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Our Ref: 3856/10

11th October, 2010

Dear Sir or Madam

Please find attached an exemption checklist for Directive 2002/95/EC, and amendment 2008 no 37

Requested for the exemption of 'Cadmium as a pigment for the use in vitreous enamel.'

The IVE is a technical institute representing manufacturers and users of vitreous enamel and vitreous enamel based products, A number of members have requested for the seeking of an exemption of "Cadmium as a pigment for use in vitreous enamel", for use on electrical and electronic products. These members are in the large household appliance sector mainly cooking products and subcontract companies supplying into this sector.

We aim to demonstrate from the checklist that this request is in accordance with article 5(1)b for the following reasons

1. There are no substitutes to Cadmium pigments for vitreous enamel for certain colourations including bright reds, orange, yellows and some greens.

2. There are no other equivalent coating materials which will provide the combination of properties which vitreous enamel possesses, namely heat resistance, abrasion resistance, chemical resistance and colour stability.

2. There are negative health and consumer safety concerns with various other 'substitute coatings' that might be considered as replacements.

In addition to this a number of our members have already had to withdraw product from the market as there was no suitable alternative. These companies are now asking about exemption as the lost sales have not been recouped with other choices of colour. The domestic appliance sector is a significant large scale user of vitreous enamel throughout Europe. Removal of the ability to use cadmium as a pigment will have a negative economic impact on this important contributor to the European economy.

Yours sincerely

Tristan Pope BSC

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ENV.G - Sustainable Development & Integration
ENV.G.4 - Sustainable Production & Consumption

DIRECTIVE 2002/95/EC ON THE RESTRICTION OF THE USE OF CERTAIN HAZARDOUS SUBSTANCES IN ELECTRICAL AND ELECTRONIC EQUIPMENT (ROHS).

CHECK LIST FOR REQUESTS FOR ADDITIONAL EXEMPTIONS

Industry has sent to the Commission's services a number of requests for exemptions from the requirements of the RoHS Directive that are additional to those currently covered by the study and the stakeholder consultation. In most cases these are not substantiated by scientific and technical evidence. The proposed check-list will enable the Technical Adaptation Committee (TAC) to carry out a first screening of the requests received. Proposals that successfully pass the screening process will then be considered for a possible exemption.

Article 4(1) of Directive 2002/95/EC on the restriction of the use of certain hazardous substances in electrical and electronic equipment[1] provides 'that from 1 July 2006, new electrical and electronic equipment put on the market does not contain lead, mercury, cadmium, hexavalent chromium, PBB or PBDE.' The Annex to the Directive lists a limited number of applications of lead, mercury, cadmium and hexavalent chromium, which are exempt from the requirements of Article 4(1).

Adaptation to scientific and technical progress is provided for under Article 5 of the Directive. Pursuant to Article 5(1): "Any amendments which are necessary in order to adapt the Annex to scientific and technical progress for the following purposes shall be adopted in accordance with the procedure referred to in Article 7(2):"

Article 5(1) (b) allows the exempting of materials and components of electrical and electronic equipment from Article 4(1) if their elimination or substitution via design changes or materials and components which do not require any of the materials or substances referred to therein is technically or scientifically impracticable, or where the negative environmental, health and/or consumer safety impacts caused by substitution are likely to outweigh the environmental, health and/or consumer safety benefits thereof;

In order to allow the TAC to consider submissions for additional exemptions, the information in Table I should be provided as a first step. The request for submissions should fulfil the criteria of Article 5(1) (b). The information provided should be supported, as far as possible, with relevant technical and scientific evidence.

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[1] OJ L 37, 13.2.2003, p. 19

TABLE I – CHECK LIST

PROPOSALS FOR FURTHER EXEMPTIONS FROM THE REQUIREMENTS OF ARTICLE 4(1) OF DIRECTIVE 2002/95/EC FOR SPECIFIC APPLICATIONS OF LEAD, MERCURY, CADMIUM, HEXAVALENT CHROMIUM.

Criteria *Information*

Please provide supporting technical and scientific evidence

1. Please describe the material / component of the electrical and electronic equipment that contains the hazardous substance. Please indicate the type and quantity of the hazardous substance used in the homogenous material. Please indicate the quantity of the substance in absolute numbers and in percentage by weight in homogenous material. Please indicate the functionality of the substance in the material of the equipment. Please also provide an estimate of the annual quantities of the hazardous substance used in this particular application.	**'Cadmium as a pigment in vitreous enamel (borosilicate glass)' Used as a vitreous enamel coating for cast iron and sheet steel for domestic appliances for the manufacture of appliance fronts, doors and utensils. The specific application seeking exemption for use in cast-iron range cookers. The pigments used are cadmium sulphoselenide-based. These undergo calcinations during processing, followed by acid washing. For this reason they have very low levels of soluble cadmium (e.g. < 0.01 % (and usually < 0.001 %) using the method in Council of Europe Resolution AP (89) 1. Cadmium pigments are the only cadmium compounds not to have designated supply hazard requirements under Directive 67/548/EEC or Regulation 12721/2008 (CLP). Cadmium pigments are highly stable, being both insoluble and resisting very high temperatures. This greatly reduces the potential for exposure. Pg 13 J316 Cadmium, attached. Depending upon the ratio of sulphur and selenium there will be 1-2% by weight of cadmium contained within the vitreous enamel layer. The amount in the specific application is 1.6% (see attached calculation) To obtain red or yellow coloration, without loss of performance and product quality the pigments used must withstand processing temperatures in excess of 800°C.**

	It must also meet touch temperature requirements for cooking products. Over a five-year period in the specific application 31.92 kg of Cadmium was used on RoHS relevant product. This is 6.385 kg per annum. (see calculation)
2. Please explain why the elimination or substitution of the hazardous substance via design changes or materials and components is currently technically or scientifically impracticable.	There are already alternatives for Cadmium yellows that give a reduced but broadly acceptable range of colour. These have been changed to cadmium-free pigments. Alternatives for red pigment in vitreous enamel exist in only a very limited form based on tin. These lack the lustre and vibrancy of cadmium pigments and can only give brown-reds and not deep vivid reds. These also have low pass rates caused by the chemical reactions of tin during the process, giving white specks and gas defects. The range of colour available does not replace the loss in sales resulting from the withdrawal of cadmium based pigmented vitreous enamels for red, but allows for elimination of cadmium pigments from some other colours requiring some redness such as purple. Alternative organic pigments will not take the temperatures required for vitreous enamel processing. Alternative coatings such as paints and powder coatings lack the durability expected by the consumer for domestic appliances. They are especially difficult for use on cast iron because of gas defects from pores in the iron. Domestic appliances, especially those at the high end of the market, are expected to

	last for a number of years and this is not possible with paint in all applications. Use of paints or powder coatings would therefore lead to products having a reduced working life. Earlier replacement would be necessary, with the associated resource, as well as possible safety and environmental costs. There are some possibilities to using paint for sheet steel parts. There are issues with touch temperatures with paint coatings as a replacement for vitreous enamel on cooking products. The absence of suitable alternative pigments for cast iron has meant product has had to be withdrawn from sale for RoHS compliance. This has created a reduction in sales, which has not been replaced with other choices of colour.
3. Please indicate if the negative environmental, health and/or consumer safety impacts caused by substitution are likely to outweigh the environmental, health and/or consumer safety benefits. If existing, please refer to relevant studies on negative impacts caused by substitution.	The cadmium pigments in vitreous enamel are first calcined and then become contained by the glass. In this form they are safe and pose no risk to the consumer. Testing to AP (89) 1 concludes that the pigments are well below the safe recommended leaching levels applicable for use in food-contact plastics. This is before they are further contained within the enamel. The process of red enamel spraying is segregated from the rest of production to ensure that no discharge is made to the atmosphere or water. Over spray enamel is collected and fused at the glass transition temperature into its glass state to ensure it is highly stable for disposal. This method, known as glass vitrification, is a proven method to contain hazardous substances and is being used for various applications including high- risk radioactive materials. Previous reviews into the use of cadmium pigments while finding no significant hazard concentrated mainly on plastics and did not consider the vitrified condition found in enamel

coatings that reduces any exposure risks even further.

The component parts have a high value for recycling at the end of their long life being metal substrates. For cast iron products it is in the manufacturer's interest to get back the product at the end of life in order to re-use it as a raw material to make more cast iron. Most companies operate buy back and trade in schemes to ensure that this is maximized and work with renovators to maintain the longevity of the product. This greatly limits the amount of cadmium going into landfill.

Vitreous enamel will form a slag during metal recycling that will continue to contain the inorganic cadmium compounds within a vitrified structure. The cadmium compounds remain stable during this high temperature processing and do not burn. The cadmium compounds present are insoluble making them difficult to become dispersed into the environment. The resultant slag can find use as a building aggregate so does not need to be land filled.

Alternative coatings would be plastic resins that will burn giving CO, CO_2 and other possible toxic decomposition products during recycling. Many plastic resins for example contain isocyanate cross linkers (polyesters, urethane) which will burn to give toxic hydrogen cyanide as a product of decomposition.

