MINI-REVIEW

M. A. Blanco · C. Negro · I. Gaspar · J. Tijero Slime problems in the paper and board industry

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Abstract The latest trends in the paper industry have been towards manufacturing by a neutral or alkaline process, greater consumption of secondary fibres and the closing-up of the process water systems. Under these conditions of papermaking, the problems of deposits, corrosion and odours due to the microbiological activity increase considerably and therefore, runnability and production problems occur. To help our understanding of the current situation in the paper industry, this paper presents a review of the microbiological activity upon the actual systems of manufacturing paper and board, and the current state of the different alternatives for its prevention and control, as well as the future trends to address environmental considerations.

Introduction

The reduction in water consumption (Kotila and Estes 1994; Mallouris 1994; McKinney 1995) coupled with increased use of secondary fibres (Meersmann 1991; Sorrelle and Belgard 1991), the increased use of surface water, the use of higher levels of filler, increased chemical addition, faster-running machines, manufacture under alkaline/neutral conditions (Goldstein 1988) etc. have considerably increased the problems of deposit formation, corrosion and odours in the papermaking process, thus affecting the runnability of the paper machine, the life of the equipment and the quality of the final product (Inman 1995; Negro et al. 1995).

Deposits within the paper industry can be separated into two main groups: non-biological (stickies, pitch and scale) and biological (slime), although both forms are often combined (Safade 1988). To solve the problems associated with non-biological deposits, papermakers add numerous chemicals, which provide a further source of nutrients for microorganisms. In order to adapt the traditional biological slime control to the actual environmental, economic and operational considerations, papermakers consider the importance not only of the identification of the microbiological population, but also of its origin and development. Therefore, prevention is an important issue as well as the application of new control systems. The Complutense University of Madrid has carried out a review of slime problems and possible solutions as part of the work carried out within the framework of the COST Action E1 "Paper recyclability" of the European Union (Blanco et al. 1995).

Microbiological population and contamination sources

The process water in paper and board mills presents ideal conditions of temperature, pH and nutrients for the growth of a great variety of microorganisms, in which the bacteria and fungi are the dominant $(10^4-10^8 \text{ microorganisms/ml})$ (Harju-Jeanty and Väätänen 1984). The main sources of microbiological contamination are:

Fresh water, especially when surface water without previous treatment is used

The cellulosic raw material, particularly when secondary fibres are used

The brokes, especially when sizing and coating additives are used

The solutions or suspensions of additives, fillers, pigments, starches, coatings, etc

The recycled water

The environment in which the paper machine is placed.

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Table 1 Main microorganisms in the paper industry

Aerobic bacteria Spore forming

Bacillus sub	, tilis, B.	cereus,	В.	megaterium,	В.	mycoides
Non-sporulati	ng					

Achromobacter, Acinetobacter, Aeromonas, Beggiatoa, Citrobacter, Corynebacterium, Enterobacter, Escherichia, Flavobacterium, Gallionella, Klebsiella, Lepthotrix, Micrococcus, Pseudomonas, Sphaerotilus, Staphylococcus, Thiobacillus

Anaerobic bacteria

Spore forming

Clostridium

Non-sporulating

Desulfovibrio, some Actinomycetes

Fungi

Moulds

Alternaria, Aspergillus, Fusarium, Penicillium, Phialophora, Phycomyces, Trichoderma

