PROBLEMS WITH PAPER ODOUR - POSSIBLE WAYS TO SOLVE THEM

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Abstract. Paper intended for food packaging should be low in odour to avoid tainting. Microbial activity under anaerobic conditions may cause odour problems in mills with closed water systems or mills using recycled paper. Direct aeration, good water circulation and addition of biocides reduce the problems. Extractives in mechanical pulp and sulphite pulp may oxidise to odorous compounds. Addition of chelating agents, pulp washing and addition of antioxidants reduce the odour caused by oxidation. Paper additives may be odorous, decompose to odorous compounds, or be contaminated by odorous compounds.

Keywords. Odour. Taint. Microbial activity. Extractives. Autoxidation. Antioxidant.

INTRODUCTION

A main purpose of food packaging is to protect and conserve the food's flavour. If the packaging material itself has any flavour, there will be a substantial risk of unacceptable flavour interactions. Odorous compounds from the packaging material may be transferred to the food and affect the food's flavour. Considerable losses may be experienced when such transfer of chemicals results in consumer dissatisfaction. The problem with odour and taste is complicated by the lack of simple and easy-to-use assessment methods. Further complications are caused by the fact that the flavour often changes during paper storage. The flavour experienced by the consumers may thus differ from the flavour detected by the mill quality control systems.

For paper and board used for packaging, there are several potential sources for flavour interactions. When problems with tainting are reported, the source most often may be traced back to printing inks and varnishes. But from time to time the problems are caused by the paper or board material itself. Paper and board will never be completely odourless, and their odorous compounds are known to taint foods. The odorous compounds in paper may originate from quite different sources. In mills with closed water system or in mills using recycled pulp, microbiological activity is frequently the main source for odour [1]. Oxidation of wood extractives is the most important odour source in furnishes containing mechanical pulp or sulphite pulp. Paper additives and degradation of paper additives are also reported as sources for odour [2]. In the following, a discussion on the different odour sources in the paper mill will be given, and strategies for odour abatement will be briefly surveyed.

PROBLEMS IN ODOUR ASSESSMENTS

Before the sources of odour are analysed, the assessment methods of odour should be briefly commented on. As yet, no chemical analysis can copy the accuracy and sensitivity of the human nose. Therefore sensory analysis is the only method which can truly be trusted. When utilizing people for assessments, great care must be taken to ensure objectivity. The assessors must be carefully selected, well trained and work under stable and well defined conditions. Given these precautions, a sensory panel can provide an objective ranking of paper samples, and a detailed description of the differences between them. Sensory analysis is especially useful when combined with an instrumental analysis. For instance a headspace purge-and-trap GC-MS system can provide detailed information on which chemical components are present in paper headspace, and combined with sensory analysis, the chemists are left with clues to what causes the odour. [3]

ODOUR CAUSED BY MICROBIAL ACTIVITY

Any papermaker may right away make a long list of problems and nuisances caused by microorganisms in the process water. If he produces food packaging, the list will be especially long. Heat resistant spores may contaminate the final product, and microorganisms may produce odorous compounds. Under anaerobic conditions many microorganisms will produce volatile fatty acids (VFA), which are smelly substances. Acetic acid (vinegar odour), butyric acid (rancid butter odour), propionic acid (Swiss cheese odour) and valeric acid are the predominant VFAs. In addition to VFAs, sulphur reducing bacteria can produce hydrogen sulphide (H_2S), with a smell like rotten eggs. [1]

VFAs may be produced by facultative anaerobic microorganisms or by strict anaerobic bacteria. However, only strict anaerobic microorganisms are able to further decompose the VFAs. The facultative anaerobic microorganisms will live both under aerobic and anaerobic conditions, whereas the strict anaerobic organisms will die if exposed to oxygen. In a paper mill, the water flow is constantly changing between direct aeration and stagnation in storage tanks. Web breaks introduce dynamic disturbances to the water system. The paper machine water system will thus tend to favour the growth of facultative anaerobic organisms, and inhibit the growth of strict anaerobic microorganisms. The consequence will be that, in closed water systems, the VFA concentration builds up in the process water, finally ending up in the products. [4]