Organic red pigments used for plastic resins are based on organic complex carbon ring structures. The most common in use are azo-pigments; These are made from absorbing azo-dye compounds that are in the main carcinogenic onto a carrier. Azo-pigments are normally regarded as non-toxic although some have been found to be mutagenic and there are studies linking azo-pigments with basal cell carcinoma. Some organic azo-pigments also contain halogen groups, e.g. Red PR254 (Chlorinated), Red PR216 (Brominated), the formation of dioxins or

	furans are therefore possible decomposition products during any high temperature recycling of the base substrate. Other possible decomposition products of organic pigments are carcinogenic aromatic amines because of the presence of Nitrogen and aromatic ring structures. REF. Eva Engel, Heidi Ulrich, Rudolf Vasold, Burkhard König, Michael Landthaler, Rudolf Süttinger, Wolfgang Bäumler (2008). "Azo Pigments and a Basal Cell Carcinoma at the Thumb". *Dermatology* **216** (1): 76–80. **For sheet steel and cast iron the most suitable substitution is epoxy polyester powder paint. This will give the best mix of properties regarding coverage, scratch resistance and temperature resistance that can be expected from paint.** **Epoxy resins are made from bisphenol A, which is subject to a number of safety concerns as a reproduction hazard being an estrogen mimic.** **Bisphenol A may also be subject to future RoHS or REACH restrictions. It is included in the Evans report as a suggested candidate for future RoHS restrictions.** **While it is possible to further speculate on negative health and environmental impacts of alternatives none have been studied to the same extent as cadmium pigments or vitreous enamel where it is known that there is a high level of safety because of the highly stable nature of both.** **For cooking appliances the door touch temperature requirements are lower for paint than for enamel. This is because of differences in thermal conductivity and it is less likely to become burnt from an enamel part. It is not always possible to maintain the lower requirement for paint without extensive design change. For a cast iron part this is less possible as there is no easy method to insert insulation or heat sinks into the door.**

	Standard EN 60335-2-6
4. Please indicate if feasible substitutes currently exist in an industrial and/or commercial scale. **Please indicate the possibilities and/or the status for the development of substitutes and indicate if these substitutes will be available by 1 July 2006 or at a later stage.**	**Currently no suitable alternatives exist to fully replace cadmium pigments in vitreous enamel for red coloration. It is unlikely that further suitable alternatives will be developed. This is limited to the availability of substances, which can perform at high temperatures during processing. Historically Uranium was used to give red colour into glass but clearly this is not a suitable alternative.** Jansen and Latchert proposed a potential alternative back in 2000 but this is still not commercially available. Abstract attached. **Alternative pigments exist for a limited application in vitreous enamel giving brown-reds and for other colours that require an element of redness these have been developed to the maximum capability of these pigments. They cannot replace cadmium pigments but have reduced the use by being used wherever possible.** **Paint does not offer a suitable alternative coating material in all cases, lacking the durability expected by the consumer especially at the high end of the market, where products are expected to last.** **Paint has lower touch temperature limits that may rule it out for completely some cooking applications.** **Paint offers neither the same durability nor the same quality as vitreous enamel.**
5. Please indicate if any current restrictions apply to such substitutes. If yes, please quote the exact title of the appropriate legislation/regulation. **6. Please indicate the costs and benefits and advantages and disadvantages of such substitutes.** **If existing, please refer to relevant studies on costs and benefits of such substitutes.**	**Alternative pigments based on tin** **The cost of this substitution is high because tin based pigments are added typically at five times the amount of cadmium pigments. They have an**

	advantage that they do not need separate processing as cadmium pigments. They do not offer the same range of colour so they have limited use. Enamel coating companies have already made use of these where possible. **Paint substitution** **Substitution to paint would require massive investment for any company undertaking this change requiring a new process and the resultant product would be less durable than vitreous enamel and have an expected lower life time. Benefits are cost per unit but this is only applicable for large volumes to cover the initial expenditure. This is not an option for some applications.**
7. Please provide any other relevant information that would support your application for an additional exemption.	**Use of cadmium pigments in vitreous enamel was not restricted in marketing and use directive 91/338/EEC. This exemption has been carried over into REACH annex XVII.** **Vitreous enamel is exempt from REACH registration in Annex V due to its recognized safety.** **This application is similar to the exemption for lead into crystal glass where the glass is binding the RoHS restricted substance into a safer form and is both decorative and functional.** **This application is almost identical in chemistry to the exemption for cadmium and lead in printing inks for enamel onto borosilicate glass, being from the same family of substances (vitreous enamel)** **Vitreous enamel is exempt from UK IPPC sector guidance note S403 relating to the release of certain metals. It is considered that vitreous enamel effectively encapsulates these metals. Section 1. page 15 section 4.2d** **Vitrification using borosilicate glass (vitreous enamel) is a recognized method to contain the release of hazardous**

	substances. **Cadmium pigments have been through two reviews under the “existing chemicals” Directive and, in both cases, it was concluded that they offer no significant hazard to human health or to the environment.**

CONTENTS

INTRODUCTION

INTRODUCTION

I. This report presents the results of the project entitled '*Assessment of the Risks to Health and to the Environment of Cadmium Contained in Certain Products, and of the Effects of Further Restrictions on their Marketing and Use'*. The project has been undertaken by WS Atkins International Ltd for Directorate General III (DG III) of the European Commission (EC) under contract number ETD/97/500536.

II. The aim of the project is to investigate the risks to health and to the environment of cadmium contained in certain products and to examine the advantages and drawbacks of further restrictions on their marketing and use. The products are those involving cadmium as a pigment in polymers, as a stabiliser in PVC and for metal plating. The project will provide the basis upon which future discussions will be founded on the possible need for further restrictions on the use of cadmium.

III. The report is divided into two parts:

- Part I: Assessment of the Risks to Health and to the Environment of Cadmium Contained in Certain Products; and
- Part II: Assessment of the Effects of Further Restrictions on the Marketing and Use of Cadmium Contained in Certain Products.

IV. These two parts are followed by overall conclusions for cadmium contained in certain products.

PART I

Assessment of the Risks to Health and to the Environment of Cadmium Contained in Certain Products

PART II

Assessment of the Effects of Further Restrictions on the Marketing and Use of Cadmium Contained in Certain Products

CONCLUSIONS

CONCLUSIONS

I. Part I of this report considered the life cycle of certain products and assessed the risks to the environment and to health arising from cadmium in certain products. The assessment has been conducted according to the principles laid down in the Technical Guidance Document in support of Commission Directive 93/67/EEC on risk assessment for new notified substances and Commission Regulation (EC) No 1488/94 on risk assessment of existing substances. The calculated losses of cadmium to the environment have been employed to assess the potential risks arising from cadmium contained in certain products at the continental scale for a generalised EU environment and at the regional and local scale for an acidic environment. The following potentially unacceptable environmental and health risks have been identified from the manufacture, use and disposal of cadmium in certain products:

- the risks from disposal of cadmium containing products in municipal landfill sites; and

- the workplace health risks associated with stabiliser preparation.

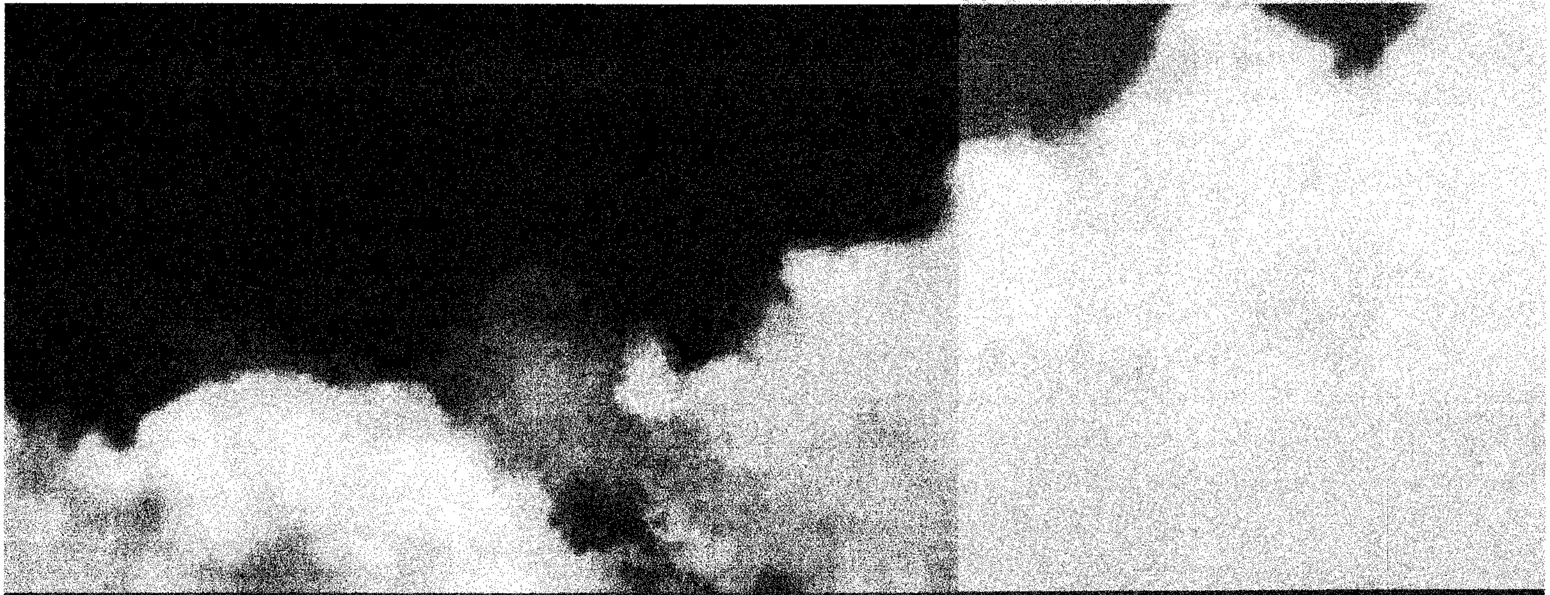
II. The regional PECs for the generalised EU environment are derived in the additional assessment of the risks of cadmium contained in the products. The derived regional PECs are then used in the additional assessment to provide the risk characterisation for the local risks arising from pigment production, stabiliser production and for plating facilities and incinerators for the generalised EU environment. The overall conclusions arising from the additional assessment and the assessment that has been undertaken in Part I of this report are presented in the additional assessment.

