Chapter 7

Toxics reduction in processes.
Some practical examples.

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Abstract

Toxics reduction aims at reduced releases of toxics substances. Toxics use reduction (TUR) has been advocated as a simple and effective method of reducing toxic pollution. Substitution and product reformulation are placed first in the TUR hierarchy based on effectiveness of reduction, product and process changes are placed second and, recycling, plant operations and maintenance are placed third. Here we analyze five examples of process modifications given by the company as an example of toxics reduction. The companies involved have a well developed environmental management system. All companies mentioned environmental legislation as a reason for toxics reduction and three mentioned also legislation aimed at the working environment as a reason. One of the companies involved used a ranking list for solvent substitution, evaluating environmental risks and risks of the working environment. Three other companies used less sophisticated lists for solvent optimalization and product development. The methods used for process modification are rather different. Three stressed input substitution and one product reformulation. These four lead to toxics use reduction. In two of the three cases that input substitution was performed the risks shifted from toxic to inflammable. In the two of the three cases that workplace legislation was mentioned as a reason for process modification, the working environment improved after process modification. Unexpectedly three of the four cases of toxics use reduction studied were said by the company to lead to increased costs. Factors to evaluate so that processes for toxics reduction be properly modified are besides risks of processes, risks of products, substitution decisions (all risks), performance and quality of products and costs. Maybe the studied companies, as they were forced by legal requirements, focused on complying with legal requirements and not on improving mentioned factors.

Introduction

Toxics may pose risks to workers and consumers and may also lead to environmental risks (1). Toxics reduction leading to reduction of risks is an issue for both governments and companies in industrialized countries. The influence of regulation has been limited in this context (2,3).

A study as to how and why companies are reducing the toxics showed that
most of the companies (nine out of ten) mentioned legal compliance as a reason for toxics reduction, product (safety) was mentioned by four companies and the working environment was mentioned twice (4).

To achieve substantial results to toxics reduction, toxics use reduction (TUR) should be part of all elements of the environmental management system (EMS) (4-8). Factors to integrate in EMS procedures for evaluation, in order to modify processes for toxics reduction are besides risks of processes, risks of products, substitution decisions (risks), performance and quality of products and costs. With risks we mean risks of releases to the general environment, risks of emissions to the working environment and risks to consumers.

TUR is an element of pollution prevention (9-11) as also shown by the comprehensive definition of pollution prevention mentioned by Gottlieb (9): pollution prevention is seeking to eliminate hazards in all environmental media along the production chain encompassing not only environmental releases but also occupational exposures and product use. The pollution prevention hierarchy is described in decreasing preference as: source reduction, recycling, treatment, ultimate disposal (10). TUR reduces, avoids or eliminates the use of toxic or hazardous substances or generation of hazardous by-products per unit of product, so as to reduce risks to the health of workers, consumers, or the environment, without shifting risks between workers, consumers or parts of the environment (12). The MA TURA accepts six techniques to achieve TUR, 1) input substitution, 2) product reformulation, 3) product unit redesign or modification, 4) product unit modernization, 5) improved operation and maintenance of product unit equipment and methods and, 6) in process recycling, reuse or extended use. OTA (The U.S. Congress Office of Technology Assessment) defines the same techniques in five methods (13, 14).

In the TUR hierarchy based on effectiveness of reduction, substitution and product reformulation are placed first, product and process changes are placed second and, recycling, plant operations and maintenance are placed third (14). Input substitution is a cornerstone of the TUR strategy (15). However substitution may be considered a highly complex process (16). Input substitution presents special concerns because chemical substitution when made without an understanding of all the issues involved, has the potential to increase rather than decrease risks (15). This has to do with the multifaceted nature of chemical substitution,
the acute or chronic health risks, safety and, fire risks (17), the limited knowledge of the toxicity of chemicals (18), the sometimes incorrect available information (19) and, the possible shift of risks from the working environment to the general environment and vice versa (14,20,21). Also functional aspects of chemicals are important. For example: with regard to substitution there is a difference in solvents used in the process (cleaning solvents), solvents in products (paints), and solvents used as chemical building blocks, for example butadiene, ethylene, and xylene. From the first two applications of organic solvents 100 % comes to be emissions or waste. The latter application is necessary for making non-hazardous products and cannot easily be replaced (15), alternative synthetic pathways are needed.

Toxic chemicals are usually closely monitored and disposed of, whereas substitute chemicals will not be subject to the same practises. Similar complexities surround product reformulation.

