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Integrated Pollution Prevention and Control

Reference Document on
Best Available Techniques for the Production of

Speciality Inorganic Chemicals

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EXECUTIVE SUMMARY

The BAT (Best Available Techniques) Reference Document (BREF) entitled 'Best Available Techniques for the Production of Speciality Inorganic Chemicals' presents the result of the work carried out by a group of European experts in a Technical Working Group (TWG) to determine the Best Available Techniques for the production of these chemicals. This document reflects an information exchange carried out under Article 16(2) of Council Directive 96/61/EC (IPPC Directive).

This executive summary describes the main findings, a summary of the principal BAT conclusions and the associated consumption and emission levels. It should be read in conjunction with the preface, which explains the objectives of the document; how it is intended to be used and legal terms.

This executive summary can be read and understood as a standalone document but, as a summary, it does not present all the complexities of this full document. It is therefore not intended as a substitute for this full document as a tool in BAT decision making.

Scope of this document

This document, together with other BREFs in the series, is intended to cover the activities described in Section 4 of the IPPC Directive, namely the 'Chemical industry'. Within the chemical industry, this document focuses on the 'Speciality Inorganic Chemicals' (SIC) sector.

Because the IPPC Directive does not define the term SIC and since there is no common understanding of this term in industry, this document proposes criteria to differentiate between SIC and Large Volume Inorganic Chemicals (LVIC). In addition, the following working definition of SIC has been used for the purpose of this document:

> '*Speciality Inorganic Chemical (SIC) is taken to mean an inorganic substance manufactured industrially by chemical processing, generally in relatively small quantities, according to specifications (i.e. purity) tailored to meet the particular requirements of a user or industry sector (e.g. pharmaceutical).*'

Given the huge variety of SIC, associated raw materials and production processes, this document focuses on a limited number of (illustrative) families of SIC and concludes on BAT for each of these specific families. From the illustrative families and the specific associated BAT conclusions, this document infers generic (or common) BAT conclusions that are considered applicable to the production of a wider range of SIC. The illustrative families developed in this document are speciality inorganic pigments, phosphorus compounds, silicones, inorganic explosives and cyanides. The exchange of information on soluble inorganic salts of nickel could not be carried out to such an extent that BAT conclusions could be drawn, and it was consequently decided to remove the section on inorganic salts of nickel from this document.

The SIC sector

Precise figures cannot be given for SIC industry sales because there is no common definition of SIC. It is thought however that, in Europe, the SIC sector represents between 10 and 20 % of the total chemical industry sales, and that sales are increasing slightly.

The SIC sector is characterised by its diversity and by its fragmentation. Thousands of SIC products are manufactured all over Europe using an immense range of raw materials and production processes. SIC installations are generally small to medium size installations using continuous or batch modes of operation. Some SIC installations produce only one type of SIC while others are multipurpose plants capable of producing many different SIC. Companies of all sizes (from very large to very small) produce SIC at standalone installations or at installations that are part of a larger industrial complex.

Production in Europe is generally highly automated and computer-controlled although there are exceptions which include explosives and pigments production. The SIC sector is highly competitive and confidential in nature as companies tend to develop niche markets and focus on their competitive advantage. Competition is generally based on quality as opposed to price.

Key environmental issues

Any substances might conceivably be a potential release to any medium because of the huge number of chemicals produced. In spite of this, the common environmental issues in the SIC sector as a whole include emissions of particulates to air (mainly dust and heavy metals); waste waters with high COD, heavy metals and/or salt loads; the consumption of energy and of water. The enormous variety of possibly produced and handled (also emitted) substances at SIC installations can also include highly harmful compounds having toxic or carcinogenic properties (e.g. cyanides, cadmium, lead, chromium (VI), arsenic). In addition, there are explosives among SIC substances. Health and safety can therefore be a crucial issue in the production of SIC substances. However, only some of these issues are relevant to individual SIC installations as shown by the illustrative families addressed in this document. The quality of end-products and the purity of raw materials are important factors influencing the environmental impact of the SIC sector.