III. A total EU ban on the marketing and use of cadmium in pigments, stabilisers and as a plating agent would have a varying impact. A ban on cadmium pigments would have an adverse economic and financial impact on manufacturers and to a lesser extent on industrial users. A ban on cadmium stabilisers would not affect economic operators as over the years both producers and users have moved towards alternatives to cadmium stabilisers. Further restrictions on cadmium as a plating agent do not seem to be technically feasible. It is likely that industry will adopt alternatives as they are developed.

	atomic weight				
cadmium	112.41				
sulphur	32.06				
selenium	78.96				
CdS	77% cadmium by weight				
CdSe	59% cadmium by weight				
					Cd ratio
	60% of a pigment is made up of these compounds.			Ratio of CdS to CdSe	0.74
into 1kg of enamel					
4% wt/wt pigment	divide by total mix wt (110)		3.6 %		
Of which is cadmium based		60%	2.16 %	multiply by 0.6	
Of the ratio		0.74	**1.5984** %	multiply by 0.74	

5 year usage		
enamel used	1995.207	
% Cadmium	1.6	
amount Cadmium	31.92	
	6.3846624	per annum

Sector Guidance Note IPPC S4.03



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Guidance for the Inorganic Chemicals Sector

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Table 0.1: Record of changes

Version	Date	Change	Template Version
Draft 1	12 May 2004		v6.2 -12 May 2004
Draft 1.1 (Consultation)	10 June 2004	Section 2.1.1 moved to 3.3, plus errors corrected	v6.2 -12 May 2004

Note: Queries about the content of the document should be made to Adrian Milner (0117-914 2681) or any member of the PIR Process Management Team.

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Executive summary

Status of this Guidance

This guidance has been produced by the Environment Agency, along with the Scottish Environment Protection Agency (SEPA) and the Northern Ireland Environment and Heritage Service (EHS) - each referred to as "the Regulator" throughout this document. Its publication follows consultation with industry, government departments and non-governmental organisations.

What is IPPC

Integrated Pollution Prevention and Control (IPPC) is a regulatory system that employs an integrated approach to control all environmental impacts of certain listed industrial activities. In the UK, the IPPC Directive is implemented through the English and Welsh, the Scottish, and the Northern Irish versions of the Pollution Prevention and Control (PPC) Regulations. It involves determination by the Regulator of the appropriate controls for those industries to protect all environmental media, through a single permitting process. To gain a PPC Permit, an Operator has to demonstrate in its Application, in a systematic way, that the techniques it is using or is proposing to use, both represent the use of Best Available Techniques (BAT), taking account of relevant local factors, and meet other relevant statutory requirements.

This Guidance and the BREF

Much UK Technical Guidance on what is BAT is based on the "BAT Reference documents" ("BREFs") produced by the European Commission. BREFs are the result of exchanges of information between member states and industry, with most covering individual industrial sectors, and some ("horizontal" BREFs) covering cross-sectoral subjects. UK Technical Guidance Notes are designed to complement BREFs, and take into account information contained in relevant BREFs in setting out indicative BAT standards and expectations for England and Wales, Scotland and Northern Ireland.

The aims of this Guidance

The aim of the Guidance is to provide Operators and officers of the Regulator with advice on indicative standards of operation and environmental performance, relevant to the industrial sector concerned. It also aims (through linkage with the Permit Application Form template) to provide a clear structure and methodology for Operators to follow to demonstrate they have addressed adequately all aspects of the PPC Regulations and relevant aspects of other environmental Regulations. Also, by expressing BAT techniques as clear indicative standards wherever possible, it aims to minimise the effort involved for both Operator and Regulator in the permitting of an installation.

To further assist Operators and officers, separate horizontal guidance is available on a range of topics such as noise, odour, waste minimisation, monitoring, calculating stack heights and so on. Most of this guidance is available free through the Environment Agency, SEPA or EHS (Northern Ireland) websites (see References).

Key environmental issues

The key environmental issues for this sector are:

- **Fugitive emissions to air** - Many inorganics installations handle solid materials, which can be the source of fugitive releases of dust and small particulates. In other processes there is the potential for escapes of acid gases, ammonia, VOCs and volatile inorganic compounds.
- **Point source emissions to air** - Most installations have abatement systems for particulates, acid gases, ammonia or volatile organics or inorganics, but there is scope for improvement in emissions from a large number of them.
- **Waste minimisation and waste disposal routes** - The Landfill Directive has reduced the options for disposal of many chemical waste streams so opportunities to minimise waste production and move up the waste hierarchy must be taken.
- **Emissions to water** - A number of installations have effluent streams containing pollutants like heavy metal compounds or complexes which need to be treated separately before being discharged to communal treatment facilities.

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1 Introduction

The status and aims of this Guidance

This Guidance has been produced by the Environment Agency for England and Wales, with the Scottish Environment Protection Agency (SEPA) and the Environment and Heritage Service (EHS) in Northern Ireland - each referred to as "the Regulator" in this document. Its publication follows consultation with industry, Government departments and non-governmental organisations.

It aims to provide Operators and the Regulator's officers with advice on indicative standards of operation and environmental performance relevant to the industrial sector concerned, to assist the former in the preparation of applications for PPC Permits and to assist the latter in the assessment of those Applications (and the setting of a subsequent compliance regime). The use of techniques quoted in the guidance and the setting of emission limit values at the benchmark values quoted in the guidance are not mandatory, except where there are statutory requirements from other legislation. However, the Regulator will carefully consider the relevance and relative importance of the information in the Guidance to the installation concerned when making technical judgments about the installation and when setting Conditions in the Permit, any departures from indicative standards being justified on a site-specific basis.

The Guidance also aims (through linkage with the Application Form or template) to provide a clear structure and methodology for Operators to follow to ensure they address all aspects of the PPC Regulations and other relevant Regulations, that are in force at the time of writing. Also, by expressing the Best Available Techniques (BAT) as clear indicative standards wherever possible, it aims to minimise the effort required by both Operator and Regulator to apply for and issue, respectively, a Permit for an installation.

1.1 Understanding IPPC

IPPC and the Regulations

Integrated Pollution Prevention and Control (IPPC) is a regulatory system that employs an integrated approach to control the environmental impacts of certain listed industrial activities. It involves determination by the Regulator of the appropriate controls for those industries to protect the environment, through a single permitting process. To gain a Permit, Operators have to demonstrate in their Applications, in a systematic way, that the techniques they are using or are proposing to use, are the Best Available Techniques (BAT) for their installation, and meet certain other requirements, taking account of relevant local factors.

The essence of BAT is that the techniques selected to protect the environment should achieve an appropriate balance between environmental benefits and the costs incurred by Operators. However, whatever the costs involved, no installation may be permitted where its operation would cause significant pollution.

IPPC operates under **The Pollution Prevention and Control Regulations** (for equivalent legislation in Scotland and N Ireland see **Appendix 2**). The three regional versions of the PPC Regulations implement in the UK the EC Directive on IPPC (96/61/EC). Further information on the application of IPPC/PPC, together with Government policy and advice on the interpretation of the English & Welsh Regulations, can be found in **IPPC: A Practical Guide** published by the Department for Environment, Food and Rural Affairs (Defra). Equivalent guidance on the Scottish Regulations is provided in PPC Regulations: A Practical Guide (Part A Activities), published by the Scottish Executive and SEPA. The Department of the Environment, Northern Ireland has published equivalent guidance on its Regulations.

Installation based, NOT national emission limits

The BAT approach of IPPC differs from regulatory approaches based on fixed national emission limits (except where General Binding Rules or Standard Permits are issued). The legal instrument that ultimately defines BAT is the Permit, and Permits can only be issued at the installation level.

Indicative BAT Standards

Indicative BAT standards are laid out in national guidance (such as this) and, where relevant, should be applied unless a different standard can be justified for a particular installation. BAT includes the technical components, process control, and management of the installation given in Section 2, and the benchmark levels for emissions identified in Section 3. Departures from those benchmark levels can be justified at the installation level by taking into account the technical characteristics of the installation concerned, its geographical location and the local environmental conditions. If any mandatory EU emission limits or conditions are applicable, they must be met, but BAT may go further (see "BAT and EQS" below).

Some industrial sectors for which national guidance is issued are narrow and tightly defined, whilst other sectors are wide and diffuse. This means that where the guidance covers a wide variety of processes, and individual techniques are not described in detail, the techniques (and their associated emission levels) which might constitute BAT for a particular operation, are more likely to differ, with justification, from the indicative BAT standards than would be the case for a narrow, tightly-defined sector.

BAT and EQS

The BAT approach complements, but differs fundamentally from, regulatory approaches based on Environmental Quality Standards (EQS). Essentially, BAT requires measures to be taken to prevent emissions - and measures that simply reduce emissions are acceptable only where prevention is not practicable. Thus, if it is economically and technically viable to reduce emissions further, or prevent them altogether, then this should be done irrespective of whether or not EQSs are already being met. The BAT approach requires us not to consider the environment as a recipient of pollutants and waste, which can be filled up to a given level, but to do all that is practicable to minimise emissions from industrial activities and their impact. The BAT approach first considers what emission prevention can reasonably be achieved (covered by Sections 2 and 3 of this Guidance) and then checks to ensure that the local environmental conditions are secure (see Section 4 of this Guidance and also Guidance Note**Environmental Assessment and Appraisal of BAT**). The BAT approach is therefore the more precautionary one because the release level achieved may be better than that simply required to meet an EQS.