Burnett states that most source reduction will come from industry as it re evaluates and redesigns its production process, performed as a continuous process of technical innovation and diffusion (22). Moreover processes may be the subject of input substitution, product reformulation and other techniques to achieve TUR. Therefore we focused our study on process modification. In order to do so we studied five modified processes in companies with a well developed EMS. The modified processes were given by the companies as examples of toxics reduction. We also looked in the practical examples at the extent that toxics risks may be replaced by other hazards and / or risks. Pollution prevention has been hailed as the most cost-effective method for environmental management (11,22,23). Theodore (24) states if a pollution prevention project cannot be justified economically after all factors and considerations have been taken into account (Total Cost Assessment), it should not be pursued. Therefore we gathered information about the costs involved in process modification.

As the use of toxics may cause problems both to the open and the work environment we asked whether the environmental department is integrated with the department of risk, safety and health. The question about quantifying techniques used by the company was to understand the possibility whether the company could estimate or calculate the environmental impacts before and after the process modification.
Method

The study was carried out with structured interviews, (table 2) and a process investigation from February 1998 until December 1998. We selected four large companies (table 1) that were known to have performed toxics reduction by modifying their (production) process. To select the companies we used the most recent corporate environmental reports. Criteria were: large company (operating internationally or belonging to an internationally operating company), a developed environmental management system, the headquarters and a large site in the Netherlands. The criteria used, large (international) company and a developed management system were intended to be sure that the company had substantial expertise in the field of the research project. After selection of the company a member of the management of the environmental department was informed about the research project by phone. In four cases the corporate environmental department and in one case the head of the Abandonment, Soil Restoration and Waste Management department was informed. Afterwards the questions for the interview were faxed and the company was asked to select one or more experts on the subject. All companies co-operated. In one case two sites of one company co-operated. Most of the time (four times) the corporate and site environmental department was visited. The companies were asked to select an example of processes modified to reduce the amount of toxics and/or toxic releases to the general environment or the working environment. The interviews were executed at the company and took about two hours. Furthermore, written material was collected (site environmental report, process descriptions, procedures). In all cases more information was obtained by a second interview at the company or by phone. When needed the questions were asked in several ways to probe the subject of the question to the bottom and to be sure the answers were reliable. The interviews were recorded, transcribed into a written text and sent back for comment. The text of the interviews was sent back to be sure there was no misunderstanding. The interview texts were finalized on the basis of these comments. Most comments were very minor with the exception of one. The interview (table 2) was structured into three parts with open questions. The first part was intended to get insight into the organisation and into the environmental organisation. The second part focused on toxics reduction. The last part was focused on the process, the process before and after the modification.
table 1

participating companies

1. NAM (Shell and Esso)
2. Océ
3. DSM Resins
4. DSM Andeno
5. Akzo (site)

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table 2

Interview

organisation

1. How is the company organised, central or decentralised, number of sites, countries, workforce.
2. How is the environmental organisation set up.

toxics reduction

3. Does the company have a policy to reduce the toxics (input, throughput (intermediates) waste and / or emission), if so how.
4. Has toxic reduction a place in the environmental management system.
5. Did you reach a reduction in the number and amount of toxics or the releases, if so how did you reach it.
6. Are you using quantifying techniques, if so which techniques are used.

process investigation

The company was asked to give an example of a process modification leading, in the companies opinion, to toxics reduction.

7. What was the reason for this process modification.

process before/after modification

8. Description of the process before/after modification.
9. Quantities toxics used, input, throughput, output (product/nonproduct).
10. Quantities of emissions (water, air) and wastes.

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Results
The results from the interviews are given below. A summary of the results is to be found in table 8.

Company 1 (NAM workforce 2700)
The main activities of the company are gas and oil exploration and production. The company is organised in business units, with 800 locations on- and off shore in the Netherlands. The information used is derived from written material and an interview with the manager of the Abandonment, Soil Restoration and Waste Management Department and the manager of the external waste treatment facility. The corporate office of Health, Safety and Environmental (HSE) Affairs includes a small staff which advises the corporate management and develops the corporate environmental policy. Every business unit has its own HSE department with a staff which advises the manager of the business unit.

The company has a corporate policy for toxics release and use reduction. The policy is focused on reduction of the effects of chemicals on the (working) environment and on reduction of the amounts of materials used by the exploration and production. The reduction of toxics releases is mainly reached by recycling (for example methanol, glycol and oil based mud). The company uses quantifying techniques in order to calculate the environmental impacts of waste and emissions. They developed their own method for quantifying the impact of the waste (25). The method is mainly based on the destination of the waste (reuse, recycling, incineration or dumping). The impact of the air emissions is calculated in EIU’s (Environmental Impact Units) as in LCAs (26). The environmental investments options are ranked in costs per EIU reduction.

