

Odor Control in Papermaking



The formation of odors in and around a paper mill are more than just an unpleasant by-product of the papermaking process. The agents at play can affect product quality and create safety problems. Identifying causes of odors and implementing corrective action is paramount to an efficient production process.

By Holger Jung and
Dr.-Ing. Johannes Kappen

In papermaking, odorous substances impair product quality and may result in complaints and reduced revenue. Odor emissions may lead to grievances from neighbors, complaints from authorities and even call the industrial location into question. Occupational safety may even be endangered in some extreme cases.

Odor problems are not a singular problem, but are rather widespread throughout the pulp and paper industry. In response to a questionnaire organized in 2007 by Paper Technology Specialists (PTS) and the German Pulp and Paper Association (VDP), approximately 20% of the participating mills indicated that they had odor problems to deal with.

Odors in paper and paperboard may be caused in principle by the following factors:

- anaerobic microbiological processes in the water and pulp systems
- odors arising from additives and coating binders
- the oxidation of wood extractives
- odor arising from printing inks (when they interact with the paper).

ANAEROBIC MICROBIOLOGICAL ODOUR GENERATION

One frequent cause of odor problems is anaerobic metabolic processes of microbes in the water circuit, in effluents and sludges which give rise to hydrogen sulphide, volatile organic acids and other compounds, some of which are truly ill smelling. Odor problems as a result of microbial processes are usually linked with increasing closure of water circuits and rising recovered paper utilization rates.

Microbial odor formation is related to a number of preconditions:

- pre-microbial growth with odor-forming micro-organisms
- an oxygen-deficient or oxygen-free (anaerobic) environment
- sufficient supply of nutrients
- sufficient dwell time
- additional factors that support environmental conditions such as specific pH and temperature ranges.

Odorous substances form microbiologically in the absence of air, whereas emission requires contact with air. Odorous substances therefore inevitably pass from the water phase to the air phase at a location other than where they form. Odorous substances, once they have formed, are therefore emitted after transport and a change of environment, at locations of high turbulence by stripping or at large boundary layers between water and air.

If the neighborhood around paper mills is affected, authorities will normally call for certifications that the mill is conforming to emissions regulations. Odor surveys can narrow down local areas in which odor emissions are being released and — as a basis for legal evaluation — the level of the odor pollution is determined in the area surrounding the mill. Such studies, however, provide little information regarding the sources and causes of odor formation because the odorous substances are simply not formed in the same process step in which they are emitted. The water circuit must be analyzed in order to identify and evaluate the underlying anaerobic microbial metabolic processes.

It is possible to obtain a meaningful inventory using the measurands redox potential, strippable hydrogen sulphide, pH and organic acids. Additional parameters confirm results and help to interpret measurements. What is important is

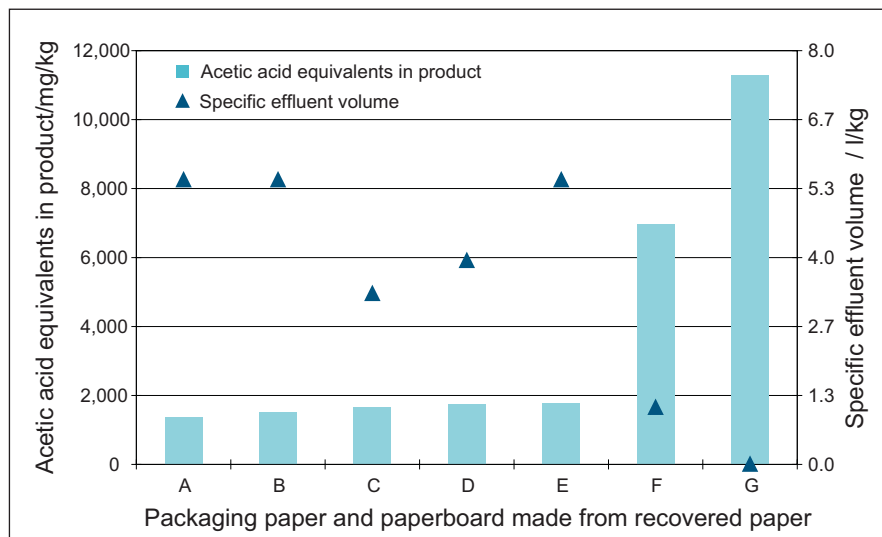


Fig. 1: Organic acids in the product of packaging paper and paperboard.

that the water circuitry and process control be evaluated at the same time the analytical parameters are being determined. Conducting and interpreting such a process analysis should be carried out by trained personnel in order to guarantee success.

DETERMINATION OF THE CONTENT OF LOW-MOLECULAR-WEIGHT ORGANIC ACIDS BY ION CHROMATOGRAPHY

Paper can contain intense smelling contents of low-molecular-weight fatty acids such as acetic acid, propionic acid, butyric acid or valeric acid. Greater amounts of these substances impart to the paper an acidic, rancid smell ranging from moldy to sewerage-like. These acids are formed as metabolic products by anaerobic and facultative anaerobic micro-organisms in water and pulp systems.