Conversely, if the application of indicative BAT might lead to a situation in which an EQS is still threatened, a more effective technique is required to be BAT for that installation. The Regulations allow for expenditure beyond indicative BAT where necessary, and, ultimately, an installation will only be permitted to operate if it does not cause significant pollution.

Further advice on the relationship between BAT, EQSs and other related standards and obligations is *given in* ***IPPC: A Practical Guide****, its Scottish equivalent, and also in Section* 3.

Assessing BAT at the sector level

The assessment of indicative BAT takes place at a number of levels. At the European level, the European Commission issues a "BAT reference document" (BREF) for each main IPPC sector. It also issues "horizontal" BREFs for a number of general techniques which are relevant across a series of industrial sectors. The BREFs are the result of an exchange of information between regulators, industry and other interested parties in Member States. Member States should take them into account when determining BAT, but they are allowed flexibility in their application. UK Sector Guidance Notes like this one take account of information contained in relevant BREFs and set out current indicative standards and expectations in the UK. At national level, techniques that are considered to be BAT should represent an appropriate balance of costs and benefits for a typical, well-performing installation in the sector concerned. They should also be affordable without making the sector as a whole uncompetitive, either within Europe or world-wide.

The BREF production programme is in progress, but is not yet complete. The BREF for the Chlor-alkali sector was published in 2000 but the 3 other BREFs for the Inorganics sector are not expected to be published before end-2004 (Large Volume Inorganic Chemicals - Ammonia, Acids and Fertilizers) or mid-2005 (Large Volume Inorganic Chemicals - Solids and Others, and Speciality Inorganic Chemicals). The "horizontal" BREF for the Treatment of Waste Water and Waste Gas has been published, and the BREF for the Storage of Chemicals should be completed in late-2004. The indicative standards laid down in this Note are therefore based on Best Available Techniques Not Entailing Excessive Cost ("BATNEEC") standards from the two IPC Technical Guidance Notes for Acids and Halogens, and Inorganic Chemicals, together with information from available BREFs (Ref 1), where relevant. When all the BREFs for this sector are published, this Guidance Note will be revised.

Assessing BAT at the installation level

When assessing applicability of sectoral indicative BAT standards at the installation level, departures may be justified in either direction. Selection of the technique which is most appropriate may depend on local factors and, where the answer is not self-evident, an installation-specific assessment of the costs and benefits of the available options will be needed. The Regulator's guidance **Environmental Assessment and Appraisal of BAT** and its associated software tool may help with the assessment. Individual installation or company profitability (as opposed to profitability of the relevant sector as a whole) is not a factor to be considered, however.

In the assessment of BAT at the installation level, the cost of improvements and the timing or phasing of that expenditure, are always factors to be taken into account. However, they should only be major or decisive factors in decisions about adopting indicative BAT where:

- the installation's technical characteristics or local environmental conditions can be shown to be so different from those assumed in the sectoral assessment of BAT described in this guidance, that the indicative BAT standards may not be appropriate; or
- the BAT cost/benefit balance of an improvement only becomes favourable when the relevant item of plant is due for renewal/renovation (eg. change to a different design of furnace when the existing furnace is due for a rebuild). In effect, these are cases where BAT for the sector can be expressed in terms of local investment cycles; or

- a number of expensive improvements are needed. In these cases, a phasing programme may be appropriate - as long as it is not so drawn out that it appears to be rewarding a poorly performing installation.

In summary, departures by an individual installation from indicative BAT for its sector may be justified on the grounds of the technical characteristics of the installation concerned, its geographical location and the local environmental conditions - but not on the basis of individual company profitability, or if significant pollution would result. Further information on this can be found in **IPPC: A Practical Guide** and **IPPC Part A(1) Installations: Guide for Applicants**, or the equivalent Scottish Guidance.

Innovation

The Regulators encourage the development and introduction of innovative techniques that advance indicative BAT standards criteria, ie. techniques which have been developed on a scale which reasonably allows implementation in the relevant sector, which are technically and economically viable and which further reduce emissions and their impact on the environment as a whole. One of the main aims of the PPC legislation is continuous improvement in the overall environmental performance of installations as a part of progressive sustainable development. This Sector Guidance Note describes the indicative BAT standards at the time of writing but Operators should keep up-to-date with improvements in technology - and this Guidance note cannot be cited as a reason for not introducing better available techniques. The technical characteristics of a particular installation may also provide opportunities not foreseen in the Guidance, and as BAT is determined at the installation level (except in the case of General Binding Rules (GBRs)), it is a requirement to consider these even where they go beyond the indicative Standards.

New installations

Indicative BAT standards apply, where relevant, to both new and existing installations, but it will be more difficult to justify departures in the case of new installations (or new activities in existing installations) - and for new activities, techniques which meet or exceed indicative BAT requirements should normally be in place before operations start.

Existing installations - standards

For an existing installation, it may not be reasonable to expect compliance with indicative BAT standards immediately if the cost of doing so is disproportionate to the environmental benefit to be achieved. In such circumstances, operating techniques that are not at the relevant indicative BAT standard may be acceptable, provided that they represent what is considered BAT for that installation and otherwise comply with the requirements of the Regulations. The determination of BAT for the installation will involve assessment of the technical characteristics of the installation and local environmental considerations, but where there is a significant difference between relevant indicative BAT and BAT for an installation, the Permit may require further improvements on a reasonably short timescale.

Existing installations - upgrading timescales

Where there are departures from relevant indicative BAT standards, Operators of existing installations will be expected to have upgrading plans and timetables. Formal timescales for upgrading will be set as Improvement Conditions in the Permits. **See Section 1.4.2** for more details.

1.2 Making an application

For the issue of a Permit a PPC Application has to:

- address the issues in Sections 2 and 3 of this guidance;
- assess the environmental impact described in Section 4 (and for England and Wales also in Environmental Assessment and Appraisal of BAT (IPPC H1));
- demonstrate that the proposed techniques are BAT for the installation.

In practice, many PPC Applications have contained far more information than is needed for determination, *yet have not addressed the areas that are most important - and this has led to extensive* requests for further information. In an attempt to focus application responses to the areas of concern to the Regulator, Application forms (templates) have been produced by the Environment Agency, by SEPA and by EHS in N Ireland. In addition, as the dates for application have approached, the operators in most industrial sectors in England and Wales have been provided with Compact Discs (CDs) which contain all relevant Application Forms and Assessment tools, technical and administrative guidance, BREFs, and the charging scheme (known as EPOPRA), hyper-linked together for ease of use.

There is such a CD for the Inorganic Chemicals sector in England and Wales. The tools and advice on the CD should steer the operator through the PPC application process, define more closely the level of detail required in the Application and help to make the process of calculating impact assessments much simpler.

For Applications where there are existing IPC Authorisations or Waste Management Licences, the previous applications may provide much of the information for the PPC Application. However, where the submitted Application refers to information supplied previously, fresh copies will have to be submitted with the PPC Application - though for issues where there is a tendency for frequent changes of detail (for example, information about the management systems), it will generally be more appropriate simply to refer to the information in the Application and keep available for inspection on site, up-to-date versions of those documents.

For further advice see IPPC Part A(1) Installations: Guide for Applicants (for England and Wales) or PPC Part A Installations: Guide for Applicants (for Scotland) or the equivalent Northern Ireland guide for Applicants.

1.3 Installations covered

The Note covers installations containing activities, described as follows in Part A(1) of Schedule 1 to The Pollution Prevention and Control Regulations (for England and Wales). For the equivalent Regulations in Scotland and Northern Ireland see Appendix 2

Installations for the manufacture or use of inorganic chemicals are listed for regulation in Section 4.2 of Schedule 1 to the Regulations, and the manufacture of chemical fertilizers is listed in Section 4.3. A few inorganic installations may also be described in Section 4.7 - "Manufacturing activities involving carbon disulphide or ammonia".

Part A(1)

Section 4.2 - Inorganic Chemicals

(a) Producing inorganic chemicals such as:

(i) gases, such as ammonia, hydrogen chloride, hydrogen fluoride, hydrogen cyanide, hydrogen sulphide, oxides of carbon, sulphur compounds, oxides of nitrogen, hydrogen, oxides of sulphur, phosgene;

(ii) acids, such as chromic acid, hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, phosphoric acid, nitric acid, sulphuric acid, oleum and chlorosulphonic acid;

(iii) bases, such as ammonium hydroxide, potassium hydroxide, sodium hydroxide;

(iv) salts, such as ammonium chloride, potassium chlorate, potassium carbonate, sodium carbonate, perborate, silver nitrate, cupric acetate, ammonium phosphomolybdate;

(v) non-metals, metal oxides, metal carbonyls or other inorganic compounds such as calcium carbide, silicon, silicon carbide, titanium dioxide;

(vi) halogens or interhalogen compound comprising two or more of halogens, or any compound comprising one or more of those halogens and oxygen.

(b) Unless falling within another Section of this Schedule, any manufacturing activity which uses, or which is likely to result in the release into the air or into water of, any halogens, hydrogen halides or any of the compounds mentioned in paragraph (a)(vi), other than the treatment of water by chlorine.

(c) Unless falling within another Section of this Schedule, any manufacturing activity involving the use of hydrogen cyanide or hydrogen sulphide.

(d) Unless falling within another Section of this Schedule, any manufacturing activity, other than the application of a glaze or vitreous enamel, involving the use of any of the following elements or compound of those elements or the recovery of any compound of the following elements - antimony, arsenic, beryllium, gallium, indium, lead, palladium, platinum, selenium, tellurium, thallium - where the activity may result in the release into the air of any of those elements or compounds or the release into water of any substance listed in paragraph 13 of Part 2 of this Schedule.

(e) Recovering any compound of cadmium or mercury.

(f) Unless falling within another Section of this Schedule, any manufacturing activity involving the use of mercury or cadmium or any compound of either element or which may result in the release into air of either of those elements or their compounds.