The example of a process modification to reduce toxics given by NAM concerns gas treatment.
In 1970 it was discovered that gas produced contained mercury. The annual production of $4.10^9 \text{Nm}^3 \text{ gas} \ (1995) \ contained \ 6500 \ \text{kg} \ \text{Hg} \ (180 \ \text{g mercury} / \text{m}^3 \text{ gas}).$ To reduce the mercury in the gas, a gas conditioning process based on cooling and filtering is used. After the conditioning a part of the mercury is to be
found in a sludge fraction. A part of the mercury is found as liquid mercury. The filters, sand and water contain a relatively smaller part of the mercury. A gas condensate fraction also containing some mercury is sent to another company. The water fraction containing some mercury is injected underground (back into the original gas reservoir). Target of the gasconditioning process is to keep the mercury concentration in the gas as low as possible. The company states that the described gasconditioning process is the best available technology. The sludge was the subject of process modification.

The original sludge treatment process was as follows. The sludge 500,000 kg/year (containing +/- 1,2 % mercury, water (20 %) and hydrocarbons (20 %) including 300 ppm benzene) was filled with bentonit (clay) and calciumsulfate to solidify. The sludge was sealed in barrels. Handling of the barrels needed personal protection due to the mercury and benzene concentrations in the working environment. The barrels are kept in a conditioned C1 dump (a depleted salt mine). The company states that the air emissions in the C1 dump are zero.

Due to new legislation dumping of the sludge was no longer allowed. A process modification was needed. Characteristics of this modification can be found in table 3. A factory was built aimed at recovering the mercury by destillation out of the sludge. The sludge is heated (with an energy of 1kWh/1kg sludge). After cooling the vapor is separated into three fractions, mercury, water and hydrocarbons. The process is kept under nitrogen and low pressure. The mercury concentration in the working environment is kept as low as possible (< 20 g/m3). The hydrocarbons and benzene concentration in the working environment are said to be 0 g/m3. Mercury (30 g/m3) and hydrocarbons (30 mgr/m3) are released to the air (output 8000 m3/year). The mercury recovered is reused, the hydrocarbons (with a mercury concentration of 10 ppb) are sent as fuel to an incinerator. The waste, 300,000 kg/year (burned sand, clay and oxidized iron) containing 2 ppm mercury is disposed of in a C3 dump. The water 100,000 kg/year polluted with mercury (10 g/m3) and hydrocarbons is sent to the waste water treatment.

The cost of the original disposal of sludge in a C1 dump were given as fl 1000,- per thousand kg sludge. The process of heating the sludge and recycling the mercury costs were stated to be fl 5000,- per thousand kg sludge.
The company is active in graphic technology and has business units in more than 30 countries. The information used is derived from written material and an interview with the manager of the consumables production and the manager R&D at the headquarters in the Netherlands. The company has no integrated corporate health, safety and environmental department but at the headquarters there is a department for product safety and environment, and a department for workplace safety and environment. The company has a corporate policy for health, safety and the environment. When developing a new product the raw materials are checked early in the project against a black list. The black list comprises the materials to be excluded by law (asbestos, cadmium, PCB’s, ozone depleting materials etc.) as well as materials the company wants to be excluded (materials likely to be excluded by law in the near future). The possibilities for dealing with the products in the post consumer stage (reuse and recycling) are considered. The company’s strategy is to design the products in such a way that the materials and parts can be reused and recycled. Hazardous materials are avoided if possible. The company has it’s own recycling facility. The materials used during the development of the product in the R&D department are checked too, for example carcinogens are allowed only in R&D under controlled conditions.

The process modification selected by the company for this study as an example of toxics reduction was executed in the supplies department. Characteristics of the two-step process modification are given in table 4. The department produces supplies for the copying machines, including polyester sheets. In some cases a light sensitive layer is needed on polyester. In order to bring a light sensitive layer on the polyester sheet (melinex) a process is used with organic solvents. First the sheet (roll of polyester) is etched with trichloroacetic acid in water. The etching is needed to prepare for attachment of a cellulose-acetate layer on both sites of the sheets. Originally the cellulose-acetate was dissolved in een 7 : 3 solution of dichloromethane and methylene glycol. In the years 1970 (until 1980) the coating process was executed as an open process. Due to environmental legislation and financial reasons associated with losses of solvents a process modification was needed. The process was closed and the vapor condensed (258 °F). The solvent was recycled and reused. Still about 5% of the solvent was lost due to evaporation during the drying process and after the process, as the sheets contained sol-
vent after drying. In 1993 465,000 l. solvent was used of which 5% (about 23,000 l.) was emitted in the working environment. Enforced ventilation was used to reduce the workplace concentrations. The reduction of the legal MAC value (legal limit for workers exposure) of dichloromethane forcefully brought home the problem of the working environment. Solvent concentration in some cleaning processes exceeded the new MAC value 100 fold.