Yeast

Candida, Geotrichum, Monilia, Rhodotorula, Saccharomyces, Torula

Algae

Blue-green Asterionella, Navicula, Oscillatoria Green Chlorococcus

The typical composition of the main paper industry microflora is shown in Table 1 (Sanborn 1965; Harhu-Jeanty and Väätänen 1984; Martin 1988; Safade 1988; Latorre 1990). When the biological contaminants become part of the process water, they find an ideal medium for their development, originating the biofouling phenomena and the slime deposits. If the water circuit is closed, the concentration of nutrients and metabolites increases, as well as the water temperature and the retention time of the microorganisms, facts that enhance the microbial growth. When the dissolved oxygen concentration is high, aerobic bacteria will be developed, which are the main producers of the slime. Alternatively, if the concentration of oxygen is decreased, the population shifts towards anaerobic species, which are responsible for the problems of odours and corrosion (Jung and Kutzner 1978; Väätänen and Niemelä 1983; Bennet 1985). If the temperature increases the population could vary from mesophilic to thermophilic species, which form spores. The reuse of the white water also increases the concentration of filamentous microorganisms present in the system. These species, which initially enter the system with the fresh water, are developed in the process, continuously contaminating the system wherever the white water is reused.

Although the fresh water is the main cause of the presence of algae in the system, the recycled pulp is the main source of bacterial and fungi contamination. The concentration of microorganisms in the recycled pulp is a thousand times higher than in the virgin fibre pulps (Sorrelle and Belgard 1991, 1992). The starches and coating products that appear in the recycled paper are an important source of microorganisms (Robertson 1994). Also, the fillers and adhesives that are present in the recycled pulps enhance the formation of slime as they are ideal places for the attachment of fungi and bacterial colonies. However, rosin and aluminium compounds generally reduce the growth of microorganisms (Hughes 1993).

The current papermaking trends have a negative influence on the treatment programmes as, for example, microbiological control in mills that use alkaline or neutral processes can end up by being seven times more expensive than that in the factories that operate in an acid medium (Goldstein 1988). Also, when secondary fibres are used as raw material, the cost of the average treatment per tonne of paper can be double that the employed if virgin fibre is used (Sorrelle and Belgard 1992).

Consequences of the microorganisms' activity

Formation of microbiological deposits

The organisms causing slimes in the paper industry are divided into two main groups, primary and secondary (Safade 1988). Primary organisms, e.g. Bacillus spp. and Sphaerotilus natans, cause the accumulation of slime by themselves. They allow the growth of colonies of secondary organisms, e.g. Klebsiella, Achromobacter and Pseudomonas. The presence of other deposits such as fibres, fillers, resins etc. also favours the attachment of microorganisms forming mixed deposits (Eklund and Lindström 1991). Although the filamentous fungi do not produce slime, organic and inorganic matter can be entangled in their structure, thus forming the deposits. The spores produced by the mycelia are responsible for the colours that appear in the moulds and, consequently, in the final product. Yeast is also present in the deposits: however, it is not directly responsible for any problem except when it develops in solutions of starch, causing fermentation (Piluso 1987). Finally, the presence of algae in the system favours, indirectly, the growth of bacteria and fungi and alters the quality of the final product owing to the presence of green spots.

The slime formation process starts with the rapid formation of a monomolecular layer upon the surfaces of the paper machine after each machine boil-out, and can originate from any furnish component. During the start of the process, the bacteria attach to this layer for feeding. Later, these bacteria produce slime that is the base for the deposits. As a consequence of the slime, damage could appear because of the plugging and fouling of felts, showers, pipes, etc. Furthermore, when the microbiological deposits are thick, the cells of the inner part die as a result of the lack of nutrients. Thus the deposit loses its capacity to attach and the microbiological deposits fall off from the surface (Hüster 1984). This can produce both web breaks during papermaking and spots or holes in the final product.

Processes of corrosion

The corrosion induced by microorganisms is directly or indirectly produced as a result of their metabolic activity and is generally associated with the microbiological deposits (Characklis and Cooksey 1983; Von Holy 1985; Ford and Mitchell 1990; Cloete et al. 1992). Sulphur oxidisers, mainly of the genus Thiobacillus, form sulphuric acid, which is a strongly corrosive agent. The aerobic iron bacteria in the genera Gallionella, Pedomicrobium and Siderococcus oxidize the ferrous iron into ferric iron, catalysing the deposition of tubercles (Herro 1991). Members of the filamentous bacteria of the genus Lepthotrix deposit ferric oxides in their sheathes. Some species of Metallogenium, Pedomicrobium and Lepthotrix oxidize the manganese, producing deposits of salts of Mn⁴⁺ out of the cellular wall. The sulphate-reducing bacteria are considered mainly responsible for the corrosion induced by microorganisms. In their presence, steel and other alloys submerged in unoxygenic waters are corroded four times more quickly than when submerged in oxygenic waters. They first act as cathodes, depolarizing, and then produce H₂S, which is very corrosive. Furthermore, the genus Clostridium produces butyric and acetic acids, which are corrosive components for the carbon steel.