(g) Unless carried out as part of any other activity falling within this Schedule -

(i) recovering, concentrating or distilling sulphuric acid or oleum;

(ii) recovering nitric acid;

(iii) purifying phosphoric acid.

(h) Any manufacturing activity (other than the manufacture of chemicals or glass or the coating, plating or surface treatment of metal) which -

(i) involves the use of hydrogen fluoride, hydrogen chloride, hydrogen bromide or hydrogen iodide or any of their acids; and

(ii) may result in the release of any of those compounds into the air.

(i) Unless carried out as part of any other activity falling within this Schedule, recovering ammonia.

(j) Extracting any magnesium compound from sea water.

Section 4.3- Chemical Fertilizer Production

(a) Producing (including blending which is related to their production), phosphorus, nitrogen or potassium based fertilizers (simple or compound fertilizers).

(b) Converting chemical fertilizers into granules.

Section 4.7 - Manufacturing activities involving Carbon disulphide or Ammonia

(a) Any manufacturing activity which may result in the release of carbon disulphide into the air.

(b) Any activity for the manufacture of a chemical which involves the use of ammonia or may result in the release of ammonia into the air other than an activity in which ammonia is only used as a refrigerant.

The installation will also include **associated activities** which have a technical connection with the main activities and which may have an effect on emissions and pollution, as well as the main activities described above. These may involve activities such as:

- the storage and handling of raw materials;
- the storage and despatch of finished products, waste and other materials;
- the control and abatement systems for emissions to all media;
- waste treatment or recycling.

Environment Agency advice on the composition of English or Welsh installations and which on-site activities are to be included within it (or them) is given in its guidance document **IPPC Regulatory Guidance Series No.5 - Interpretation of "Installation" in the PPC Regulations.** Operators are advised to discuss the composition of their installations with the Regulator before preparing their Applications.

This Note contains some information from the Chlor-alkali sector BREF and also from other relevant BREFs or draft BREFs (Ref 1) but it leans most heavily on the IPC Technical Guidance Notes for Inorganic Chemicals and Inorganic Acids and Halogens (Ref 21).

1.4 Timescales

1.4.1 Permit review periods

Permits are likely to be reviewed as follows:

- for individual activities not previously subject to regulation under IPC or Waste Management Licensing, a review should be carried out within four years of the issue of the PPC Permit
- for individual activities previously subject to regulation under IPC or Waste Management Licensing, a review should be carried out within six years of the issue of the IPPC Permit

However, where discharges of Groundwater List I or List II substances have been permitted, or where there is disposal of any matter that might lead to an indirect discharge of any Groundwater List I or II substance, a review must be carried out within four years as a requirement of the Groundwater Regulations.

These periods will be kept under review and, if any of the above factors change significantly, they may be shortened or extended.

1.4.2 Upgrading timescales for existing plant

Existing installation timescales

Unless subject to specific conditions elsewhere in the Permit, upgrading timescales will be set in the Improvement Programme of the Permit, having regard to the criteria for improvements in the following two categories:

1 *Standard "good-practice" requirements, such as, management systems, waste, water and energy audits, bunding, housekeeping measures to prevent fugitive or accidental emissions, good waste-handling facilities, and adequate monitoring equipment.* Many of these require relatively modest capital expenditure and so, with studies aimed at improving environmental performance, they should be implemented as soon as possible and generally well within 3 years of issue of the Permit.

2 *Larger. more capital-intensive improvements, such as major changes to reaction systems or the installation of significant abatement equipment.* Ideally, and where there is considerable divergence from indicative BAT standards, these improvements should also be completed within 3 years of Permit issue but longer time-scales may be allowed by the Regulator, where justified in objective terms.

Local environmental impacts may require action to be taken more quickly than the indicative timescales above, and requirements still outstanding from any upgrading programme in a previous permit should be completed to the original time-scale or sooner. On the other hand, where an activity already operates to a standard that is close to an indicative requirement a more extended time-scale may be acceptable. The requirement by the Regulator for capital expenditure on improvements and the rate at which those improvements have to be made, should be proportionate to the divergence of the installation from indicative standards and to the environmental benefits that will be gained - except where there are statutory deadlines for compliance with national or international requirements.

The Operator should include in the Application a proposed programme in which all identified improvements (and rectification of clear deficiencies) are undertaken at the earliest practicable opportunities. The Regulator will assess BAT for the installation and the improvements that need to be made, compare them with the Operator's proposals, and then set appropriate Improvement Conditions in the Permit

1.5 Key issues

The Inorganic Chemicals sector comprises a large number of specifically different installations with relatively few common factors. With the majority of activities undertaken by only one or two operators and only a handful undertaken by more than 3 operators, the main environmental issues tend to be site-specific. However a few general issues are:

1.5.1 Fugitive emissions to air

Many inorganic processes involve the handling of solid materials and fugitive releases of dust and small particulates from joints in conveyors systems, from stock-piles, from packages, etc. are significant issues on many plants. In other processes, where gases or liquids with moderately high vapour pressures are handled, there is always the potential for releases of acid gases, ammonia, VOCs or volatile inorganic compounds from flanges, pumps, agitators and valves with seals, storage tanks, tanker connections, sample points, etc.

These fugitive releases can occur through relaxation or progressive wear-and-tear of sealing materials, through sloppy operation, maintenance or design, or through failure of equipment. Apart from releases of material through accidental mal-operation or equipment failure, fugitive losses from individual pieces of equipment are often small - but on a large-scale plant the aggregated effect can be very significant.

Section 2.2.4 - Control of fugitive emissions to air - of this Guidance Note covers relevant issues and, in addition, prevention and control of fugitive emissions is covered in the Emissions from Storage BREF and in other relevant BREFs. (Ref 1)

The basic rules are:

- Operators should aim to minimise fugitive releases of solids, liquid and gaseous substances at the design stage by the specification of the right equipment and the right materials of construction. The priority is environmental protection rather than financial savings from material that is not lost.
- For on-going fugitive emission prevention, operators should have formal inspection/detection programmes in place and, where necessary, replace equipment which continues to generate significant fugitive emissions, with higher quality items.

1.5.2 Point source emissions to air

As with fugitive emissions, many inorganic processes involving the handling of solid materials release significant quantities of dust, fume or wet particulates from process vents - and some of these contain toxic substances such as heavy metal compounds. Other installations release significant quantities of acid gases, ammonia or volatile inorganic or organic compounds from process vents on vessels, storages and abatement system exhausts. On most plants, gaseous emissions from point sources have been individually characterised and significantly reduced (in total) since the introduction of the IPC regime across the sector in the mid-1990s. However, areas remain where considerable improvement can still be made - and for some installations IPC Improvement Programme conditions are still in the process of being completed.

Individual sources of air emissions from particular processes are indicated in Section 2.1 - In-process controls - in this Note, and further details are provided in the relevant BREF, where available. (Ref 1)

1.5.3 Waste minimisation and waste disposal routes

The Inorganics sector is diverse and wastes are very process-specific, but some parts of the sector do generate significant quantities of waste and in most cases they are non-combustable so there are major disposals of waste to landfill. The Landfill Directive reduces the options for disposal of many chemical waste streams so operators must maximise all waste minimisation opportunities and move their waste up the waste hierarchy.

Operators should assess their activities against the BAT criteria laid out in Section 2.4, Section 2.5, and Section 2.6 of this Guidance Note.

1.5.4 Emissions to water

Many inorganic installations have small or easily treatable aqueous waste streams but a number have effluent streams containing more difficult pollutants such as heavy metal compounds or complexes. Where it is not practicable to prevent the generation of these difficult waste water streams in the first place, they need to be segregated and treated separately, before being discharged to communal effluent treatment facilities. Effluent streams specific to individual process are identified in Section 2.1 and its sub-sections in this Note, and treatment techniques are covered in Section 2.2.2. More detail on available techniques is provided in the Waste Water and Waste Gas Treatment BREF, and in other relevant BREFs, where available. (See Ref 1)

1.5.5 Odour

Some of the substances produced or used in installations covered by this Note have the odour potential to cause offence to neighbouring communities This is a key issue for some installations, though probably not for the majority in the sector. The issues are covered in the Odour section in this Technical Guidance Note (Section 2.2.6) and in more detail in Horizontal Guidance Note H4 covering Odour (see Ref 22).

1.5.6 Energy efficiency

Some Inorganics installations are very large users of energy and the direct or indirect release to air of combustion products often is the biggest single environmental impact arising from their production activities - but other installations in the sector are very significant net generators of energy. Most installations will be participants in a Climate Change Agreement or have an Emissions Trading Scheme permit (which, together with basic energy efficiency measures, are generally deemed to meet the PPC requirement to use energy efficiently). However, even at these installations there may be some issues which need to be addressed in the PPC Permitting process. (See **Section 2.7**.)

1.5.7 Noise and vibration

Noise and vibration are constant features of most large volume inorganics plants - from compressors and other machinery, steam relief valves, large combustion units, flares, etc. Guidance is provided in the Noise section in this Technical Guidance Note (**Section 2.9**) and in greater detail in the Horizontal Guidance Note H3 covering Noise (see **Ref 15**).

1.5.8 Chemical analysis and monitoring of emissions

The Inorganics sector is very diverse but even where there are similarities, emissions monitoring has been rather variable within the sector, to date. With national reporting and comparison (via databases like the Pollution Inventory) becoming the norm, it is important that there is consistent measurement of comparable release streams, both in terms of substances monitored and methods of analysis used. Further guidance is being developed but interim guidance is provided in **Section 2.10** - Monitoring - in this Note.