Again a process modification was needed. The only choice perceived was substitution of the solvents. The solvent chosen is a 8:2 mixture of acetone and ethanol. The emission to the working environment (and therefore into the general environment) is still 5% of solvent used. The choice of the acetone and ethanol mixture was mainly based on the solvability of the celluloseacetate in the solvent and the high MAC values of acetone and ethanol. Acetone and ethanol however are inflammable and/or explosive. (The company had the knowledge and experience to work with inflammable solvents.) Investments were needed for the new process to reduce the risks of inflammability and explosiveness. The oxygen concentration is critical, monitoring of the working environment is executed. The process and solvent stock is kept under a nitrogen atmosphere. After modification the process costs are higher due to the investments. R&D will be started to substitute the organic solvents with water.

**company 3 DSM Resins, Zwolle (workforce 1800)**

The company out of the chemical industry has its production sites mainly in Europe and the USA. The main production sites and the headquarters are located in the Netherlands. The information used was derived from an interview with the Safety, Health and Environment and Quality manager from the business unit Industrial Resins & Compounds and a product specialist 'Insert resins'. The company has a corporate Safety, Environment Health & Technology department at the headquarters with a small staff. The business unit Industrial Resins was visited (workforce 1000). Every business unit has a small HSEQ (one person) staff, the same holds for the production units. The business unit staff 'translates' the corporate policy for the business unit, co-ordinates and stimulates and advises. The business unit produces about 130,000 ton of polyester resin. The business unit does not have a management system for toxics reduction but the R&D of new products is aimed at toxics reduction. The business unit uses the company's prio-
rity substances lists (black list European Union). The reasons for toxics reduction are legislation (environmental and working conditions) and problems of the customers with toxic materials (additives to the polyester resin). About 500 types of different polyester are produced. The chemicals and amounts used for producing the different types of polyester depend on the customer’s specification of the polyester and price. The process is as follows: the chemicals are mixed, polycondensation takes place at a temperature of 200-220 °C in a closed process. The vapour of the process holds water and some organic acids, the vapour is mixed with the fuel of the incinerator. After the polycondensation the polyester is mixed with the styrene in a closed process. After adding some chemicals and, if necessary, some styrene dependent on the viscosity, the polyester is delivered to the customer as a polyester in 40 % styrene solvent. To start the hardening of the product at the customers site (crosslinking of the polyester with the styrene) some additives are needed. The polyester resin may be polymerised at the customers in moulds or in open systems, for example by spraying or by spreading. About 50 % of the amount of polyester in styrene is used in open systems. When the polyester styrene solution is used with open techniques about 7 % of the styrene evaporates. Most of the time the customers are small to medium sized companies. In many cases the knowledge and means to take the right measures for limiting the impact of styrene on the working conditions is not sufficient.

Due to European environmental legislation which reduced the allowable emissions of styrene (volatile organic compounds) and changing requirements for the working environment (a reduced MAC value of styrene, from 50 to 25 ppm) a process modification was needed. (In Germany the monitoring of styrene emissions is obligatory by law, in the Netherlands the monitoring of the total emissions of volatile organic compounds is obligatory.) A possibility to reduce the styrene concentrations in the working environment is changing the open techniques into closed systems and improving the enforced ventilation. End of pipe technology may be used to reduce the emissions into the general environment. Other possibilities were to develop a resin without styrene, a resin which causes a reduced styrene emission by using an open system, or a resin with a reduced concentration of styrene. The company decided to modify the polyester resin in order to reduce the styrene emission. This process was chosen by the company as an example of toxics reduction. Main characteristics of the process change are given in
To modify the resin a process was developed with a modified chemical composition and a reduced concentration of styrene (a 25-30% solution instead of 40%). The technology of the process was not modified. (In order to get a polyester resin solution with the same viscosity the molecule weight of the polyester was reduced.) Moreover parafins and waxes (C25 - C35) were added to form a film on the surface of the polyester during the hardening, thereby reducing evaporation. (However most of the evaporation of styrene occurs during the spraying or spreading.) After the modification the evaporation of the styrene, during the spraying or spreading and hardening, is 3-4%. The costs of the modified resins are increased with 30-35%. The higher cost are due to the change in chemicals. Still R&D has to be done to reduce the costs.