Common applied techniques, consumption and emission levels

Although processes for the production of SIC are extremely diverse and sometimes very complex (e.g. silicones), they are typically composed of a combination of simpler activities (or process steps) and equipment. These activities include dissolution of raw materials, mixing, synthesis/reaction or calcination, washing, drying, milling/grinding (wet or dry), sieving, condensation, distillation, evaporation, filtration, hydrolysis, extraction, compaction, granulation and briquetting. These process steps can be grouped under five general process stages which form the core activities in a SIC production process: raw and auxiliary materials supply, handling and preparation; synthesis/reaction/calcinations; product separation and purification; product storage and handling; and emissions abatement. This document briefly describes these activities and general process stages and highlights the associated environmental issues. This document also briefly describes the process equipment and infrastructure commonly used in the SIC sector, as well as the characteristics of its energy supply and management system.

Generic consumption and emission levels reflecting the whole SIC sector are difficult to provide because consumption and emission levels are specific to each SIC production process and only a few illustrative SIC processes have been examined in this document. This document therefore presents instead a checklist of possible emission sources and components against which assessments of any SIC production process can be made.

Common techniques to consider in the determination of BAT

The generic techniques that have been considered in the determination of BAT for the whole SIC sector are generally presented in line with the generic approach in order to understand a SIC production process. Each technique is presented following the same outline to facilitate its evaluation and, when it is possible, to enable comparisons to be made between techniques.

Most of the common techniques are used in other chemical industry sectors and are described, generally in more detail, in other BREF documents (especially in the CWW BREF).

Generic Best Available Techniques (BAT)

This document presents Best Available Techniques (BAT) at two levels: generic BAT valid for the whole SIC sector, and specific BAT valid for the illustrative families of SIC selected. BAT for the production of a speciality inorganic chemical pertaining to one of the illustrative SIC families is therefore the combination of the generic BAT elements and the specific BAT elements that can be found in this document. For the production of a SIC that does not pertain to one of these illustrative SIC families, only the generic elements apply.

In addition to the BAT referenced in this document, BAT for a SIC installation may also contain elements from other IPPC documents such as the BREFs on Emissions from Storage (ESB), Common Waste Water and Waste Gas Treatment/Management Systems in the Chemical Sector (CWW BREF).

With regard to the CWW BREF, it is worth noting the following points:

- the SIC BREF takes a more in-depth look into the application of some of the techniques identified in the CWW BREF for the production of speciality inorganic chemicals
- in order to reduce the need for the reader of this document to consult the CWW BREF, techniques used both in the SIC sector and in other chemical industry sectors are briefly described in this document. For more detailed information, the reader should refer to the CWW BREF.

The main conclusions reached for the generic BAT are summarised below.

<u>Raw and auxiliary materials supply, storage, handling and preparation</u>
BAT is to reduce the amount of packaging materials disposed of by, e.g. recycling 'hard' and 'soft' used packaging materials, unless safety or hazard considerations prevent it.

<u>Synthesis/reaction/calcination</u>
BAT is to reduce emissions and the amount of residues generated by implementing one or a combination of the following measures: using high purity feedstock; improving reactor efficiencies; improving catalyst systems.

For discontinuous processes, BAT is to optimise yields, lower emissions and reduce waste by sequencing the addition of reactants and reagents. BAT for discontinuous processes is also to minimise cleaning operations by optimising the sequences for addition of raw and auxiliary materials.

<u>Product handling and storage</u>
BAT is to reduce the amount of residues generated, for example by using returnable product transportation containers/drums.

<u>Waste gas emissions abatement</u>
This document presents BAT conclusions and associated emission levels for the abatement of HCN, NH_3, HCl and Particulate Matters (PM). As an example, for PM BAT is to minimise emissions of total dust in off-gases and achieve emission levels in the range of 1 – 10 mg/Nm^3 by using techniques described in this document. The lower end of the range may be achieved by using fabric filters in combination with other abatement techniques. However, the range may be higher, depending on the carrier gas and particulate characteristics. Using fabric filters is not always possible, e.g. when pollutants other than dust have to be abated or when the off-gases present humid conditions. The PM recovered/removed are recycled back into production when this is feasible. The scrubbing medium is recycled when this is feasible.

Waste water management and water emissions abatement
Waste water treatment in the SIC sector follows at least three different strategies:

- pretreatment within the premises of the SIC installation and final treatment(s) in a central WWTP within the premises of a larger site where the SIC installation is located
- pretreatment and/or final treatment(s) in a WWTP within the premises of the SIC installation
- pretreatment within the premises of the SIC installation and final treatment(s) in a municipal WWTP.