1.6 Summary of emissions

The Inorganic Chemicals sector is very wide and across the sector almost any substance might conceivably be a potential release to any medium. It is considered, therefore, that there is little value in providing a releases summary of the type used in some other sectoral Guidance Notes.

1.7 Technical overview

More than 50 different processes are covered by this Note and it is not possible to provide detailed descriptions of them. Instead, brief outline descriptions and flow diagrams are given for the main Inorganics processes operated in the UK, together with an indication of their main emissions and any the techniques which are special to those processes.

The larger Inorganics processes are continuous and are often co-located on large integrated sites, so that they can beneficially exchange raw materials, products, by-products and wastes. In some cases, the sharing of energy streams and other utilities is the main benefit. They represent a wide range of different chemical processes based on combinations of unit operations. There are, however, several key issues common to many processes such as the control of acid gas and particulates emissions and the minimisation and reuse of wastes.

Brief descriptions of the various processes together with their pollution potential are provided in **Section 2.1**.

1.8 Economics

Inorganic processes, even the large volume ones, are not part of a single homogeneous industry and there is a wide range of process types and of plant sizes. A few of the large volume products - for example, ammonia, sulphuric and nitric acids, ammonium nitrate, chlor-alkali, titanium dioxide, sodium carbonate - can be described as industrial sub-sectors with some comparable characteristics (albeit mostly internal to that sub-sector) but the majority of inorganic chemicals are manufactured in Europe on a relatively small scale by just one to three companies, with most of the competition coming from outside the EU. For most of these processes, apart from the application of abatement systems to remove common pollutants like particulates or acid gases, there are few financial characteristics which can meaningfully be used across the board to compare them - and even then, whilst certain abatement techniques are common to many processes, the large variations in scale and technical duty can result in very large differences in cost per tonne of product or cost per tonne of pollution abated.

This variability makes prescriptive approaches to the identification of what is BAT very difficult but a number of issues related to the industry structure, the product market and the operating conditions of the sector can be highlighted. Frequently, individual processes are part of a larger operation, so there needs to be careful consideration of the whole range of associated operations when assessing cost impacts.

SMEs are important in the sector so to avoid over-burdening small companies, in particular, careful consideration needs to be given to making environmental improvements cost-effective in relation to the environmental benefits to be gained. Increasingly there is foreign ownership of companies in the sector so another factor which may need to be considered is the choice that international companies have regarding investment -and changes in ownership and management structures lead to changes in attitudes to environmental performance - both positive and negative - and these present opportunities for review of environmental performance (by both operators and Regulators).

Apart from smaller niche products, new inorganics installations are likely to be few and far between and most developments will continue to be extensions to existing plants - so the opportunities provided by such developments should be used to review BAT overall and to implement environmental improvements.

Economic issues specific to some of the sub-sectors are noted below. In the absence of BREFs covering most of the Inorganics sector, the information has been taken from IPC Technical Guidance Notes S2 4.03 and S2 4.04 (Ref 21).

1.8.1 Sub-sectors

1.8.1.1 Sulphuric acid and related businesses

The current UK market for sulphuric acid is now a little over 1Mtpa - which represents a very sizeable fall from the 4Mtpa market of the 1970s and 80s. This is mainly due to the cessation of phosphoric acid manufacture and decline of other UK fertilisers production, to lower steel production and a general decline in tonnage chemical manufacture which used sulphuric acid. The number of sulphuric acid manufacturers in the UK has declined to just 3, which together produce around a half of UK demand, the other half being imported as 96% acid (mainly from European smelter plants).

One producer obtains most of its SO_2 raw material by thermal destruction of waste acid from methacrylate production and recycles the majority of its acid and oleum to that co-located methacrylates plant; the others are sulphur burners and produce a significant proportion of their outputs as specialist grades of sulphuric acid or 100% sulphur dioxide or trioxide.

Basic 96% or 98% sulphuric acid is a mature commodity, most of which is now satisfied by-product acid from non-ferrous metal production overseas. UK production has moved towards specific sulphuric acid-related products where importation is expensive or impractical, or to production which meets a specific local need.

1.8.1.2 Ammonia production

Ammonia production in the UK is around 1Mtpa and is undertaken by two foreign companies on 4 separate sites. On the 3 largest sites, ammonia production is closely integrated with nitric acid and ammonium nitrate production - and the ammonia business environment is closely allied to that of the nitric acid and ammonium nitrate businesses. As well as nitrate outlets, ammonia is used in significant quantities in the manufacture of other chemicals and polymer intermediates, and the overall market is balanced by imports.

1.8.1.3 Nitric acid and related businesses

Nitric acid production in the UK is similar in size to sulphuric acid production, and again there are just 3 or 4 producers (none of which are UK companies). Most weak nitric acid is used captively to manufacture fertilisers (mainly granular ammonium nitrate) or intermediates in the manufacture of polyurethanes or fibres, but it is also sold for the manufacture of explosives and other chemicals, and for the surface treatment of metals. Most concentrated (i.e 96%) nitric acid is also for merchant sales.

1.8.1.4 Fertilizer business

Western European fertilizer production and consumption have declined by at least a third since the end of the 1980s. The availability of cheaper imported fertlizers, particularly ammonium nitrate and particularly from Russia and former Eastern Bloc countries, had a disastrous effect on prices with consequential closure of a significant proportion of EU production capacity. It is possible that the European fertiliser environment is now stabilising, albeit at a lower demand level, and that the oversupply situation is improving - but it is not absolutely clear.

Within the UK, the fertilizer industry comprises 3 large overseas-owned concerns that manufacture granular ammonium nitrate and related fertilizers, together with a small number of independent blenders or granulators. With fertilizer consumption estimated to fall at a rate of 0.5% - 1%pa to around 1.3Mtpa (as N) by 2007, it seems unlikely that much new investment is likely to occur in the near future - though there will probably be opportunities for environmental improvements as existing plant is revamped.

1.8.1.5 Chlorine and sodium hydroxide

Chlorine is a large-volume commodity chemical for which prices fluctuate widely. The chlorine production business is cyclical (recently around 8 year cycles) and the business cycle is fairly closely related to the manufacture of vinyl chloride monomer (VCM), its largest end-user, and thus to the demand for PVC.

A major feature of the industry is that a tonne of chlorine is always co-produced with 1.2 tonne of equally valuable caustic soda. Thus when one is in demand and its price is high, the other has to be produced and outlets found for it - so its price is usually low. For this reason, it is not so much the fluctuating price of chlorine which dictates the profitability of the business as the combined prices of chlorine and sodium hydroxide - and this tends to fluctuate rather less.

Electricity costs are typically over half of total manufacturing costs for chlor-alkali producers, whereas feedstock costs are usually less than 15%. In recent times, as a result of electricity deregulation and a significant increase in generation from natural gas, electricity costs in the UK have been amongst the lowest in Europe so the UK chlor-alkali industry has been reasonably competitive within European markets - but the forecasts for future electricity pricing and perhaps, therefore, for chlor-alkali businesses, are not so sanguine.

Apart from the major end-use, the manufacture of PVC plastic, there are a number of other significant users of chlorine plus many small-volume applications within industry. Many of the other uses for chlorine have already declined under environmental pressure, e.g. chlorine for pulp and paper bleaching, chlorinated solvent manufacture, hypochlorite bleaches, chlorine in water treatment and, of course, the manufacture of CFCs and other ozone-depleting substances. However, other uses for chlorine within the chemical industry are likely to show above-average growth, e.g. for titanium dioxide, phosgene, propylene oxide, pharmaceuticals and other organics.

In the UK, sodium hydroxide is used in most industrial sectors as well as being one of the major raw materials in many chemical production processes, but in a global context there are a few major uses, such as in the processing of aluminium ore, which can have a significant effect on prices.

The major debate within the chlor-alkali industry worldwide concerns the replacement of mercury electrolytic cells by membrane or diaphragm cells for environmental reasons. Europe has a large proportion of its capacity based on mercury cells and in the UK, apart from 2 or 3 small membrane cell-rooms, all the 700-800 ktpa of chlorine production is now via mercury cells and, as a proportion of chlor-alkali capacity, mercury-based production has actually risen over the last decade. There is a Recommendation from PARCOM (the Paris Convention, now known as OSPAR) to phase out the use of mercury cells by 2010 but, in practice, the replacement of mercury cells in many European countries has been patchy over the last 15-20 years. The Chlor-alkali BREF states that BAT for new plant is the use of membrane cells and, whilst mercury losses to the environment have been significantly reduced by recently-installed abatement and recovery techniques, none of the 3 primary UK producers has yet undertaken to replace existing cell-rooms with membrane units. Their argument has been, hitherto, that the environmental gain is too small for the capital cost entailed (estimated to be around £300 million for the currently installed capacity).

1.8.1.6 Titanium dioxide manufacture

Titanium dioxide is a widely used pigment, with demand closely linked to growth in housing, the automobile and the coatings industries. It is a typical commodity product with major product price and profitability cycles. The cycles are not always in phase with the overall chemicals industry cycle. In recent cycles, good profitability in mid/ late 1980s led to major new-plant investment, which resulted in overcapacity and lower profitability in the early 1990s and, since then, prices and profitability have oscillated. Some planned new plants, particularly in the US, have been delayed or abandoned and some capacity, particularly sulphate-route, has been removed. In Europe most investment has been to boost output by debottle necking existing facilities by introducing new process technology, catalysts, etc.

On a worldwide basis, the sulphate process has dropped from about two-thirds of total capacity in 1985 to nearer one-third now. It is likely that there will always be a residual market for the sulphate-based TiO_2, where there is still demand for the anatase pigment, but markets for their by-product materials (i.e. ferric sulphate and gypsum) will be an important factor.