**company 4 DSM, Andeno, Venlo (workforce 400)**
The company out of the chemical industry has its production sites mainly in Europe and the USA. The main production sites and the headquarters are located in the Netherlands. The information used is derived from written material and an interview with the manager Quality, Environment, Safety and Health and the environmental specialist of the dependent site. The company has a corporate Safety, Environment, Health & Technology department at the headquarters with a small staff. Every business unit of the company has its own (small) QESH (Quality, Environment, Safety, Health) staff, the same holds for every site. The business unit visited belongs to the business group fine chemicals. The business unit visited (3 sites) produces pharmaceutical intermediates. The strategy of the company is emission reduction of the toxics but also reduction of the number and amounts of toxics. The business unit is working to eliminate all materials which have an impact on the ozone layer (corporate requirement). Directives exist to start in the R & D phase of a new process with the non or less toxic solvents. There is not a ban on a solvent, but investments are higher with toxic solvents. The corporate list with priority substances (European Union black list) is used in the R&D stage of a new process to optimize the process solvents. Optimization of solvents in existing processes is more difficult, substituting solvents can lead to other unwanted by-products. The production site used 6 solvents from the priority substances list. Two toxic solvents are completely eliminated, carbon tetrachloride and...
1,2 dichloroethane. The process modification chosen by the company as an example of toxics reduction concerns a process to produce an intermediate of an antibiotic. Characteristics of the process modification are given in table 6. The original process produces the intermediate FGZ (d-phenylglycinechloride-hydrochloride) out of d-phenylglycine. Out of the FGZ (mol.weight 206) another company produces an antibiotic (ampicillin). Carbontetrachloride and 1,2 dichloroethane are used as a solvent for the production of the FGZ. There is a net consumption of solvents (0.1 kg carbontetrachloride and 0.027 kg 1,2 dichloroethane per kg FGZ) due to several losses. Most of the solvents was recycled (98%, calculated out of the needed extra input) and reused. An emission into the air remained, 72 ton/year. The concentration in the air of the workplace was monitored on 50% of the MAC value for both solvents.

A process modification was needed due to legislation, as carbontetrachloride was no longer allowed. A possible modification considered was to use methylenechloride instead of carbontetrachloride or just 1,2 dichloroethane. However the use of a 100% methylenechloride solvent needed high investments. Furthermore the possibility existed, at the time of the process modification, that methylenechloride should also be excluded due to legislation. 1,2 Dichloroethane was not chosen as a substitute due to high investments needed for a process with a toxic solvent. This drew attention to an alternative process existing on the site, the production of FGkze (mol.weight 301) which may be used as another intermediate for ampicillin. For this closed process the solvent 2-propanol is used. However in the process 2.2 liter 2-propanol is lost per kg FGkze. In the beginning most of the releases of 2-propanol were carried off as waste. Nowadays 70% of the 2-propanol is recycled and reused. The first process was closed and the second process expanded. The working environment associated with the second process is not monitored. A reason for this was said to be the high MAC value of 2-propanol. The vapour of 2-propanol is inflammable. As a location for inflammable processes already existed (the so called multipurpose department) it was not necessary to make safety investments. After the modification the process costs are lower due to lower investments. The extent to which the efficiency of the production of ampicillin differs with the different intermediates was not a subject of our study (mol.weight of FGZ 206 and FGkze 301).
Company 5, Akzo site, workforce 1200

The site visited belongs to the business unit which produces active pharmaceutical ingredients. The business unit has a workforce 2000 worldwide and seven sites. The business unit has to fulfil the requirements of the FDA (Food and Drugs Administration, U.S.A.). The information used is derived from written material and an interview with the manager of the HSE (health safety, environment) department of the site visited. The business unit does not have a central HSE staff department. All the sites have their own HSE staff departments, the size of the HSE department depends on the size of the site. The sites may use the HSE expertise of the other sites. The company has a corporate strategy for toxics reduction, there are some quantified targets. The corporate strategy aims at the reduction of the impact of non-product output, hazardous waste, hazardous emissions to air and water. The company works with 'product stewardship' (27). There are no requirements for suppliers and no lists with unwanted hazardous or priority materials for the company as a whole. Several sites have developed their own lists in this field.

At the site visited many different batchwise processes are executed. The processes are chemical reactions in a solvent. After reaction the materials are crystallized, filtered and dried. Alcohols are the largest amount of solvents used. The process modifications chosen by the company as an example of toxics reduction were its dealing with organic solvents.

The site executed several process modifications in order to reduce the releases of solvent to the working environment and the general environment. Characteristics of process modifications are given in table 7. The site eliminated some organic solvents (benzene, trichloromethane, dichloroethane). It is stated that it is impossible to eliminate or substitute chlorinated hydrocarbons (such as trichloroethylene and methylenechloride) completely. The reasons for substitution and elimination in the past were, most of the time, requirements for the working environment, because most processes were open processes at that time. Later on legal and other environmental requirements formed reasons to substitute and/or eliminate solvents. Nowadays the processes are as much as possible closed (the reactors were and are closed but the filtering and drying not, nowadays most handling is controlled or closed).

In the R&D phase of a new process, the main streams of organic solvents are
screened. For this purpose a ranking list of solvents was developed for the business unit. The use of the list is embedded in the management system. The ranking of the solvents on the list depends on quantified legal requirements for the working environment and open environment. The main ranking criteria are RIR index (relative inhalation risk, this describes the probability limits are exceeded) and emission potential (g/m³). Other criteria are presence on black lists, reprotoxic risk, fire danger and explosive risk. (Carcinogenics are not used.) All these criteria are assimilated in a health and safety score (the water score is 0, the highest score of dichloromethane is 10). The list is frequently updated (minimal once per 2 years). The update frequency is also dependent on alterations in the MAC values of the solvents on the list.