All three strategies are BAT when properly applied to the actual waste water situation.

No generic BAT conclusions on the abatement of heavy metals in waste water were derived. However, BAT conclusions on heavy metals abatement from waste water specific to three of the five illustrative families of SIC addressed in this document have been drawn, namely for speciality inorganic pigments, silicones and inorganic explosives. For information on heavy metals abatement in waste water in the production of substances not covered in the illustrative families sections of this document, it is recommended to refer to the CWW BREF.

As a general measure, BAT is to allocate contaminated waste water streams according to their pollutant load. Inorganic waste water without relevant organic components is segregated from organic waste water and ducted to special treatment facilities.

This document also presents BAT conclusions for the collection and treatment of rainwater.

Infrastructure
BAT is to minimise diffuse dust emissions in particular from the storage and handling of materials/products by applying one or more of the following techniques: storing materials in closed systems, using covered areas protected from rain and wind, having production equipment totally or partially enclosed, having equipment designed with hooding and ducting to capture diffuse dust emissions and abating them, carrying out housekeeping regularly. BAT is to reduce fugitive gaseous and liquid emissions by applying one or more of the following measures: having periodic leak detection and repair programmes, operating equipment at slightly below atmospheric pressure, replacing flanges by welded connections, using seal-less pumps and bellow valves, using high performance sealing systems, carrying out housekeeping regularly.

For new installations, BAT is to use a computerised control system to operate the plant. However, this does not apply where safety issues do not permit automatic operations (e.g. in the production of SIC explosives).

For installations where solid hazardous compounds can build up in pipelines, machines and vessels, BAT is to have in place a closed cleaning and rinsing system.

Energy
BAT is to reduce the consumption of energy by optimising plant design, construction and operation, for example by using pinch methodology, unless safety issues prevent it.

Cross-boundary techniques
Where substances which represent a potential risk of contamination of ground and groundwater are handled, BAT is to minimise soil and groundwater pollution by designing, building, operating and maintaining facilities, in such a way that material escapes are minimised. This document provides the specific list of techniques that are considered BAT.

BAT is to have a high level of education and continuous training of personnel. This includes having personnel with sound basic education in chemical engineering and operations, continuously training plant personnel on the job, regularly evaluating and recording the performance of personnel, and regularly training personnel on how to respond to emergency situations, health and safety at work, and on product and transportation safety regulations.

BAT is to apply the principles of an Industry Code if available. This includes the following: applying very high standards for safety, environmental and quality aspects in the production of the SIC; carrying out activities such as auditing, certification, training of plant personnel.

BAT is to carry out a structured safety assessment for normal operation and to take into account effects due to deviations of the chemical process and deviations in the operation of the plant. In order to ensure that a process can be controlled adequately, BAT is to apply one or more of the following techniques: organisational measures, control engineering techniques, reaction stoppers, emergency cooling, pressure resistant construction, pressure relief systems.

A number of environmental management techniques are determined as BAT. The scope and nature of the Environmental Management System (EMS) will generally be related to the nature, scale and complexity of the installation, and the range of environmental impacts it may have. BAT is to implement and adhere to an EMS that incorporates, as appropriate to individual circumstances, features that include the definition of an environmental policy, planning, establishing and implementing procedures, checking performance and taking corrective action, having the management system and audit procedure examined and validated by an accredited certification body or an external EMS verifier.

Illustrative families of Speciality Inorganic Chemicals

<u>Speciality inorganic pigments</u>

General information and applied processes and techniques

The information contained in this document focuses on speciality inorganic pigments produced industrially by chemical processes (such as iron oxide pigments, complex inorganic coloured pigments, zinc sulphide, barium sulphate and lithopone pigments). Other (non-speciality) inorganic pigments, in particular titanium dioxide and carbon black pigments, are in the scope of the Large Volume Inorganic Chemicals – Solid and Others (LVIC-S) BREF. In Europe, speciality inorganic pigments are produced in small to large installations using a continuous or a batch mode of operation. Production is mainly located in Germany, Italy and Spain. Pigments production is considered a mature industrial sector where little new development is foreseen.