1.8.2 Costs of pollution abatement

This industry sector covers a range of different processes with different scales of operation - ranging from small-scale batch facilities through to large continuous manufacturing processes. A very wide range of chemical species with differing physical, chemical and lexicological properties are stored, handled and processed. The costs of abatement techniques vary widely according to process duty and site-specific factors. The following information is therefore very general and relate to data collected in 1997. The costs of abatement on individual installations may be significantly different and to demonstrate BAT, it is the operator's responsibility to develop robust cost estimates that correspond to its own specific processes and circumstances.

1.8.2.1 Particulate matter

Within the inorganic chemicals industry one of the main abatement issues is that of abatement of particulate matter from gaseous streams. There are a number of alternative technologies available (as described in Section 2.2 and in a number of BREFs (Ref 1)) and the choice will depend upon technical, site-specific and economic considerations. A number of appropriate criteria for consideration are given below:

- volumetric flowrate, temperature and humidity;
- size and nature of the particulates;
- presence of other chemical species;
- required efficiency of particulate removal;
- waste disposal considerations;
- control and monitoring requirements;
- utility requirements; and
- space availability and civil engineering work.

One of the main factors in the choice of technique is that the efficiency of particulate capture varies enormously with particulate size for some techniques - but for most techniques, the capital cost of particulate matter abatement is very dependent on the flowrate (Figure 1.1) and, generally, rather less dependent on the loading.

Different techniques have differing energy requirements. Figure 1.2 gives a general comparison of the total annualised costs of the same types of equipment.

Figure 1.1: *Installed cost of equipment for capture of Particulates*

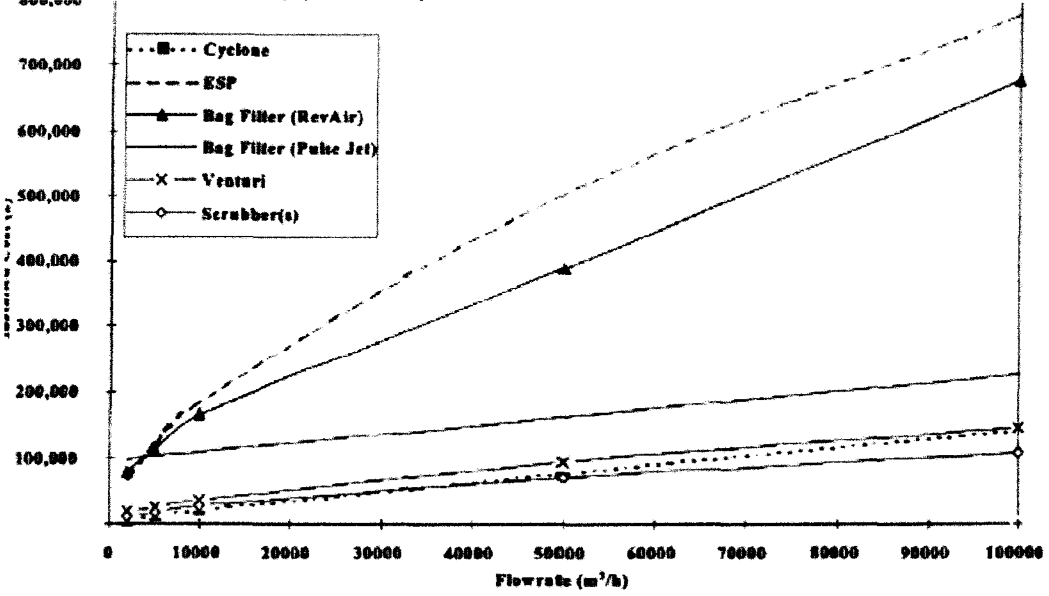
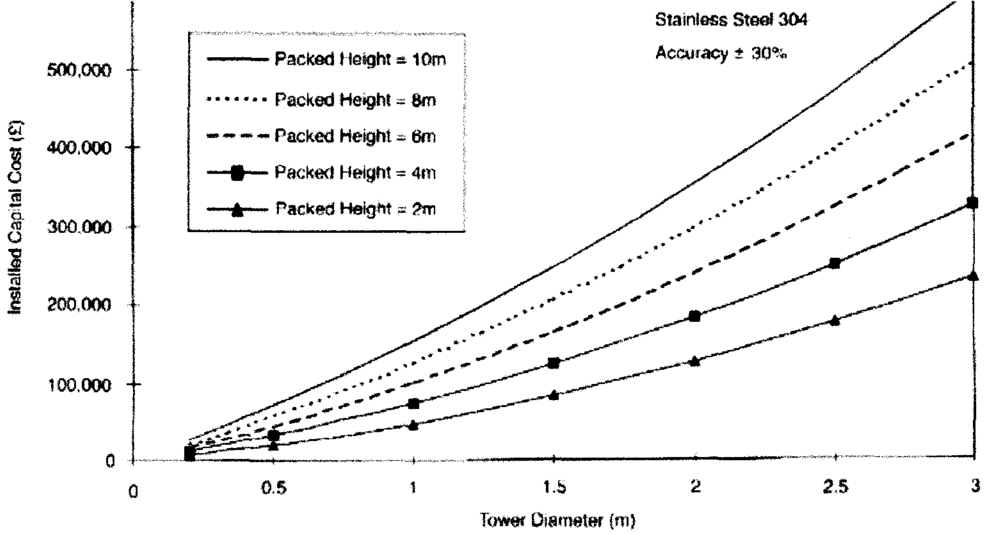


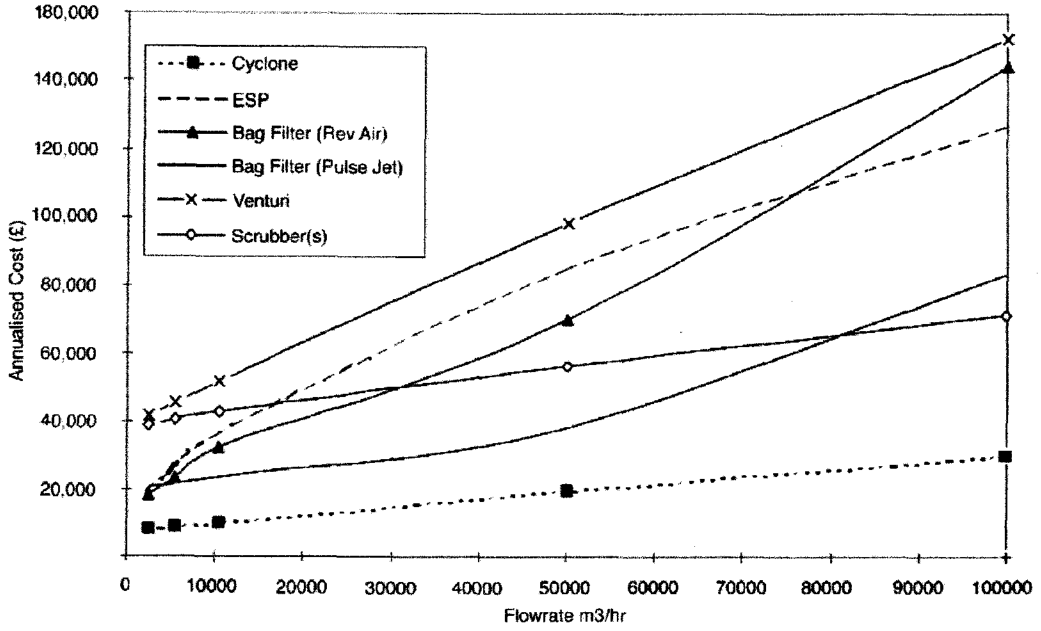
Figure 1.2: *Total annualised costs for capture of Particulates*



1.8.2.2 Gas scrubbing

Scrubbing techniques are widely used in the sector for gaseous pollutants but the diverse nature of the pollutants, the scrubbing medium and operating conditions make it impracticable to give typical annualised costs so Figure 1.3 shows just the installed capital costs for various sizes of a common type of scrubbing equipment constructed in stainless steel.

Figure 1.3: Installed cost of stainless steel scrubbers



1.8.2.3 Volatile organic compounds

Some Inorganics processes have significant releases of organic compounds to air. The capital cost s of different types of VOC abatement are a function of gas flowrate, the properties and concentration of the VOCs concerned, specific site issues, and issues relating to the partyicular technique. The costs given in Table 1.1 are approximate costs for non-halogenated VOCs. Equipment to treat halogenated VOCs is generally more expensive owing to the larger sizing of equipment required by some of the technologies or to the materials of construction required by others.

Table 1.1: Examples of VOC Abatement techniques - approximate costs

Technique	Flow (m^3/hr)	Capital costs (£)	Operating costs (£/annum)	Annualised Total costs (£/annum)
Adsorption - canister	200	1000	100	260
Adsorption - regenerable fixed bed	10000	900000	26000	173000
Absorption	5000	550000	17000	107000
Condensation - refrigerant	1000	400000	13000	7800
Condensation - cryogenic	200	200000	–	–
Thermal oxidiser	25500	750000	278000	400000
Catalytic oxidiser	34000	750000	300000	420000
Biological oxidiser	3600	300000	5000	54000

1.8.2.4 Water treatment

Aqueous effluent from Inorganics activities can be very varied and often are passed to a site waste-water treatment plant where a mixture of wastes are treated so incremental costs arising from the subject processes are difficult to identify. Major components of waste steams are metal compounds and other species specific to the Inorganics process, and specific treatment techniques will be required. Some relative comparative costs for a 100 m^3/day facility are shown as examples in Table 1.2.

Table 1.2: Examples of specialised waste-water treatment - approximate costs.