For the working environment the MAC value is used as an exposure limit. For materials without a known MAC value the site develops their own limits as much as possible conforming to the method of the MAC value. Some materials used (or produced) in the process are (biologically) very active. In many situations personal protection remains needed, because it is technically impossible to reduce unprotected exposure. Monitoring the working environment of every process is impossible, due to the large amount of different processes. With reference exposures and worst cases (materials and levels), processes and work situations are evaluated. Procedures and work instructions are developed based on the most critical materials used in processes.

Furthermore an activity program was developed for all solvents focusing on the main releases. For example the solvent emissions were reduced by applying technology for reduced nitrogen use in processes. To reduce the emissions of chlorinated organic solvents to water the waste water streams with the chlorinated solvents were separated from the other waste water streams. Distillation was used to separate these solvents from the waste water. The amount of chlorinated solvent in waste water was reduced from 82 ton (1986) to 600 kg at present. Nowadays about 12,000 ton of organic solvents are used. Half of the amount of the solvent used, about 6000 ton, is recycled and reused. The total purchase of organic solvents in a year is about 6000 ton. Emissions into the air are about 300 ton. These emissions are calculated out of input and output data. In spite of enlarged production the solvents consumed in processes remained approximately constant. There is no quantified accounting of the amounts of solvents elimina-
ted or substituted. It is stated that due to the use of the ranking list, the mix of organic solvents used must be less hazardous nowadays. Biotechnology is applied more in processes but it is not the strategy. (The strategy is to minimize the releases to the open environment and the risks for the working environment, biotechnology might be a choice.) The process costs are said to be higher after modifications due to higher investments in technology and experts.

Table 3

Main characteristics of process modification at NAM.

<table>
<thead>
<tr>
<th>process 1</th>
<th>impact</th>
<th>process 2</th>
<th>impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>500,000 kg Hg sludge/year</td>
<td>working environment exposure mercury and benzene, personal protection needed</td>
<td>500,000 kg Hg sludge/year</td>
<td>working environment exposure mercury &lt; 20 microgr./m³</td>
</tr>
<tr>
<td>open process</td>
<td></td>
<td>closed process</td>
<td>emissions air, 8000 m³/year</td>
</tr>
<tr>
<td>*adding 150,000 kg clay and calciumsulfate</td>
<td></td>
<td>*mercury 6000 kg, *hydrocarbons incl. 150 kg benzene total 100,000 kg</td>
<td>*mercury 30 microgr./m³</td>
</tr>
<tr>
<td>*sealed in barrels</td>
<td></td>
<td>*hydrocarbons 30 mg/m³</td>
<td></td>
</tr>
<tr>
<td>*C1 dump</td>
<td></td>
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</tbody>
</table>

Table 4

Main characteristics of process modification at Oce

<table>
<thead>
<tr>
<th>process</th>
<th>impact</th>
<th>process</th>
<th>impact</th>
<th>process</th>
<th>impact 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>open process dissolving cellulose-acetate in a solution of dichloromethane/ methyleneglycol 7:3</td>
<td>*open environment the evaporated solvent is enforced emitted into the open air working environment exposure to the solvent</td>
<td>process closed solvent dichloromethane/ methylene glycol 7:3</td>
<td>5% of the solvent evaporates into working environment and then in open, MAC value exceeded in some cases</td>
<td>closed process solvent acetone/ethanol 8:2</td>
<td>5% of the solvent evaporates into working environment and then in open, extra measures to reduce fire and explosion risk</td>
</tr>
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Table 5

Main characteristics of process change at DSM Resins

<table>
<thead>
<tr>
<th>process 1</th>
<th>impact</th>
<th>process 2</th>
<th>impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>production polyester resin, 130.000 ton process polycondensation polyester resin and dissolving the polyester in 40% styrene in closed processes use at customers about 50% of the resin is used in open systems</td>
<td>+/- 7% of the styrene evaporates into the working and general environment (open system).</td>
<td>production polyester resin, 130.000 ton process polycondensation polyester resin with a shorter chain length due to a change in chemicals and dissolving the polyester in 25-30% styrene in closed processes, adding paraffins and waxes use at customers unchanged</td>
<td>3 - 4% of the styrene evaporates (open system)</td>
</tr>
</tbody>
</table>

Table 6

Main characteristics of process modification at DSM Andeno.