Although many production processes have been developed to manufacture the very large variety of inorganic pigments, production may be broken down in two main processes: pigment synthesis followed by pigment processing. The synthesis of pigments is carried out using a wet precipitation process or a dry calcination process each having a different environmental impact. The wet chemical process requires a large amount of water and generates a large amount of waste water, whereas the dry calcination process requires less water but more energy and gives rise to more off-gas emissions. Pigment processing includes washing, drying, calcination, mixing/milling, filtration/screening, and drying operations. Pigment processing gives rise to emissions to air and water. Of particular concern is the emission of particulates containing heavy metals to air.

Consumption/emissions levels and techniques to consider in the determination of BAT

This document provides consumption and emission levels from a sample of plants producing pigments in Europe. Techniques to consider in the determination of BAT include the use of non-carcinogenic raw materials, fluoride abatement by lime washing, the use of distilled water coming from the evaporation/concentration system for washing pigments, the removal of chromium from waste water, the recycling of precipitation sludge back into production, the biological treatment of waste water loaded with nitrates, the pretreatment and final treatment of waste water loaded with heavy metals.

Best Available Techniques

In some instances, the diversity of the production processes and raw materials used led to BAT conclusions which are only applicable to certain pigments and/or when certain processes are carried out. Examples of BAT that have a wider applicability are presented below (i.e. concerning PM, acid gases and waste water).

BAT is to capture dust in the work areas and duct it to abatement. The abated dust is then recycled back into production. BAT is also to carry out regular housekeeping of the work areas.

BAT is to minimise the emission of acid gases and fluorides by using sorbent injection techniques for example.

BAT is to minimise the emission of total dust from the activities carried out at the installation and achieve emission levels of 1 – 10 mg/Nm^3 by using techniques such as cyclone, fabric filter, wet scrubber, ESP. The lower end of the range may be achieved by using fabric filters in combination with other abatement techniques. Using fabric filters is not always possible, for example when other pollutants have to be abated or when the off-gases present humid conditions.

For waste water, BAT is to (pre)treat waste water contaminated with Cr(VI) and achieve a Cr(VI) concentration of <0.1 mg/l by flow buffering and reducing Cr(VI) to Cr(III), for example using sulphite or iron (II) sulphate. BAT is also to pretreat the waste water loaded with heavy metals before discharging to the receiving water by a combination of techniques indicated in this document. The filtration residues recovered from the waste water treatment may be recycled back into production.

Phosphorus compounds

General information and applied processes and techniques

The phosphorus compounds addressed in this document are phosphorus trichloride (PCl_3), phosphoryl chloride ($POCl_3$) and phosphorus pentachloride (PCl_5). All three substances are very toxic. They are produced in Europe by six companies at seven sites. The main markets for phosphorus compounds are in agriculture and in the production of flame-retardants. Production is carried out at multipurpose plants using a continuous mode of operation.

Production of PCl_3, $POCl_3$ and PCl_5 are closely related as PCl_3 is the starting material for the production of the other two compounds. PCl_3 is manufactured in Europe either using the gas-liquid or the gas phase reaction process. Elemental phosphorus and chlorine are the raw materials used to produce PCl_3.

Consumption/emission levels and techniques to consider in the determination of BAT

The main environmental issues of concern in the production of phosphorus compounds are HCl and phosphorus oxide emissions to air, as well as chlorides and phosphorous emissions to water. Techniques to consider in the determination of BAT include the use of hot condensate water to melt elemental phosphorus and to keep it in liquid form, the use of different systems to blanket elemental phosphorus, the use of elemental phosphorus with low organic and inorganic impurities, the use of scrubbing systems to abate phosphorus compounds in the waste gases, and storage measures.

Best Available Techniques

BAT for phosphorus compounds relate mainly to the minimisation of waste, energy savings, the prevention of accidents, the production yield as well as the minimisation of chloride, and phosphorus emissions to the environment. Examples of these are presented below.

BAT is to reduce the consumption of energy required to melt the solid white/yellow elemental phosphorus raw material by using hot condensate water coming from other parts of the process.

BAT is to minimise the risk of fire by blanketing the elemental phosphorus raw material with an inert medium up to the reaction step.

BAT is to reduce HCl emissions to air from the production of phosphorus compounds and achieve emission levels of 3 – 15 mg/Nm^3 by alkaline scrubbing. To minimise emissions in all production conditions, flowrates through the scrubber system and alkali concentration in the scrubbing medium have to be sufficiently high.

