### 4.5.5 Substitution for sodium hypochlorite and chlorine-containing compounds in bleaching operations

**Description**

The application of hypochlorite gives rise to subsidiary reactions leading to the formation of a number of chlorinated hydrocarbons such as the carcinogenic trichloromethane (which is also the most frequently formed as it is the end of the reaction chain). Most of these by-products can be detected as adsorbable organic halogens by means of the sum parameter AOX. Similar contributions to the formation of hazardous AOX come from chlorine or chlorine-releasing compounds and strong chlorinated acids (e.g. trichloroacetic acid). Halogenated solvents are a different category of problematic AOX (see also Section 2.6.1.2).

Sodium hypochlorite was for a long time one of the most widely used bleaching agents in the textile finishing industry. Although it has been largely replaced in Germany and many other European countries, it is still in use not only as a bleaching agent, but also for cleaning dyeing machines or as a stripping agent for recovery of faulty dyed goods.

In certain conditions, sodium chlorite may also give rise to the formation of AOX, although to a lesser extent than hypochlorite. However, recent investigations have shown that the cause is not sodium chlorite itself, but the chlorine or hypochlorite present as impurities (from non-stoichiometric production) or used as activating agent. Recent technologies (using hydrogen peroxide as the reducing agent of sodium chlorate) are now available to produce ClO₂ without generation of AOX [18, VITO, 1998], [59, L. Bettens, 2000].

Hydrogen peroxide is now the preferred bleaching agent for cotton and cotton blends as a substitute for sodium hypochlorite.

When a single-stage process using only hydrogen peroxide cannot achieve the high degree of whiteness required, a two-stage process with hydrogen peroxide (first step) and sodium hypochlorite (second step) can be applied, in order to reduce AOX emissions. In this way the impurities on the fibre – which act as precursors in the haloform reaction – are removed, thus producing a reduction in AOX in the effluent. Nevertheless, a two-stage bleaching process using only hydrogen peroxide is today possible, thus completely eliminating the use of hypochlorite (cold bleaching at room temperature followed by a hot bleaching step).

There is also increasing support for peroxide bleach under strong alkaline conditions, which achieves a high degree of whiteness after careful removal of catalysts by a reduction/extraction technique. The additional advantage claimed is the possible combination of scouring and bleaching. The reduction/extraction followed by a strong oxidative combined bleaching/scouring step (high alkali and high active oxygen concentration) is applicable for bleaching highly contaminated textiles in all make-ups and on all types of machines (discontinuous and continuous). This method takes the oxidative route and uses the active oxygen.

**Main achieved environmental benefits**

The presence of hazardous AOX such as trichloromethane and chloroacetic acid in the effluent is avoided.

**Operational data**

Particular attention needs to be paid to the combination or sequence of pretreatment operations and to the mixing of streams containing hypochlorite or chlorine. For example, the application of the two-step bleaching method where hypochlorite as well as peroxide is used, is potentially hazardous if the hypochlorite bleaching is performed when large quantities of organohalogen precursors are still present on the substrate. The risk would thus be reduced if hypochlorite
bleach came as a last step after an alkaline peroxide bleach that removes the precursors from the fibre. However, no data were made available that show the importance of reversing the sequence of the two steps from hypochlorite → peroxide into peroxide → hypochlorite. It is actually more important to avoid mixing hypochlorite bleach waste water with certain other streams and mixed effluents, in particular from desizing and washing, even when the right sequence of pretreatment and bleaching is adopted. The formation of organohalogens is highly possible in combined process streams.

For chlorite bleach, handling and storage of sodium chlorite needs particular attention because of toxicity and corrosion risks. Machinery and equipment need to be inspected frequently because of the high stress to which they are subjected (see also Section 2.6.1.2).

Cross-media effects

Complexing agents (e.g. EDTA, DTPA, phosphonates) are normally applied as hydrogen peroxide stabilisers. The main concerns associated with the use of these substances arise from their ability to form stable complexes with metals (remobilisation of heavy metals), their N- and P- content and their often low biodegradability/bioeliminability. The addition of strong sequestering agents, however, can be avoided by fine control of the pH conditions during the bleaching process (see Section 4.5.6) and with the assistance of silicates, magnesium, acrylates or biologically degradable carboxylates, slowing down the uncontrolled decomposition of hydrogen peroxide (see Section 4.3.4).