One possible method of determination is ion chromatography. In this procedure, the aqueous sample is passed through a suitable separation column where the dissolved organic acids are adsorbed for different lengths of time, thus separating them. The presence of the organic acids is verified by conductivity. The low-molecular-weight organic acids contained in the paper are previously dissolved by hot water extraction. **Figure 1** shows the content of low-molecular-weight organic acids as acetic acid equivalents in packaging paper and paperboard produced from recovered paper.

ORGANOLEPTIC ANALYSIS

Organoleptic analysis can provide helpful evidence to explain the causes of an off-odor coming from a product. For this purpose, samples are subjected to an odor test in accordance with DIN EN 1230-1, a sample that is found

to be unobjectionable and odorless being used as a standard reference sample. The additives and raw materials used during production can be employed as reference samples with the product odor being compared with them.

INPUT OF ODOROUS SUBSTANCES BY WAY OF ADDITIVES

Depending on their composition, chemical additives may carry substances into the process which bring with them an off-odor or may react in the product to form aldehydes, producing in this way an off-odor. Such substances include aldehydes such as hexanal and unsaturated fatty acids. Studies have shown that especially the unsaturated fatty acids, oleic

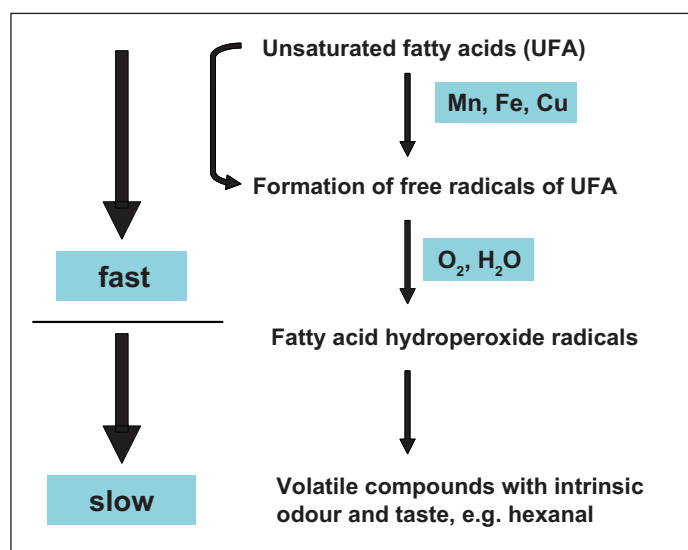


Figure 2: Degradation pathway of the unsaturated fatty acids of wood lipids.

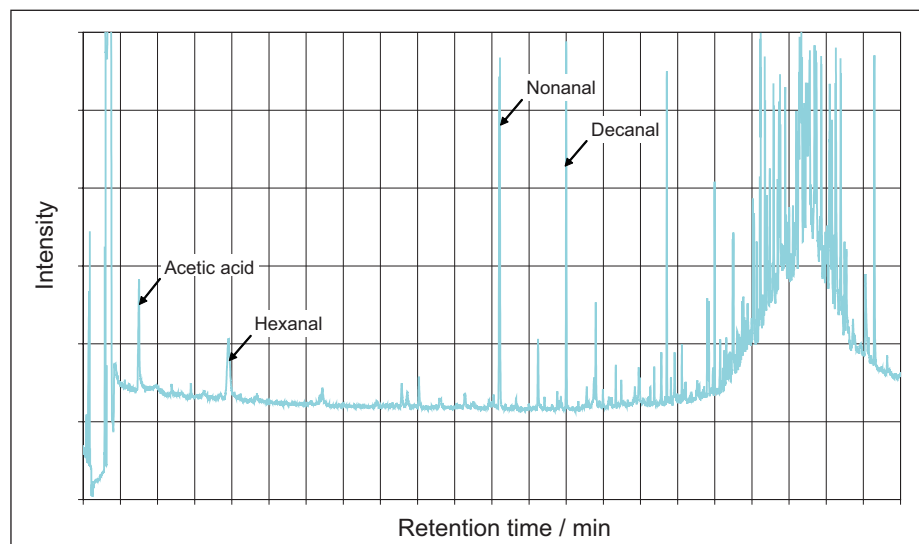


Figure 3: Determination of volatile organic compounds by thermal desorption GC MS.

acid, linoleic acid and linolenic acid can be converted to form aldehydes. Analytical determination of the content of hexanal and organic acids (with a minimum length up to C20) provides starting points for optimization. A preliminary selection of the additives to be examined can be carried out on the basis of the safety data sheets and organoleptic analysis.