Ways to reduce odour from microbial activity

The nicest way to reduce odour caused by microbial activity will be to avoid VFAs being formed. VFAs are formed only under anaerobic conditions. To avoid VFA production, adequate oxygen concentration in the system should be ensured. Good water circulation, direct aeration, and avoiding stagnant water volumes are all actions that can easily be implemented [5]. The VFAs are soluble and mix well in the process flows. Without sufficient concentration gradients, it may be difficult to trace the origin of the VFAs by monitoring the actual VFA concentration in the water system. Available technology exists for monitoring by-products of the anaerobic activity. It is claimed that the problem with insufficient concentration gradients may be overcome [4]. It should be noted that excess of oxygen in the water phase does not ensure oxygen surplus inside biological films and aggregates of microorganisms [1]. Biological films thus may exhibit an aerobic surface and an anaerobic interior, as the oxygen is consumed while diffusing inwards. This effect has been demonstrated in relatively thin films, less than 0.2 mm thick [6]. Minimization of biological film growth and biological activity in general is thus necessary to avoid local anaerobic conditions with resulting VFA production.

Thus, aeration is not a complete strategy. Even biocides have to be applied to avoid build up of microorganisms in the water system. However, care must be taken, as even some biocides have strong odour. Biocides should also be added to chests during shut down periods. [5]

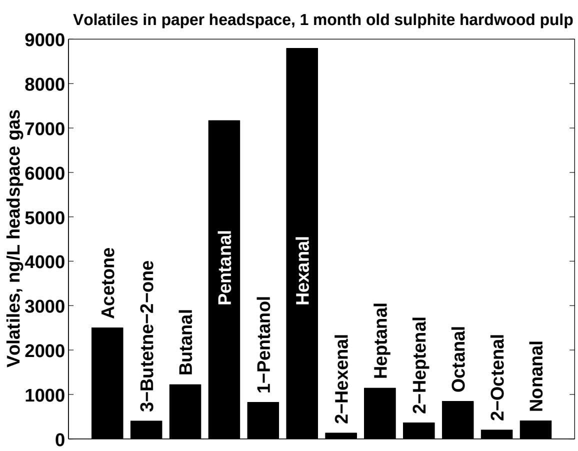

Figure 1. Typical volatiles in headspace of sulphite hardwood pulp

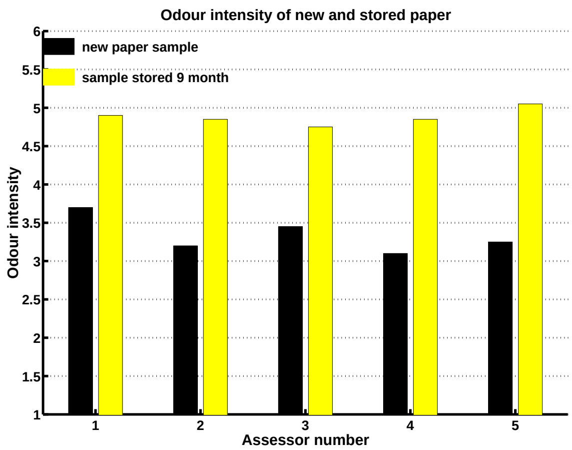

Figure 2. Odour intensity analysed by five assessors at a mill.

Addition of nitrates has been suggested as an action against formation of sulphides. The nitrate ion has a redox potential making it favourable as a terminal electron acceptor compared to the sulphate ion [1]. I am not aware of any mill scale implementation of this hypothesis. Avoiding alum is also recommended, being a major sulphur source [7].

Water system closure has been expected to increase the odour problem caused by microorganisms. The risk for anaerobic conditions is increased by higher concentrations of nutrients, and the concurrent reduced solubility of oxygen caused by increased temperature [8].