BAT is to minimise emissions of phosphorus and chlorine to the receiving water by treating water effluents in a WWTP equipped with biological treatment and achieve emission levels of phosphorus to the receiving water of 0.5 – 2 kg/t of raw elemental phosphorus and emission levels of chlorine to the receiving water of 5 – 10 kg/t of raw elemental phosphorus.

Regarding waste, BAT is to achieve emission levels of waste distillation residues from PCl_3 production of 4 – 8 kg/t of raw elemental phosphorus and to incinerate distillation residues.

<u>Silicones</u>

General information and applied processes and techniques

Silicones are a special variety of polymers. They differ from polymers as the backbone of their structure does not contain carbon, but is a chain of alternating silicon and oxygen atoms. Several thousands of different silicone products are on the market and a production site often manufactures over a thousand different silicone products. This document addresses the most important ones, namely polydimethylsiloxane (PDMS). Applications of silicones include electric isolators, lubricants, elastomers, coatings, additives in lacquers, paintings and cosmetic products. Four companies produce silicones in Europe, all using a continuous mode of operation.

PDMS is produced through the following process steps: methyl chloride synthesis, grinding of elemental silicon, direct synthesis (Müller-Rochow synthesis), distillation, and hydrolysis/condensation. The main raw materials are elemental silicon, HCl and methanol.

Consumption/emission levels and techniques to consider in the determination of BAT

The main environmental issues are dust, chlorides and NO_X emissions to the air, as well as emission of copper and zinc to the receiving water. Techniques to consider in the determination of BAT include measures for the storage of elemental silicon, pinch methodology to optimise energy consumption, a dry dedusting system for the storage, handling and grinding of elemental silicon, different ways of recovering methyl chloride, thermal treatment of off-gases containing light hydrocarbons and chlorinated compounds, treatment of waste water, re-use/recovery of water and HCl, prevention of accidents.

Best Available Techniques

BAT for the production of silicones mainly relate to the maximisation of the efficiency of the chemical reaction, the minimisation of materials used, the prevention of accidents, the minimisation of waste, the efficient use of energy, the reduction of emissions to air and water. Some examples are presented below.

BAT is to minimise diffuse dust emissions from the storage and handling of elemental silicon by applying measures indicated in this document. BAT is to reduce channelled dust emissions from elemental silicon grinding, storage and handling, and achieve emission levels of 5 – 20 mg/Nm^3 (yearly average) by using fabric filters, for example, and recycling the separated dust back into production.

To achieve maximum efficiency of the chemical reaction in the direct synthesis, BAT is to use elemental silicon raw materials with a particle size of <1 mm.

Regarding the prevention of accidents, BAT is to minimise the sources of ignition energy from elemental silicon grinding and to minimise the sources of explosions from grinding and conveying elemental silicon by maintaining the oxygen and/or elemental silicon dust content in the equipment atmosphere at a safe level below the LEL.

BAT is to reduce the consumption of energy by recycling the energy produced in the direct synthesis.

For waste water treatment, BAT is to minimise emissions of copper and zinc to water by pretreating the water effluents from PDMS production by precipitation/flocculation under alkaline conditions followed by sedimentation and filtration. BAT is also to reduce the BOD/COD content of the water effluent coming out of the pretreatment by applying a biological treatment step.

SIC explosives

General information and applied processes and techniques

The inorganic explosives covered in this document are lead azide, lead trinitroresorcinate and lead picrate which are of industrial and economic importance in Europe. These substances are classified as ‘primary explosives’ whose main function is to initiate a ‘secondary explosive’ (e.g. in dynamites). Other uses include applications in air-bag inflators and seat-belt pretensioners. Inorganic explosives are produced batch wise.

The raw materials used are lead nitrate and sodium azide in the production of lead azide, lead nitrate and trinitroresorcine in the production of lead trinitroresorcinate and lead nitrate and sodium picrate in the production of lead picrate. SIC explosives are produced by a precipitation reaction. The resulting product is then purified and dried.

Consumption/emission levels and techniques to consider in the determination of BAT

The main environmental issues associated with inorganic explosives production are emissions to water of lead, nitrates, sulphates, COD and suspended solids. Techniques to consider in the determination of BAT include the removal of lead from waste waters by precipitation with sulphuric acid or sodium carbonate, the removal of traces of explosive materials containing lead from waste waters using a neutralisation station, and ground protection measures.

