system. The onboard computer rotates the OFM disc every hour, momentarily lifting the water-wetted segment into the path of an LED transmitter/detector beam. Measurements of the transmitted light are carried out and the resultant absorbance recorded in the monitor's memory. Four measurements are taken during rotation and an average value calculated, thus avoiding spurious data from, for example, foam deposit buildup at the water line. The whole measurement operation takes less than one minute, after which the disc is rotated back to its original position. Any deposition present is untouched, and deposit growth continues undisturbed.

The average measurement for the most recent set of readings is displayed on the monitor screen for the duration between hourly disc revolutions. All stored measurements can be downloaded via serial port to a computer to allow rapid, meaningful evaluation of the collected data.

Obviously, the rate of change of absorbance over time is directly related to the rate and type of deposition on the disc. Care needs to be taken to ensure the application point for the monitor is suitable and will accurately replicate conditions found in the paper machine system.

This OFM provides early warning of microbiological problems, provided that the water flow rate and quality is representative of that section of the system under investigation. For example, a low velocity water flow will encourage a far faster rate of deposition.

The second measuring tool is the TRA-CIDE® unit. This is a portable diagnostic unit that measures both microbiological activity and system toxicity in a matter of minutes, at any sample point in the paper machine water system. The information is used to determine both the levels of toxicant present at that point and the efficacy of the determined level of biocide. Studies over the period of the dosing cycle provide an accurate indication of how the program is performing and can immediately suggest purposeful modifications to dosage amount, dosage frequency, or dosing point.

TRIAL PREPARATION

Laboratory evaluations

Screening work was conducted to determine the optimum program for the system and give an indication of probable addition rates. Results indicated that a peak of 150 to 200 ppm of the peroxygen product would reduce microbiological populations by a log factor of 5. On-site testing with all additives to the machine system were also carried out to ensure that no problems or unwanted reactions would affect paper quality during a trial. Handsheets were prepared at various product addition levels to determine the effect on sheet properties. Laboratory evaluations were also carried out to determine the presence of any reducing agents that would affect the oxidizing biocide when added to the paper machine stock. No contra-indications were found in any of the studies.

Evaluations of pH were carried out to determine the effect of the peroxyacetic acid blend on system pH. Laboratory testing showed a drop of around 0.1 pH may be observed if the addition level was twice the expected addition level, i.e., 400 ppm. This was not expected to cause any major difficulties if careful control of addition levels was maintained.

Feed/storage system

Peroxyacetic acid/hydrogen peroxide blend is classified as an organic peroxide, with consequent handling hazards, so safety is of paramount importance. A stainless steel bulk storage and feed system was installed that had been approved via an exhaustive HazOp review. Dosing lines were installed, allowing addition to one of two addition points. The selected addition points chosen for the trial were the blend chest inlet and the backwater silo.

Background information

The Optical Fouling Monitor had been installed into the backwater silo on PM6 for several months prior to the trial to establish the microbiological fouling rate of the system. In conjunction with several separate microbiological contamination evaluations, this monitor gave a good indication of the background condition of the paper machine system.

The trial was scheduled to start immediately after a routine maintenance shutdown and system boilout. However, time constraints prevented the boilout from taking place. It was likely, therefore, that there would be some areas of the machine where deposition was present. If the program was too harsh, this deposition could be broken away, causing sheet holes, defects, or even breaks. Both the mill and Nalco agreed to start the trial anyway, as the abnormally dirty conditions would provide a good test of the new program due to the extra deposition and microbial loading. Trial progress would be observed using the Optical Fouling Monitor (OFM).

The OFM gave an early indication that the machine system was gradually starting to become cleaner, with a steady reduction in the thickness of the microbial deposit film on the OFM disc. Days later, the machine crew indicated that they believed the system was becoming cleaner, based on visual inspection.

Initial stages of the machine trial were designed to select the most effective addition point and most cost-effective dosing period and quantity. The fast-acting nature of the peroxyacetic acid/hydrogen peroxide product meant that a rapid addition would give a high initial peak concentration, which would work more effectively against the microbiological contamination present in the paper machine system.