The odour problems caused by microorganisms have been reported to increase when switching to alkaline papermaking, as a result of raised microbiological activity at a more favourable pH level. [6]

ODOUR CAUSED BY OXIDATION OF WOOD EXTRACTIVES

Wood extractives are the dominating sources for odour in paper grades containing mechanical pulps or sulphite pulps. The problems are especially severe for unbleached pulps because of the higher extractive and metal ion content [2]. The following discussion considers how these odorous volatiles are formed and how to reduce the problems caused by wood extractives.

Fats and waxes constitute a major fraction of the wood extractives. There are also some free fatty acids in wood. The amount of fats, waxes and free fatty acids in wood vary depending on

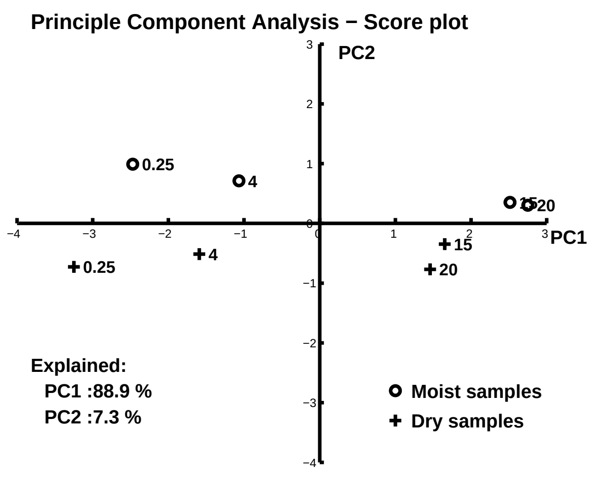

Figure 3. PCA analysis. Numbers by the data points state time of storage in months.

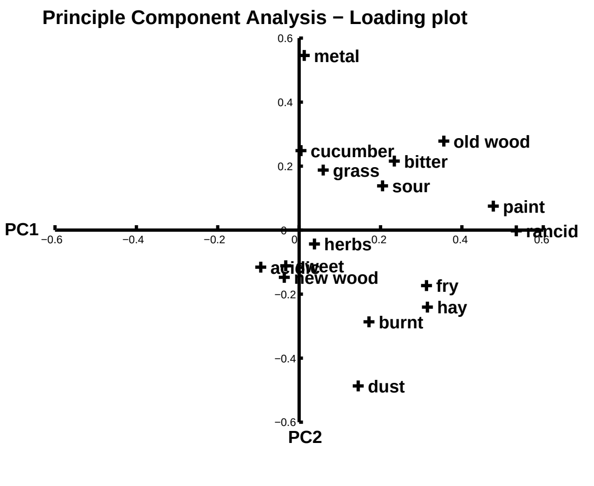

Figure 4. PCA analysis - score plot for the samples of Figure 3.

many factors like wood species, season, place of growth, weather condition and others. In general, quite large variations are observed. Some of the fatty acids are unsaturated [9-13]. These fatty acids are susceptible to oxidation, a reaction during which many odorous volatile compounds are formed [14]. The oxidation of the fatty acids by the air oxygen, often referred to as autoxidation, is what we ordinarily term fats going rancid. Paper is exposed to hot air during drying, and is later continuously exposed to air during storage and use. The fats in the paper will therefore inevitably go rancid.

The autoxidation is a very complicated free radical chain reaction. The free radical mechanism is not very specific, but the reaction takes place at a carbon atom in the vicinity of a carbon-carbon double bond. The final step in the oxidation process cleaves the carbon chain of the former fatty acid, thus producing smaller and more volatile compounds. The break occurs near the former carbon-carbon double bond [14]. As the unsaturated fatty acids in wood are typically linoleic acid (C18:2 ω3), oleic acid (C18:1 ω6) and linolenic acid (C18:3 ω9), one may expect the volatiles to have typically about three to nine carbon atoms. And analyses prove indeed such volatiles to be present in paper headspace, Figure 1, [15]. Several of the volatiles seen in Figure 1, have flavour threshold levels in the order of a few ppb. The composition of the gas in Figure 1 resembles that of rancid edible oils, thus exhibiting a pronounced smell.