Optical brighteners are often applied when peroxide bleaching is not sufficient to achieve the required level of whiteness. The resulting COD load and smoke during fixation in the stenter have to be taken into account. Moreover, optical whiteners are potentially irritating and thus not always acceptable for white goods coming into close contact with the skin (e.g. underwear, bedsheets).

Applicability

Substitution for hypochlorite as bleaching agent is applicable to both new and existing installations.

Hydrogen peroxide is a valid substitute for bleaching yarn and woven fabric made of most cellulosic and wool fibres and most of their blends. Today a full hydrogen peroxide bleaching process is also applicable to cotton & cotton-blend knitted fabric and a high degree of whiteness (>75 BERBER Whiteness Index) can be obtained (with a strong alkaline scour/bleach after removal of the catalyst).

Exceptions are flax and other bast fibres that cannot be bleached using peroxide alone. Unlike chlorine dioxide, the anionic bleaching agent is not strong enough to remove all coloured material and does not preferentially access the hydrophobic region of the fibre. A two-step hydrogen peroxide-chlorine dioxide bleaching is an option for flax.

It is claimed that a sequence where precursors of halogenation are removed with a peroxide bleach followed by a hypochlorite bleach (or a peroxide pre-bleach followed by a combined hydrogen peroxide/hypochlorite bleach) is still necessary for high whiteness and for fabrics that are fragile and would suffer from depolymerisation.

Sodium chlorite is an excellent bleaching agent for flax, linen and some synthetic fibres.
Economics

In general, bleaching with hydrogen peroxide is no more expensive than with hypochlorite because of market saturation.

The two-stage bleaching process with hydrogen peroxide proposed for knitted fabric is reported to be from two to six times more expensive than the conventional process using hydrogen peroxide and hypochlorite [179, UBA, 2001].

If using chlorine dioxide as bleaching agent, investment may be needed (in existing installations) for equipment resistant to the highly corrosive conditions in which this bleaching agent is used.

As far as the production of elemental chlorine-free chlorine dioxide is concerned, this process is fully investigated and described in another BREF (pulp & paper industry).

Driving force for implementation

Market demands for chlorine-free bleached textiles and the requirements set by legislation (regarding waste water discharge) are the main driving forces for the implementation of this technique.

Reference plants

Many plants in Europe and worldwide largely use substitutes for sodium hypochlorite as bleaching agent.

Reference literature


4.5.6 Minimising consumption of complexing agents in hydrogen peroxide bleaching

Description

When bleaching with hydrogen peroxide, oxygen species of differing reactivity may be present in water (O2**, H2O2/HOO-, H2O/OH-, HOOC/O2*-, OH*/O*-, O2/O*-). The kinetics of formation and disappearance depend on concentration of oxygen, energy for activation, reduction potential, pH, catalyst and other reagents. These processes are very complex and can only be explained with dynamic simulation models. It is widely accepted that the OH* radical is responsible for attacking the cellulose fibre and leading to its damage (depolymerisation) and that the formation of the OH* radical is mainly due to the reaction of H2O2/HOO' with transition metals such as iron, manganese and copper. The prevention of “catalytic” damage of the fibre as a consequence of the uncontrolled formation of OH* radical is usually achieved by using complex formers that inactivate the catalyst (stabilisers). See also Section 8.5.

Complexing agents (see Figure 4.6) that are typically applied in finishing mills are based on polyphosphates (e.g. tripolyphosphate), phosphonates (e.g. 1-hydroxyethane 1,1-diphosphonic acid) and amino carboxylic acids (e.g. EDTA, DTPA and NTA). The main concerns associated with the use of these substances arise from their N- and P- content, their often-low biodegradability/bioeliminability and their ability to form stable complexes with metals, which may lead to the remobilisation of heavy metals (see also Section 8.5).