OXIDATION OF WOOD EXTRACTIVES

A rather large number of low-molecular-weight compounds contribute to product odors. In addition to the organic acids and sulphur compounds mentioned above, low-molecular-weight aldehydes from unsaturated fatty acids of wood extractives are frequently the cause of odor. Hexanal is frequently used as an indicator substance to analytically trace the source of these odors. Wood contains approx. 0.5 – 9% of extractable constituents dependent on the type and origin of the wood and also depending on the season of year. Residual amounts (approx. 0.1 – 0.5 %) of extractable constituents still exist in the pulps even after digestion.

Analyses have shown that these extractable constituents contain resin acids in addition to relatively large amounts of saturated and unsaturated fatty acids in some cases both in free and in esterified form (waxes, triglycerides). This explains why paper products made of virgin fiber can develop odors depending on the production and storage conditions. The starting point is the low-molecular-weight oxidation products of the unsaturated fatty acids from the parenchyma resin as part of the wood extractives.

Whereas hydroperoxides are formed quickly as the oxidized precursors of malodorous aldehydes, the reaction leading to these ill-smelling aldehydes is a reaction that proceeds

slowly at room temperature (Figure 2). As far as the formation and release of these ill-smelling substances is concerned, this means that the fatty acid-hydroperoxide precursor depends on the concentration of the reactants unsaturated fatty acid and oxygen as well as on the presence of the heavy metal catalysts Mn, Fe and Cu.

Determination of volatile organic compounds by thermal desorption GC MS Thermal desorption GC MS is ideal for determining volatile organic compounds in samples of product and raw materials (Figure 3). This measuring procedure was developed to determine highly and medium volatile organic

substances that can be released from paper. The solid sample is heated in a helium flow and the substances released are cryofocused at $-150\text{ }^{\circ}\text{C}$, then separated by gas chromatography and detected using a mass spectrometer. The randomly sampled study of paper by thermal desorption GC MS provides valuable information about the presence of individual substances in the paper. Accurate quantification of individual substances, however, requires both calibration for precisely the substances that are being looked for and in particular examination of a large number of samples.

CORRECTIVE ACTION

In the experience of PTS experts, measures that affect the conditions in unit operations favoring the formation of odorous substances are suitable for effective and economical optimization to avoid anaerobic microbiological processes in the water circuit. Such measures include the following:

- reduction of dwell times
- avoidance of biofilms and dead zones
- stirring and ventilation.

Chemical additives can then be used in the next step. Nitrates and hydrogen peroxide should be taken into account in addition to conventional biocides. Subsequent measures such as enclosing the emission sites do not prevent odorous substances from forming. They only prevent them from being released. In order to analytically monitor the effect of the optimization measures, samples should be taken at regular intervals prior to and shortly after measures have been implemented. The parameters mentioned above should be measured at critical locations in the system as part of routine analysis.

If the cause of the off-odor of the product does not lie in the anaerobic microbiological processes, then the input of odor-causing substances must be reduced first of all.

Attention should be focused on both substances that have an off-odor themselves (e.g. aldehydes) or those that react during the production process, thus forming substances with an off-odor (e.g. unsaturated fatty acids). The raw materials used as well as the chemical additives constitute the starting point.

Yet another starting point for guaranteeing organoleptic product quality is to avoid or reduce the formation of fatty acid-hydroperoxides that form from the unsaturated fatty acids of wood extractives as a precursor to hexanal formation. The reaction path offers the following points of departure, making it possible to reduce or prevent the unsaturated fatty acids from forming hydroperoxide:

- effective complexation and removal of the heavy metals (especially Cu, Fe and Mn) that greatly accelerate the

formation of hydroperoxides and hexanal

- reduction in the extractive contents in the raw material
- the use of antioxidants to block the oxidation and autoxidation reactions.

When using complexing agents and antioxidants, attention must be given not only to the efficacy and economy of their use but also to the ecological consequences, since some of the complexing agents now on the market are virtually non-biodegradable and the use of some antioxidants causes AOX substances to form.

For internal quality control purposes, it is advisable to set up an odor panel to monitor the organoleptic quality of the product. It is recommended that pH-dependent odor tests be carried out by the panel. In addition to these tests, the raw materials should also be included with check samples being tested at regular intervals in order to trace the time-dependent development of the off-odor. ■

Holger Jung is Project Manager - Energy and Water Use at PTS. He can be contacted at: holger.jung@ptspaper.de. Dr.-Ing. Johannes Kappen is Division Manager, Resources Management. He can be reached at: johannes.kappen@ptspaper.de.

Paper Technology Specialists (PTS) is a research and consultancy firm with pilot plants in Munich and Heidenau, Germany. With a staff of 150 highly qualified specialists, PTS carries out product development, process optimization and materials testing in its research laboratories and pilot plants using highly efficient analytical techniques.



NEW CITY.
FRESH PERSPECTIVES.

PAPER2011
WHERE THE INDUSTRY MEETS
MARCH 28-30 CHICAGO

PRESENTED BY

American Forest & Paper Association

npta ALLIANCE
Paper • Packaging • Supplies