Approach to substitution

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Content of presentation

- Background and general considerations (extracts from Contract No B3-4305/2000/293861/MAR/E1 report)
- Overview of BREFs regarding hazardous substances and substitution
- “Green chemistry”
- Practical aspects of substitution
- Available tools

Background setting

- Substitution of hazardous substances by less hazardous alternatives appears to be a straightforward approach when enterprises consider management and reduction of chemicals related risks.
- At the same time, various stakeholders' perceptions differ widely about the definition of substitution and concerning the question whether substitution should be a “fundamental principle”, a “duty to both producers and users of chemicals”, a “preferred risk reduction strategy” or whether it is “just another tool for managing risk”.

- For achieving the general goal of reducing risks from hazardous chemicals, the various guidance documents suggest a large range of measures, ranging from elimination, modification or replacement of processes or products to exposure reduction by personal protection measures. Based on the observation that in the management of chemical risks it is useful to distinguish between the technical strategies of hazard reduction by emission control and hazard reduction by substitution, the following definition of substitution is suggested:

  "Substitution means the replacement or reduction of hazardous substances in products and processes by less hazardous or non-hazardous substances, or by achieving an equivalent functionality via technological or organisational measures."

- The key aspect in this definition is the functional equivalence , i.e. the achievement of the same functionality by less hazardous means

Key drivers and barriers

- Key drivers and barriers towards substitution are identified particularly with regard to:
  - economic factors
  - technical functionality
  - communication and social factors,
  - risk information
  - the regulatory framework, that is set by legislation and standardisation.

- Legislation is found to be one of the most powerful drivers in many cases, often inducing substitution as a side-effect even where it is not explicitly addressed as the main goal.
- Another strong driver can be serious public concern about perceived chemical risks.

- In the absence of such robust drivers, short term economic considerations are often the main barrier, and a general tendency of downstream users prevails to stick to well-established conventional substances, rather than undergoing any risks with respect to quality and liability by experimenting with less hazardous substitutes.
- In several cases, there is a considerable imbalance between the available risk information on

  1) substances which have been found to be problematic and thus became subject to substitution efforts, and

  2) their potential substitutes for which less information is available, partly due to the fact that they have never been used on a similar scale as the conventional substance.
- Even where functionally equivalent substitutes are readily available, economically viable and proven to be less hazardous, their introduction in a certain process or product is often hampered by the fact that complex communication along the supply chain is a prerequisite for implementation.

- The motivation of companies to substitute specific substances differs significantly from other stakeholders’ attitudes. Decisions taken in enterprises are influenced by policy, regulation and enforcement, technology development, economy and market,scientific finding and the public debate. Both environmental legislation and public pressure are seen as relevant external factors.

General considerations

Why substitute?

- Substitution of currently-used materials with less hazardous materials is one of the most effective ways of eliminating or reducing human and environmental exposure to materials that are toxic or pose other hazards
- All other methods reduce or eliminate the risk of harm by interrupting the path of exposure between the hazardous material and the recipient, and rechannel the pollution. Substitution removes the hazard at the source

Scope of the task

- Care must be taken to ensure that one hazard is not being exchanged for another, especially one that could even be a more serious hazard. Before deciding to replace a chemical, one must know the risks of the chemical to the employees, the environment, and the risks for damage to equipment and facilities. If the risks are serious, then alternatives should be considered and their risks must also be understood.
- The selection of a substitute can be a very complex process. In large organizations the selection process may involve a committee with representatives from engineering, purchasing, industrial hygiene, safety, maintenance, research and development, environmental control, waste management, shipping and the supervisors and workers who directly work with the material. In smaller organizations, one person may carry out many of these functions