Best Available Techniques

This document presents BAT in areas that include accident prevention, waste minimisation and reduction of lead emissions to water. Some examples of BAT are presented below.

In order to avoid the ‘domino effect’ in the case of an explosion, BAT is to separate production and storage buildings on the production site. BAT is also to reduce the risk of explosions of electric origin by storing SIC explosives in buildings equipped with electrical protection and safety systems.

BAT for waste water includes the collection and treatment of used process waters, the removal of traces of explosive impurities in the waste water, the reduction of organic impurities in the waste water by using activated carbon. BAT is also to recycle waste water back into the production process where the production scale and/or the ratio between energy-cost/water-cost justifies this. Finally, BAT is to send the waste water to a central WWTP for treatment. If the central WWTP does not have denitrification treatment (and nitrification if necessary), BAT is to subsequently treat the waste water in a biological WWTP (on-site or off-site, e.g. municipal WWTP) with denitrification (and nitrification if necessary).

Cyanides

General information and applied processes and techniques

This document focuses on water soluble sodium cyanide (NaCN) and potassium cyanide (KCN). The other inorganic cyanide salts are not addressed due to their low production volume. Cyanides are mainly used in Europe in the chemical synthesis industry as well as in electroplating and metal hardening. NaCN and KCN are produced at less than a dozen sites in Europe in medium sized facilities using a continuous mode of operation.

This document addresses the production of NaCN and KCN by the water solution process which includes two main steps for the production of a solution of cyanides (i.e. neutralisation followed by filtration) and subsequent steps for the production of cyanides in solid forms (i.e. drying, compaction, granulation, separation from fine dust, sieving or briquetting). The raw materials are HCN and NaOH or KOH.

Consumption/emission levels and techniques to consider in the determination of BAT

Emissions from the production of cyanides mainly consists of HCN and NH_3 to the air and of cyanides to the receiving waters. Techniques to consider in the determination of BAT include the destruction of cyanides from waste gases and waste waters using hydrogen peroxide, the thermal treatment of off-gases containing VOCs, the cleaning-in-place system for equipment contaminated with cyanide, the use of returnable packaging for the transport of solid cyanides, the use of a computerised control system to operate the plant, the application of the International Cyanide Management Code, storage measures for cyanides, the use of raw materials with low contents of heavy metals, the high level of education and continuous training of personnel.

Best Available Techniques

This document presents BAT on waste reduction, minimisation of raw materials as well as on the abatement of NO_X, HCN, NH_3 and VOCs. This document also presents BAT associated emission levels for these pollutants.

Regarding emissions of cyanides to water, this document concludes that BAT is to minimise these emissions by using techniques that oxidise cyanides. Using hypochlorite is also considered BAT when the cyanide-effluent stream is free of organic material and when no free hypochlorite is left in the effluent after the oxidation reaction. The associated BAT emission levels are also indicated in this document.

Several BAT for the prevention of soil pollution are also presented. Other BAT conclusions relate to water and energy consumption, product storage and packaging, plant operation and training of personnel.

Emerging techniques

Some emerging techniques have been identified in the course of the work. These are: the decontamination of exhaust gases and waste water by chemically modified inorganic ion exchangers and active carbon, the utilisation of industrial waste as fuel, air filtration for the abatement of volatile chromium compounds, the development and application of advanced ceramic electrodes for the electrochemical elimination of cyanides in waste water.

Concluding remarks

The information exchange on BAT for the production of SIC was conducted in a period of about two years, from October 2003 to November 2005. The exchange of information was challenging because confidentiality concerns hampered the collection of actual consumption and emission data from individual SIC installations. However, this did not prevent the drawing of generic BAT conclusions valid for the whole SIC sector as well as BAT conclusions for the specific families of SIC addressed in this document. Consensus has been achieved on BAT and no split views were recorded.

The EC is launching and supporting, through its RTD programmes, a series of projects dealing with clean technologies, emerging effluent treatment and recycling technologies and management strategies. Potentially these projects could provide a useful contribution to future BREF reviews. Readers are therefore invited to inform the European IPPC Bureau of any research results which are relevant to the scope of this document (see also the preface of this document).