The microstructural factors also influence the process of metal corrosion by, for example, increasing the solubility of the hydroxides. The formation of oxygen concentration cells initiates corrosion by pitting (Piluso and Nathan 1974).

The production of gases

The production of explosive gases and bad odours, as a result of bacterial activity, is important in the mills that use secondary fibres as raw material and have a closed water system. The growth of bacteria of the genus *Clostridium* and of bacteria that produce methane has been the cause of serious accidents in several board mills (Cox 1989; Rochibaud 1991; Sorrelle and Belgard 1991; Rowbottom 1989, 1993). This problem can be avoided with correct ventilation of the chests to reduce the build-up of dangerous gases, by aerating the water to avoid the development of the anaerobic bacteria, or with the proper use of biocides. The generation of H₂S and volatile fatty acids in the paper mills gives rise to odour problems in the system, which can remain in the final product. The economical losses as a consequence of the growth of the microorganisms in the paper and board mills can be summarised by:

Reduced production due to a greater number of web breaks, down time for cleaning and maintenance of the machinery, loss of yield, production of paper out of specification etc.

Higher production costs due to a larger consumption of additives, higher energy consumption, spoiling of chemicals etc.

The reduction of the equipment life caused by corrosion, scale, fouling and plugging

Reduction in the quality of the final product as a result of spots, holes, odours, inferior optical properties, presence of moulds etc.

Safety problems

The drop in sales as a result of the loss of clients.

Microbiological survey of the mill

The microbiological survey of the mill aims to determine the infection level of the plant as well as its origin; and consists of a macroscopic and microscopic analysis of the system. This study is necessary to achieve optimum microbiological control and is applied not only to the paper machine but also when dealing with problems in the coating division, in starch preservation and with smell problems in the final product.

The microbiological survey in a paper mill starts with a macroscopic analysis of the whole system, gathering all the information concerned with the fabrication process, the machine and the operational conditions. The deposits found are analysed microscopically to identify the type of infection. Finally, the infection level and the contamination source are determined by analysing the following samples: fresh water, pulper, headbox, white water, clarifier input and output, brokes, kaolin, calcium carbonate, starch etc. The critical areas of the process are the wet end, the coating section and the size emulsion. In the wet end it is important to inspect the machine frame under the wire, the surface of the foils, the suction boxes, the whitewater tanks and the clarifiers, in order to detect any possible presence of deposits and, if these are present, the aspect of the deposits e.g. smell, texture, and colour. In the coating division area, the presence of bad smells indicates the existence of microbiological problems. The infection of the solutions can also be checked by measuring the pH and the viscosity. Besides the traditional techniques used to study the microbiological contamination there are also some devices to monitor the development of biofilms in the white-water systems, e.g. the devices of Robbins and the modified Pedersen device and the insertion of ceramic tiles in the interior of the piping system (McCoy et al. 1981; Harris and Garnett 1989; Von Holy and Cloete 1988; Cloete et al. 1992; Wolfaardt et al. 1993).

The control of microbiological problems

Any programme of microbiological control requires a good knowledge of the papermaking system. Once the sources of contamination (e.g. treatment of fresh water and additives, control of the residence time in the storage tanks, control of the stagnant-flow areas) have been minimised the papermaker can control the microbiological population through the systematic maintenance and cleaning of the system and by using different chemicals. Alternatively, the application of other control systems, such as enzymatic degradation of the microbiological deposits and population control by the limitation of nutrients, can also be considered.