BREFs about substitution

Chlor-Alkali Manufacturing Industry

- The co-production of chlorine and sodium hydroxide in fixed proportions, 1.128 tonnes of caustic (as 100% NaOH) per tonne chlorine produced, has always been a problem for the chloralkali industry. Currently the best option to deal with this is considered using chlorine absorption units that contain weak caustic soda. As a result sodium hypochlorite is produced through neutralization reactions. Other important issue is reducing Hg emissions from caustic soda leaving mercury cells. This issue is dealt with carbon filtration which allows reducing the Hg content in caustic soda to 0.05 ppm.
- BAT TECHIQUE WITHOUT HG

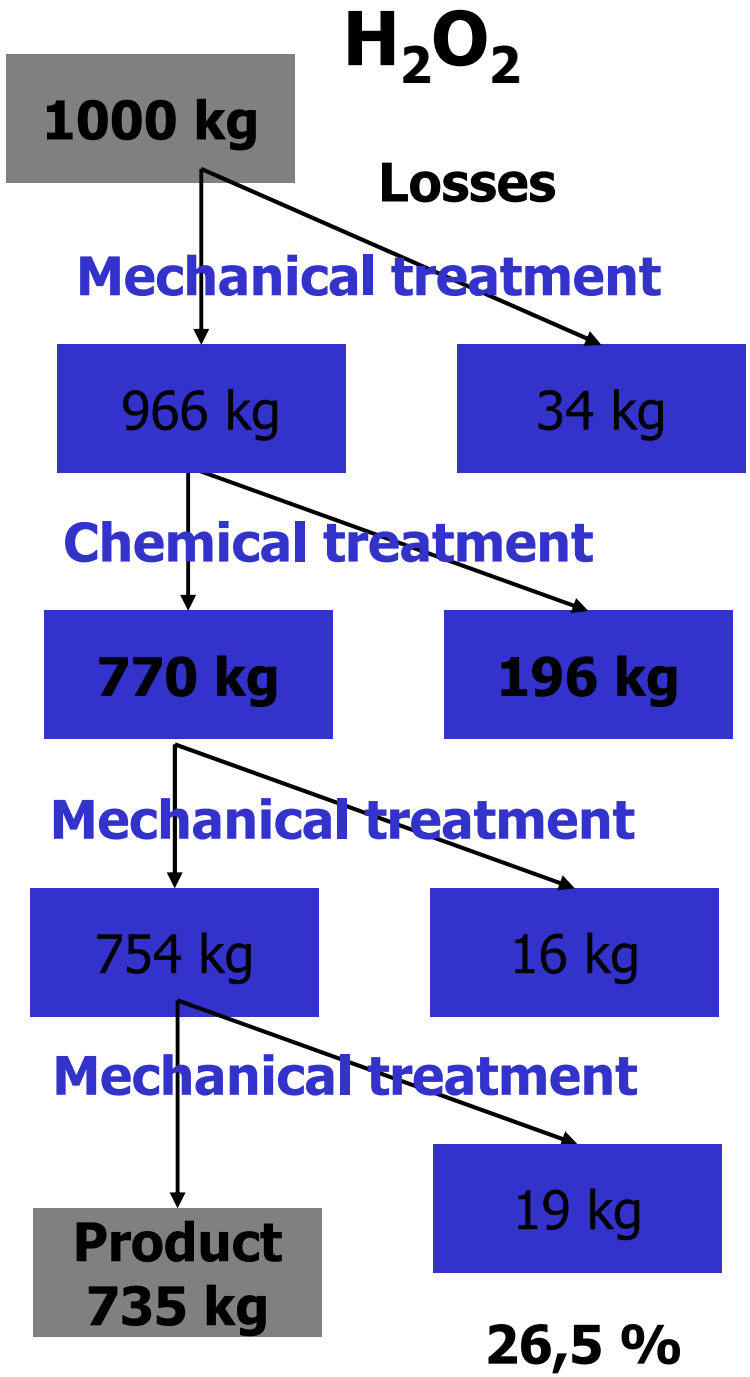
Textile industry

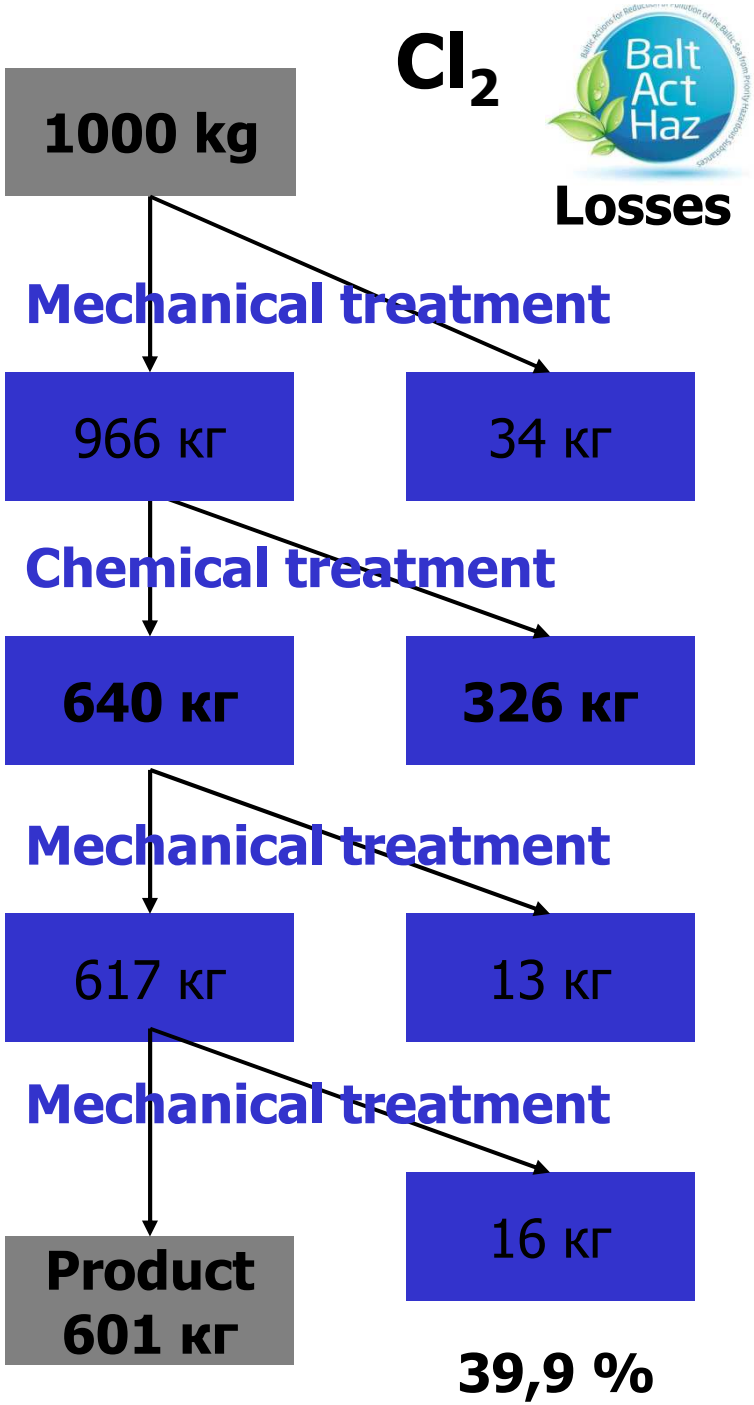
Pretreatment - bleaching

- Hydrogen peroxide is now the preferred bleaching agent for cotton and cotton blends as a substitute for sodium hypochlorite, although it is claimed that sodium hypochlorite is still necessary for high whiteness and for fabrics that are fragile and would suffer from depolymerisation. In these cases, a two-stage process first with hydrogen peroxide and then with sodium hypochlorite can be applied, in order to reduce AOX emissions (the impurities on the fibre – which act as precursors in the haloform reaction – are removed in the first step). A two-stage bleaching process using only hydrogen peroxide is also possible today, which completely avoids the use of hypochlorite. This option is however reported to be from two to six timesmore expensive.