<table>
<thead>
<tr>
<th>process 1</th>
<th>impact</th>
<th>process 2</th>
<th>impact</th>
</tr>
</thead>
<tbody>
<tr>
<td>production intermediate of an antibiotic (PGZ, mol.weight 206) process solvents carbon tetrachloride/1,2 dichloroethane 1:1</td>
<td>working environment carbon tetrachloride, 1,2 dichloroethane 1:1 (monitored at 50% of the MAC value) general environment emissions (72 ton/year) of carbon tetrachloride and 1,2 dichloroethane</td>
<td>production another intermediate of the same antibiotic (FGkze, mol.weight 301) in a closed process process solvents 2-propanol</td>
<td>working environment 2-propanol (not monitored due to the high MAC value) environment emission 2-propanol waste *before recycling about 2.2 liter 2-propanol/kg FGKze *after recycling 0.3 liter/kg</td>
</tr>
</tbody>
</table>
Table 7
Main characteristics of process modifications at a site of Akzo

<table>
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<tr>
<th>process</th>
<th>modified process 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>process</td>
<td>process</td>
</tr>
<tr>
<td>many different processes in batches</td>
<td>many different processes in batches</td>
</tr>
<tr>
<td>impact</td>
<td>impact</td>
</tr>
<tr>
<td>solvent emissions to working environment, air and water, waste</td>
<td>solvent emissions to working environment, air and water, waste</td>
</tr>
<tr>
<td>modifications</td>
<td>closing processes, in process and end of pipe technology, recycling of the solvents, use of ranking list of solvents</td>
</tr>
<tr>
<td>impact</td>
<td>impact</td>
</tr>
<tr>
<td>less exposure working environment, less releases</td>
<td>less exposure working environment, less releases</td>
</tr>
<tr>
<td>reduced use of organic solvents</td>
<td>reduced use of organic solvents</td>
</tr>
</tbody>
</table>

Discussion

In this study we try to analyze some examples of toxics reduction in processes of a number of companies. In order to do so we selected companies with a.o. the criteria developed environmental management system. These criteria will influence the results of the study as probably the selected companies will be leaders. The sample studied is small, but it may well be that the results are representative of the state of affairs of toxics reduction by process modification. The companies were asked to select an example of a process modified to reduce the amount of toxics or toxic releases to the general or working environment. All the companies studied had, more or less, toxics reduction integrated in the EMS.

All companies mentioned environmental legislation as a reason for the process modification. The working environment was mentioned three times. In the cases the working environment was mentioned the working environment improved in two of the three cases after the process modification.

The methods used for process modification are very different. Company 1 gave as an example for toxics reduction in a process an off-site waste treatment. The toxic materials concerned are mercury and benzene. The modification was needed caused by changing environmental legislation. However the toxic components are co-products of gas exploration. This makes all TUR techniques impossible. The changed process leads to the production of usable by-products. The mercury is reused, the other fractions, hydrocarbons and benzene are sent to the
incineration. In the pollution prevention hierarchy the modified process is increas­
ing one step from ultimate disposal to treatment (10). The waste is less toxic
after treatment. In the working environment there is still exposure to mercury
(about half of the MAC value). The costs after modification are 5 times higher.
The company states there was no other possibility.

Company 2 started with an open process and lost a lot of solvent. One of the
solvents used methylene chloride is a confirmed carcinogen (28). Using a closed
process was overtaken by legal requirements for the working environment. The
solvent was substituted with a less toxic solvent. The first modification (closing
the process, TUR hierarchy 3) reduced the toxic releases and use (source reduc­
tion). By the second modification input substitution was adjusted (TUR hierarchy
1). However the risk shifted from toxic to inflammable. This was facilitated by the
experience of the company with flammable solvents.

Company 3 uses product reformulation (TUR hierarchy 1) to get a lower emis­
sion of styrene to the working environment and to the general environment. The
毒ological properties of styrene are: suspected carcinogen, skin and eye irritant,
and the material has been involved in several industrial explosions (28). After
modification compared with before product modification still half of the amount
of styrene evaporates into the working environment and into the general envi­
ronment. The modified product is more expensive.

Company 4 uses product reformulation (TUR hierarchy 1) to substitute the
solvent, halogenated hydrocarbons with an alcohol. The risk for the working envi­
ronment shifted from toxic to inflammable (28). The modified process was alre­
dy operational on the site.

Company 5 takes several measures, including substitution, improved operation,
on site recycling and waste water treatment (10,12).