An issue of great importance at present is the regulation of the biocides at worldwide level, because of their effect upon human health and their disposal in the environment. Therefore, not only are the efficiency, the compatibility of the biocide with the process and the cost important, but the toxicity and the ecotoxicity must also be considered (Hoeckstra 1992). To control the efficiency of a treatment, the analysis of white water would be sufficient, and eventually that of the brokes, the fresh water in summer and the suspensions of starch and coatings. The biocides are dosed in two ways: continuously, e.g. for the preservation of the sizing and coatings, or discontinuously as, for example, in the wet end. Figure 1 shows the dosing points most widely adopted in the paper mills.

To reduce the toxicity of the deposits-control systems, biodispersants are used. The main characteristic of the dispersant is its capacity to reduce the size of dispersed particles, reducing the possibility of the formation of microbiological deposits. The dispersants also act as biopenetrators, opening the biofilms and allowing the biocides to penetrate through the exopolysaccharidal layer toward the interior of the cells (Barnes 1984). The non-ionic dispersants inhibit or reduce the formation of the microbiological deposits, forming deposits of less thickness and consistency, although in the presence of calcium carbonate greater amounts of dispersant are required. However, the lignosulphonates are not very efficient under papermaking conditions, and may even enhance the growth of these under certain circumstance because of the presence of sugars that serve as nutrients to the microflora (Cardoso 1992; Robertson and Taylor 1994).

The use of enzymes to control the microbiological deposits in the paper industry is efficient under the current operating conditions of the mills (Colasurdo and Wilson 1988). The most extended enzyme is called EDC-1 and was developed by Moor and Hach (1984). The EDC-1 hydrolyses and depolymerizes the fructose of the levan, one of the components of the biofilm, to its lower-molecular-mass soluble forms and continues hydrolysing the soluble polymer to form fructose, which is not sticky (Colasurdo and Wilton 1988). The effect of this enzyme can be increased by adding 10% of the normal dose of biocides to the system, because of the synergetic effect (Freis 1984).

The control of biofilms by the limitation of nutrients was also developed as an alternative to the application of biocides. It is based upon the biological equilibrium between the levels of bacteria and the concentration of available nutrients. The control of bioavailability of the nutrients is accomplished through the chelation of metallic ions, the complexation of biomolecules that participate in the cellular respiration and the tensoactive effect that influences the cell membrane and its exchanges with the medium. This process is not directly aggressive to the bacteria and therefore the microorganisms' resistance to the treatment is avoided. Furthermore, the development of fungi is also reduced by the limitation of the bacteria, which is their main nutrient source. The implementation of this treatment in the mills can be accompanied by the addition of a biocide



Fig. 1 Main dosification points of biocides

at a different point of the machine. This treatment is particularly appropriate in paper mills with closed water systems as the necessary biological equilibrium for this treatment is easily achieved (Oberkofler 1990; Morros 1995; Porton and Dubout 1995).

Conclusions and the future

The control of the microbiological activity in the paper industry is necessary in modern mill conditions to reduce maintenance costs and downtime and to increase the production and quality of the final product. Therefore, slime control is not a non-profit-making expense but an integral part of a successful mill. The methodology for an optimum control system takes into account the following aspects: identification of the type of microorganisms that cause the problem; minimization of the contamination sources; control of the additive slurries, keeping a clean system by means of an adequate maintenance shut-down programme, prevention of the growth of anaerobic bacteria, especially of spore-forming species and selection of the most suitable control programme.

To optimize the microbiological control in paper and board mills a wide knowledge of the mechanism of formation of the biofilms is required and it is necessary, therefore, to improve the methods that allow observation *in vivo* of the bacterial deposits.

Because of the resistance of microorganisms to the traditional control systems based on biocides, the environmental considerations and the biological treatment of the effluent, other types of systems to control microbiological deposits have to be applied, e.g. enzymatic treatments and the limitation of nutrients. Furthermore, the synergetic effect of the combination of these treatments has to be established in order to increase the efficiency by using minor concentrations of chemicals.

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