BAT for bleaching

- Use hydrogen peroxide bleaching as preferred bleaching agent combined with techniques for minimising the use of hydrogen peroxide stabilisers, or using biodegradable/bioeliminable complexing agents
- Use sodium chlorite for flax and bast fibres that cannot be bleached with hydrogen peroxide alone. A two-step hydrogen peroxide-chlorine dioxide bleaching is the preferred option. It must be ensured that elemental chlorine-free chlorine dioxide is used. Chlorine-free chlorine dioxide is produced using hydrogen peroxide as the reducing agent of sodium chlorate
- Limit the use of sodium hypochlorite only to cases in which high whiteness has to be achieved and to fabrics that are fragile and would suffer depolymerisation. In these special cases, to reduce the formation of hazardous AOX, sodium hypochlorite bleaching is carried out in a two-step process in which peroxide is used in the first step and hypochlorite in the second. Effluent from hypochlorite bleaching is kept separate from the other streams and mixed effluents in order to reduce formation of hazardous AOX.


H_2O_2
1000 kg
Losses
Mechanical treatment
966 kg
34 kg
Chemical treatment
770 kg
196 kg
Mechanical treatment
754 kg
16 kg
Mechanical treatment
Product
735 kg
19 kg
26,5 %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1000 kg
Losses
Mechanical treatment
966 кг
34 кг
Chemical treatment
640 кг
326 кг
Mechanical treatment
617 кг
13 кг
Mechanical treatment
Product
601 кг
16 кг
39,9 %

Industrial Cooling Systems

- The most concerning part regarding hazardous substances in this industry sector is additives to the cooling liquids. The used amount of these substances must be carefully evaluated together with the chemical and toxicological properties. Common approach to reduce the use of hazardous substances is to avoid using any materials that contain Hg, Cd, Cr, wood, preserved with CCA or TBTO. In general, a very important aspect is to prevent any leakages from the cooling system.

Surface Treatment of Metals and Plastics

- It is a general BAT to use less hazardous substances. It is BAT to substitute for EDTA by biodegradable alternatives or to use alternative techniques. Where EDTA has to be used, it is BAT to minimise its loss and treat any remaining in waste waters. For PFOS, it is BAT to minimise its use by controlling additions, minimising fumes to be controlled by techniques including floating surface insulation sections: however, occupational health may be an important factor. It can be phased out in anodising and there are alternative processes to hexavalent chromium and alkali cyanide-free zinc plating

Manufacture of Organic Fine Chemicals

- Mass balance of all input and output materials must be made to get information about hazardous substances emissions and possibilities of replacing them. In many cases process intensification can help in reduction of reactor volume for potentially hazardous processes.

Green chemistry
(or sustainable chemistry)

- A chemical philosophy encouraging the design of products and processes that reduce or eliminate the use and generation of hazardous substances
- Seeks to reduce and prevent pollution at its source
- Three key developments in green chemistry:
  - use of supercritical carbon dioxide as green solvent,
  - aqueous hydrogen peroxide for clean oxidations
  - use of hydrogen in asymmetric synthesis.

12 principles of Green Chemistry

The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up in the product;
- the use of safe, environment-friendly substances, including solvents, whenever possible;
- the design of energy efficient processes;
- the best form of waste disposal: do not create it in the first place.

Practical aspects of substitution

- What are some major considerations to look at when considering the suitability of potential substitutes?
  - **Effectiveness.** Will the material meet the technical requirements (e.g., solubility, drying time) for the job or process?
  - **Compatibility.** The substitute must not interfere or react with the process, the other materials or the equipment.
  - **Existing Control Measures**. Existing control methods may not adequately control the substitute (e.g., a less toxic substitute may evaporate more rapidly and the existing ventilation system may not adequately capture the vapours).
  - **Waste Disposal**. Will the current waste disposal system meet technical and regulatory requirements when dealing with any new waste created by using the substitute?
  - **Hazard Assessment**. A hazard assessment should be done to decide whether to substitute a different chemical or material.