Some metal ions catalyse rancidity. This is especially true for iron, copper and manganese, which are catalytically active even at the concentration levels often observed in paper mill water systems. [14,16]

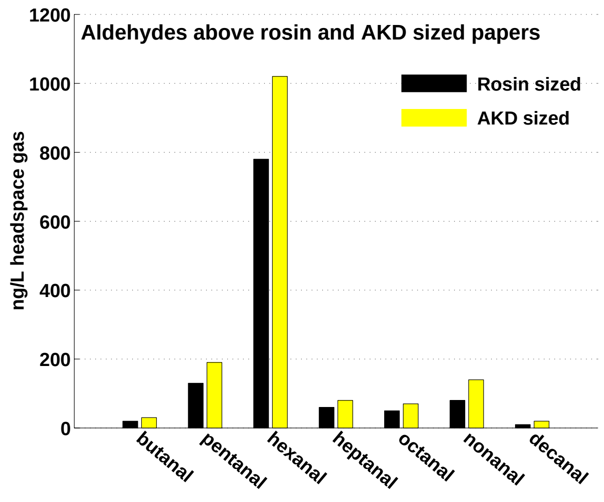

Figure 5. Volatile aldehydes in paper headspace of AKD and rosin sized paper

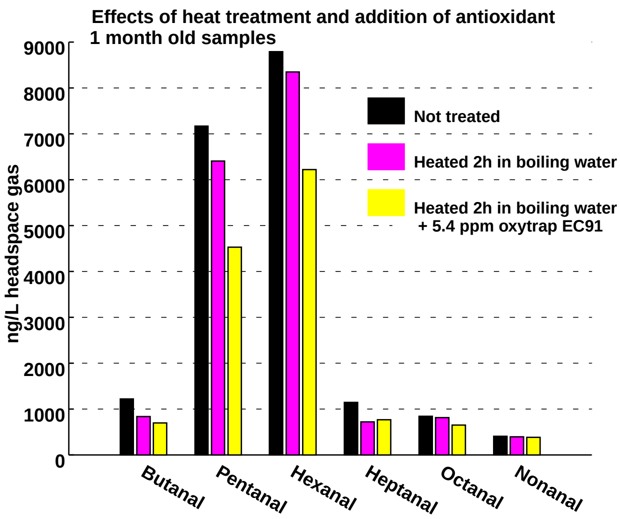

Figure 6. Effects of heat treatment and addition of antioxidant.

It is very important to realize that the oxidation of the fatty acids continues after the paper has been produced. Therefore, both the odour intensity (Figure 2) [17], and the odour characteristics (Figures 3 and 4) [3], change during storage. Paper converters may thus experience higher odour levels than the quality control systems have detected at the paper mill. Attributes such as *paint* and *rancid* become more prominent upon storage (Figures 3 and 4). Both are attributes commonly associated with oxidised samples.

Ways to reduce odour from wood extractives

The obvious solution to the odour problems caused by wood extractives is to remove the extractives. Unfortunately, this is not an easy task. A large fraction of the extractives are contained inside parenchyma cells, making these extractives hard to reach by washing chemicals. Extractives are also present as dissolved and colloid substances, as well as precipitated on fibres. A combination of thorough pulp washing and fines removal by screening may be beneficial, however hardly acceptable from an environmental point of view. Both pulp washing and fines removal have proven to reduce the odour.

As certain metal ions have a strong catalytic effect on the odour causing reactions, washing with chelating agents such as EDTA or DTPA is proven to be very efficient [18,19]. The metal ions lose the catalytic effect when chelated, making the chelating agents beneficial even without subsequent washing [16].