THE TRIAL

Over the first three days, several dose configurations (time period/dose amount) were used to gain data to enable a sensible dosing regime to be established. Close monitoring of oxidizer residuals and microbiological plate counts were used in conjunction with OFM data to give an insight into program performance.

An initial dose of the oxidizer was added to the backwater silo over a 7 min period with samples taken from headbox and backwater silo itself every 3 min. The samples were measured for peak concentrations of residual oxidizer, then plated on several different culture media to allow differential microbiological determination. This would give an insight into the populations being most readily affected by the program and an early warning of any resistant or troublesome strains. This initial regime gave good results for the thin stock loop but had little effect in the blend chest or thick stock system.

The addition point was changed to the blend chest. In this machine system, this point was found to offer better protection in the thin stock loop, though subsequent work in a wide variety of paper machine systems in Europe and North America has demonstrated that each requires its own unique approach to get the best from the program. Thus, the initial program of three doses per 24 h to the backwater system was replaced by three similar doses to the blend chest.

Several days of close monitoring followed, with adjustments of the biocide addition level and addition time period to determine the optimum microbiological control program. After five days, the most effective addition point was judged to be the blend chest, with four more smaller additions per day.

These results showed a much higher kill level when compared to the conventional program. Microbial levels within the paper machine system of 10^8 prior to the dose were reduced to less than 10^3 with the new program, while the previous one had only managed a 2 log reduction. There was an improvement in the OFM absorbance levels, demonstrating reduced slime buildup and improved cleanliness, which was borne out by visual inspections. Over the first month, the typical background levels of all species of microorganisms were reduced, from 10^7 to 10^8, down to 10^4 to 10^5, seen in samples taken throughout the system.

Despite the fast-acting nature of the oxidizer, low level residuals could be measured in the backwater tank and in the thick stock, sampled 90 min after the dose had been added. Residual oxidizer was carrying forward from the backwater tank and returning via pulpers to the paper machine, causing a slight decrease in populations up to 2 h after the initial slug dose. During each dosing cycle, microbial populations were reduced to below 1000 total count for up to 20 min in the thickstock samples and up to 45 min in the headbox samples.

This control program was used successfully for a year. The mill then made what seemed to be an insignificant change to one of their additives, moving from a cationic starch with a relatively low degree of substitution to one having a higher degree of substitution, i.e., more branched in nature. This new additive seemed to be slightly susceptible to oxidation. A reduction in starch effectiveness contributed to small blips in the ash retention, as measured by a Chemtronics analyzer, each time the product was added to the blend chest. This was exacerbated by the parameters in the process control computer, which overcompensated by adding excess filler to the white water.

Several modifications were made to prevent these retention effects—for example, by better controlling the feedback loop that pumped filler into the system. This single change made a significant difference, almost removing the drop altogether. Changes were also made to the dosing schedule by extending the time period for dosing, yielding lower peak concentrations of residual oxidizer. This had a slightly adverse effect on program performance, but the program remains highly effective to this day.

BENEFITS TO THE MILL

Among the benefits observed were the following:

- Reduction in microbiological control cost per unit metric ton of produced paper
- Improved cleanliness of the paper machine—visually more impressive and having fewer quality and production problems
- Simple, safe installation and dosing equipment
- Reduction in the number of chemicals being handled
- Improved control of microbiological populations across the mill's four-week production cycle
- Positive environmental impact by reducing the quantity of nonoxidizing biocide being used.

PROBLEMS/INTERFERENCES

Some of the problems observed include:

- Problems may occur with brightness control if the oxidizer is allowed to come into intimate contact with the optical brightening agent prior to being thoroughly mixed with the stock. No problems occur after either product is mixed.
- The starch used at the start of the trial was HiCat 135. There were no problems until the starch was changed to HiCat 145. The more branched version seems more susceptible to attack by the oxidizer.
- Calcium carbonate is susceptible to attack by any acid, which could cause some difficulties if high peak levels are maintained. Careful monitoring and control of oxidizer addition and dosing point avoids problems.
- In terms of wet strength, it is easily oxidizable and may cause rapid loss of oxidizer residuals with a consequent loss of program effectiveness. **TJ**

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