Hazard assessment

- Use material safety data sheets (MSDSs) and other sources of chemical information to compare the hazards of various materials. For easier comparison, set up a table with the following categories for each potential substitute. The important properties to compare are:
- Physical properties like vapour pressure, log(Kow), etc.
- Accute health and environmental effects
- Long term effects
- CMR properties …

Steps to take

- From "7 Steps to Successful Substitution of Hazardous Substances", HS(G) 110, Health and Safety Executive, United Kingdom, 1994.
- **1. Identifying hazards and assessing risks.** This step involves deciding whether the current substance or process is a hazard. Is there a significant risk involved in storing, using or disposing of a substance? A hazard is defined as "the potential a substance or process has to harm someone or damage the environment." Risk is "how likely this is to happen."

2. Identifying alternatives

- Investigate a wide range of options. Compare all of the hazard assessment information as previously mentioned in this document. Compare the different states of a chemical (e.g., will a granular form create less dust than a powder form?) Also consider whether the job is necessary or not (e.g., can the part be replaced rather than cleaned). If you are a supplier, you may need to select options according to your customers' needs as well as those of your own employees.

3. If to use the alternative …

- **Think about what could happen if you use the alternatives.** It is important that you have gathered all available information before this step so that you can make a realistic comparison of both the good and bad points. Remember that you must also consider the way employees use it and how likely it is that they may be exposed. Choosing an alternative chemical may require changes in:
  - the way the work is done,
  - the kind of equipment or parts (e.g., O-rings, gaskets or hose materials) needed to be compatible with the substitute chemical,
  - the ventilation system that may be required,
  - the disposal methods, and
  - regulatory requirements that may apply.

4. Comparing alternatives

- In this step, compare the alternatives with each other, and with the substance or process currently being used. HSE recognizes that it is hard to compare the risks of one chemical that is very flammable with one that is very toxic. They recommend thinking of the effects in simple terms such as "Is the substitute going to explode, or poison people? Will it only affect people who work with it, or could it affect other people in the area?" Remember to consider how and where the alternative will be used.

5. Decide whether to substitute

- This step is the most difficult. Remember that a change in one step of a process can affect many others. Consult with the workers who will be handling the material directly for their input. It may be a good idea to introduce the substitute on a trial or small quantity basis at first.

6-7. Final steps

- **6. Introducing the substitute.** Plan the change in material or process carefully. Remember to train and educate the workers involved.
- **7. Assessing the change.** Check to see if the substitution has produced the intended results. You may find monitoring the health of the workers, monitoring the level of contaminants in the air, or fulfilling legal requirements useful parameters to measure

Tools for substitution - general

- **Column pattern for chemical substitutes**
  - Worker's health related initiative
  - The BGIA - Institut für Arbeitsschutz has developed the so-called column pattern to provide industry with a practical aid for the identification of possible substitutes. Only little information on the products is needed to carry out the assessment by means of this table
  - http://www.dguv.de/bgia/en/pra/spalte/spaltmod.pdf

Tools for substitution - specific

- **CLEANTOOL – Optimisation of metal surface cleaning**
  - EU 5th Action programme financed project 2001-4
  - CLEANTOOL is a Europe wide database for parts cleaning, metal surface cleaning, component cleaning and degreasing, based on real processes in numerous European companies
  - When searching for processes you can choose selection criteria meeting your individual needs, and you have the possibility to evaluate the listed processes according to your individual point of view
  - Links to other similar sites

http://www.cleantool.org/en/index.php

SAGE - Solvents Alternative Guide

- US-EPA link (http://sage.rti.org seems to be not working)
- SAGE is a comprehensive guide designed to provide pollution-prevention information on solvent and process alternatives for parts cleaning and degreasing.
- Use its well-designed "expert system," which asks a series of questions, and will assist you in determining those solvent/process alternatives most likely to work for your particular circumstances.
- There are separate indexes for alternative processes and solvents, each containing a great deal of valuable information.
- The site may be searched for a particular topic or phrase