Alkaline paper has been found to be slightly higher in volatiles and odour compared to acidic paper, Figure 5. The effect is probably caused by an increased pH value in the AKD sized paper. Thus, in some packaging paper grades, rosin sizing is preferred from an odour point of view. However, rosin sizes seem to taint tobacco, and should be avoided in tobacco packaging.

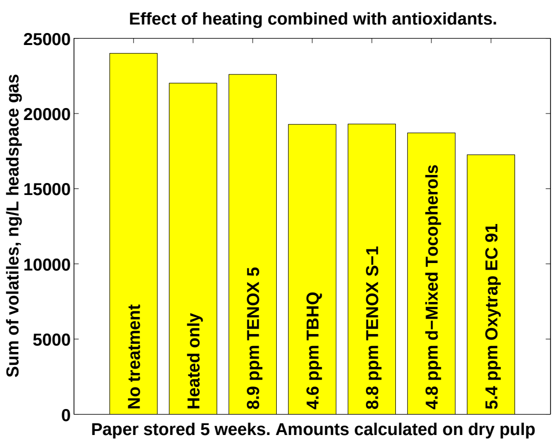

Figure 7. Comparison of different antioxidants added after the pulps had been heated at low oxygen concentration.

Antioxidants are chemicals that can protect fats against oxidation [16]. Addition of antioxidants have been found to improve the sensory properties of ground wood during the initial paper storage [2]. However, antioxidants can not repair already damaged fats. That probably explains why some trials that we performed with addition of antioxidants to TCF bleached sulphite pulps showed no beneficial effects. The oxidative bleaching prior to the treatment may have damaged the fats beyond repair. If, however, the pulp is treated by heat at low oxygen concentration in order to reduce the amount of damaged fats and intermediates, subsequent addition of antioxidants has proven to be beneficial, Figure 6. We have tested several antioxidants as additives to paper, Figure 7. The observed decrease in odorous volatiles has been confirmed by a sensory panel. Even though the effect of the antioxidants is small, the technique is interesting because the cost of the chemicals is very low, and several of the antioxidants are of food grade. [15]

ODOUR CAUSED BY PAPER ADDITIVES

Paper additives are the third main cause for paper odour besides microbiological activity and degraded extractives. Published literature on odour caused by paper additives is very limited. Sour starch is a familiar problem. Defoaming agents have been reported to cause odour. Monomers of styrene-butadiene latexes used in coating have been found to cause tainting. [18]

The papermaker should be aware that paper additives may decompose in the paper. For the assessments, some storage time must therefore be allowed before conclusions are drawn.

The papermaker also should be aware that paper additives may be contaminated with compounds having flavour. Thus, sensory testing of the paper additives should be incorporated in the quality control systems.

SUMMARY

Paper odour is a problem of raising importance. The odour may originate through many different sources. Some sources are rather trivial to eliminate, such as changing the brand of defoaming agent. Other sources are very difficult to eliminate like the oxidation of wood extractives, where present technology merely can offer a reduction in odour. However, by careful choice of furnish, production technology and paper additives, it is possible to produce paper low in odour.

Table 1: Factors affecting paper odour

Process	Possible effects	Odour response
Bleaching	Alkaline stages remove extractives Chelating agents remove metal ions Oxidative chemicals initiate rancidity	Overall odour reduction
Sizing	AKD sizing increases pH in the paper	Increased odour
Paper storage	Autoxidation proceeds	Increased odour
Washing	Fines and extractives are removed	Decreased odour
Biocides	Decreased microbiological activity Some biocides have odour	Reduced odour caused by microorganisms Increased biocide odour
Recycled paper	Spores and bacteria are fed to system	Potential increase in odour
Chelating agents	Metal ions lose catalytic activity	Decreased odour
Coating	Latexes contaminated by volatile monomers	Increased odour

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