Only one company (NAM) uses on a regular bases techniques quantifying
environmental impacts (waste and emissions to the air).
<table>
<thead>
<tr>
<th>Company</th>
<th>Toxic policy</th>
<th>Toxic reductions</th>
<th>Reason process modification</th>
<th>Process modifications</th>
<th>Change in working environment</th>
<th>Change in emissions</th>
<th>Change in waste</th>
<th>Change in costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAM</td>
<td>yes</td>
<td>releases</td>
<td>environmental legislation</td>
<td>waste treatment (off site)</td>
<td>?</td>
<td>?</td>
<td>*less mercury</td>
<td>increase strong</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>*hydrocarbons are incinerated instead of dumped</td>
<td></td>
</tr>
<tr>
<td>Ocê</td>
<td>yes</td>
<td>use and releases</td>
<td>costs and legislation</td>
<td>*open process to closed (process 2), *input substitution chemicals (process 3)</td>
<td>process 2, +/- process 3, +</td>
<td>*reduction (process 2), *substitution, less env. impact (process 3)</td>
<td>increase</td>
<td></td>
</tr>
<tr>
<td>DSM Resin</td>
<td>yes</td>
<td>use and releases</td>
<td>legislation</td>
<td>modifying chemical composition of the resin, less styrene as a solvent is needed</td>
<td>+/-</td>
<td>reduction of styrene emission</td>
<td>increase strong</td>
<td></td>
</tr>
<tr>
<td>DSM Aden</td>
<td>yes</td>
<td>use and releases</td>
<td>environmental legislation</td>
<td>production of another intermediate for the same antibiotic, solvent substitution</td>
<td>+</td>
<td>2-propanol instead of carbon tetra chloride and 1,2 dichloro ethane emissions</td>
<td>less 2-propanol</td>
<td>decrease</td>
</tr>
<tr>
<td>AKZO (site)</td>
<td>yes</td>
<td>use and releases</td>
<td>legislation</td>
<td>*closing processes *in process and end of pipe technology *recycling of the solvents *ranking list of solvents</td>
<td>+</td>
<td>emission reductions to air and water</td>
<td>less</td>
<td>increase</td>
</tr>
</tbody>
</table>

? = not clear  
+/− = more or less  
+ = improvement
Costs

In 4 of the 5 cases the production costs increased after modification. (In 3 of the 4 cases where TUR was involved). This is unexpected in view of the opinion that pollution prevention is found to be the most cost-effective method for environmental management (11), and in view of the findings of Gray (17) showing the most important factors in chemical substitution decision making are regulatory compliance and costs. We did however not perform a total costs assessment (24). We just asked the companies if the cost increased or decreased after modification. Costs involved in using toxics are: engineering controls to minimize releases, regulatory reporting requirements, worker training requirements, secondarily contained storage facilities, and disposal restrictions (23). Most of these costs remain until the last toxic or hazardous chemical is eliminated or substituted. Two companies stated the costs increased due to investments (company 2 and 5). This is contrary to the statement of company 4 that investments are higher with toxic solvents and the findings of Higgins (23). The reformulated product of one company was more expensive (due to more expensive chemicals) and, the waste treatment process of NAM was more expensive. Higgins (23) identified in a review of corporate practices, five corporate decision models based on the following goals: minimize near term costs, minimize long term costs, reduce total waste, limit total expenditures to a fixed amount, achieve other corporate objectives (e.g. public image, reduced liability). From these goals only the reduced liability is reached by 3 of the 4 companies. For the fourth company even the reduced liability is doubtful. Financially the process modifications studied are no success stories. There are so far few, if any, examples in literature of cases where TUR ended up costing a company significant amounts of money. However it may be that the present literature is biased towards success stories (15).

Substitution

Three companies (2,4,5) substituted solvents. Only company 5 used a ranking list for solvents evaluating environmental risks and risks of the working environment. Company 3 and 4 use the corporate priority substances list (black list EU 76/464). Company 2 uses a black list for product development. The use of such lists is in line with the finding of Gray (17) that substitution decisions may range from ad hoc procedures to procedures that are defined, structured, and documented.
More elaborate decision making systems are found in the comparatively larger firms, which have many resources, often including an environmental, health, and safety department (HSE) (17). The companies studied were large companies with HSE or similar departments.

Conclusions

Obviously one of the biggest challenges for companies addressing process modification is not only solving the problem for which the modification was needed but improving or innovating the processes in such a way that more aspects of company performance improve. Factors to integrate in procedures for evaluation, in order to modify processes for toxics reduction are besides risks of processes, risks of products, substitution decisions (all risks), performance and quality of products and costs. Maybe the companies studied, as they were forced by legal requirements, focused on complying with legal requirements and not on improving mentioned factors. A more comprehensive response to toxics reduction than shown in the examples seems indicated. This is in line with TUR legislation in Massachusetts which stipulates that companies should develop plans identifying programs and goals to discontinue or reduce the generation, per unit of product, of any agent that appears on a defined list of toxic compounds provided that a comprehensive evaluating procedure is developed and the programs and goals are integrated in the EMS.

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20. Hoet, H. and all. Epidemic of liver disease caused by hydrofluoro-