Technique	Capital costs (£)	Operating costs (£/annum)	Annualised total cost (£/annum)
PAC	3500	800	1300
GAC	1900	3000	6200
Chemical coagulation	120000	2500	22300
Ozone	150000	5800	30000
Air stripping	10500	–	17000

Some waste streams contains high concentrations of organics or other compounds which are similarly oxidisable and which need to be almost completely removed. Table 1.3 illustrates the relative costs of alternative (or additional) techniques to treat effluent with a high organic (or oxidisable) content. The flow is 5 m^3/h with an organics content of 5000 mg/l.

Table 1.3: *Cost of Treatment of a high-organic or oxidisable aqueous effluent*

Technique	Capital Cost (£000)	Annual Cost (£000 per annum)	Annualised cost (£000 per annum)	Unit Cost £,/m^3)
Incineration	4000	1750	2400	60
Wet air oxidation	5000	360	1170	29
Supercritical water oxidation	7000	690	1830	46

COUNCIL OF EUROPE
COMMITTEE OF MINISTERS

(PARTIAL AGREEMENT IN THE SOCIAL AND PUBLIC HEALTH FIELD)

RESOLUTION AP (89) 1

ON THE USE OF COLOURANTS IN PLASTIC MATERIALS COMING INTO CONTACT WITH FOOD

(Adopted by the Committee of Ministers on 13 September 1989
at the 428th meeting of the Ministers' Deputies)

The Representatives on the Committee of Ministers of Belgium, France, the Federal Republic of Germany, Italy, Luxembourg, the Netherlands and the United Kingdom of Great Britain and Northern Ireland, these states being parties to the Partial Agreement in the social and public health field, and the Representatives of Austria, Denmark, Ireland, Norway, Spain, Sweden and Switzerland, states which have participated in the public health activities pursued within the above-mentioned Partial Agreement since 1 October 1974, 2 April 1968, 23 September 1969, 11 July 1979, 21 April 1988, 10 June 1975 and 5 May 1964 respectively,

Considering that the aim of the Council of Europe is to achieve a greater unity between its members and that this aim may be pursued, amongst others, by common action in the social and public health field;

Having regard to the provisions of the Brussels Treaty signed on 17 March 1948, by virtue of which Belgium, France, Luxembourg, the Netherlands and the United Kingdom of Great Britain and Northern Ireland declared themselves resolved to strengthen the social ties by which they were already united;

Having regard to the protocol modifying and completing the Brussels Treaty, signed on 23 October 1954 by the signatory states of the Brussels Treaty, on the one hand, and the Federal Republic of Germany and Italy, on the other hand;

Observing that the seven states parties to the Partial Agreement which have continued, within the Council of Europe, the social work hitherto undertaken by the Brussels Treaty Organisation and then by Western European Union, which derived from the Brussels Treaty as modified by the protocol mentioned in the fourth paragraph above, as well as Austria, Denmark, Ireland, Norway, Spain, Sweden and Switzerland, who participate in Partial Agreement activities in the field of public health, have always endeavoured to be in the forefront of progress in social matters and also in the associated field of public health, and have for many years undertaken action towards harmonisation of their legislation;

Having regard to the fact that colourants are used to impart a colour to plastic materials coming into contact with food;

Forty years
Council of Europe

Considering that plastic materials coming into contact with food may, by reason of their colouration, pose a risk to human health if not used under normal conditions or if the colourants used do not meet purity criteria based on good manufacturing practice;

Taking the view that each member state faced with the need to introduce regulations governing this matter would find it beneficial to harmonise such regulations at European level,

Recommend that the governments of the states parties to the Partial Agreement as well as the governments of Austria, Denmark, Ireland, Norway, Spain, Sweden and Switzerland take into account in their national laws and regulations the principles set out in this resolution and the analytical methods and, in particular, specifications on the use of inorganic cadmium pigments set out in the appendix to this resolution.

Appendix to Resolution AP (89) 1

I. Field of application

This resolution applies to the use of colourants in plastic materials and articles coming into contact with food. Colourants are substances which are intentionally added to plastics to impart colour: they include dyes, organic and inorganic pigments.

II. General principles

1. *Migration from the final plastic material or article*

Under normal or foreseeable conditions of use, plastic materials and articles should not, by reason of their colouration, pose a risk to human health or bring about either a deterioration in the organoleptic characteristics or an unacceptable change in the nature, substance or quality of the food with which they come into contact.

Colourants should be sufficiently integrated within plastic materials and articles so as to preclude any visible migration into foodstuffs under normal conditions of use, as determined by an appropriate method.[1]

2. *Specification*

The colourants to be tested should be the active ingredients and not the active components predispersed in a medium to facilitate good distribution during processing of the plastic materials.

The colourants should meet the purity criteria of the provisions 2.1 — 2.4 and be based on good manufacturing practice.

2.1. *Metals and metalloids*

The content of metals and metalloids soluble in 0.1M hydrochloric acid, determined as a percentage in relation to the colourant, should not exceed:

antimony: 0.05%
arsenic: 0.01%
barium: 0.01%
cadmium: 0.01%
chromium[2]: 0.1%
lead: 0.01%
mercury: 0.005%
selenium: 0.01%

The analytical method is described in section III, paragraph 2.

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[1] It should be noted that, under normal or foreseeable conditions of use, the specific migration of aromatic amines and of metals from the finished plastic materials or articles should not exceed the limits specified in the Council of Europe booklet *Substances used in plastics materials coming into contact with food* (1).

[2] The use of chromium VI pigments may pose a risk to human health and should be discouraged.

2.2. *Aromatic amines*

The content of primary unsulphonated aromatic amines soluble in 1M hydrochloric acid and expressed as aniline should not exceed 500mg/kg. The content of benzidine, ß-naphthylamine and 4-aminobiphenyl, singly or in total, should not exceed 10mg/kg.[1] The analytical methods are referred to in section III, paragraph 3.

2.3. *Sulphonated aromatic amines*

Sulphonated aromatic amines are defined as those compounds sulphonated on all aromatic or conjugated ring structures.

The total content of sulphonated aromatic amines extracted by a suitable solvent and determined by an appropriate test, expressed as aniline sulphonic acid, should not exceed 500mg/kg. This limit can be exceptionally exceeded if adequate supporting data on the technological need are provided. An analytical method is discussed in section III, paragraph 4.

2.4. *Carbon black*

Carbon black should comply with any national requirement for food grade material. Furthermore, the toluene-extractable fraction of carbon black should not in any case exceed 0.15% in accordance with the method described in section III, paragraph 5.

2.5. *Polychlorinated biphenyls (PCBs)*

The content of extractable polychlorinated biphenyls should not exceed 25mg/kg, expressed as decachlorobiphenyl, as determined by an appropriate method indicated in section III, paragraph 6.

2.6. *Inorganic cadmium pigments*

A number of national and international authorities have recommended that the intake of cadmium by man should be reduced as far as possible. Furthermore, environmental contamination by cadmium is a recognised international problem. Consequently, a number of regulatory authorities have either taken steps to reduce the total industrial use of cadmium or are actively considering such measures.

The use of inorganic cadmium pigments in plastic materials and articles coming into contact with food is small but, in certain applications, such use is claimed to offer major technological advantages. The migration of cadmium from the use of such pigments is, in general, very low but extraction can vary from plastic type to plastic type. Thus, the use of inorganic cadmium pigments in plastics coming into contact with food will probably make only a minor contribution to man's total intake. However, in order to keep the contamination of food with cadmium in general as low as possible, the use of such pigments should be restricted to applications where their special technological advantages cannot be met by alternative products.

3. *Toxicological tests*

Toxicological data should be obtained from pages 71 to 77 of the Council of Europe booklet *Substances used in plastics materials coming into contact with food* (1).

III. **Analytical methods**

1. *Determination that there is no visible migration*

1.1. *Apparatus*

- filter paper for qualitative analysis, of medium porosity such as *Weissband Mittel* (Schleicher and Schull), chromatography paper (Archer, 302), etc.;
- glass desiccator or other suitable sealed container;
- oven regulated at 50° ± 2°C.

1.2. *Simulants*

- distilled water or water of equivalent quality;
- 3% acetic acid (w/w) in aqueous solution;
- 15% ethanol (v/v) in aqueous solution;
- decolourised edible oil or fat or a comparable synthetic triglyceride.

If foods do not correspond to the above simulants, for example because of high acid or alcohol content, the simulants should be modified accordingly.

1.3. *Contact surface*

At least $10cm^2$.

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[1] In normal use, therefore, the quantity of these substances which may migrate into food will be toxicologically insignificant.

1.4. *Operating procedure*

Impregnate strips of filter paper with the simulant(s) for the food(s) intended to come into contact with the material. These strips should have a contact surface of 10 to 15cm². Eliminate excess simulant by wringing the strips between two glass rods.

Place the impregnated strips onto the food contact surface of the material or article to be tested, so that there is intimate contact, and fix with non-coloured adhesive tape. Ensure that there are no air bubbles between the surface of the sample and the impregnated paper and verify that the latter exerts an even pressure on the sample after the adhesive tape is affixed.

A simpler method of attachment may be applied in the case of flat samples. On a glass plate, place consecutively 100cm² of sample and a few impregnated strips, cover with a further flat glass plate and apply a weight of approximately 1kg.

Impregnate additional strips of filter paper with simulant to act as blanks. It is important that these do not come into contact with any coloured materials or articles.

Place samples and blanks in a desiccator and maintain for five hours in an oven regulated at 50° ± 2°C. Where an aqueous simulant is used, it is necessary to transfer a portion to the desiccator and maintain at 50° ± 2°C for thirty minutes prior to use. This will ensure that the atmosphere in the desiccator is saturated with the vapour of the simulant.

After the set contact time, separate the strips of impregnated filter paper from the samples and isolate the blank strips. In the case of aqueous simulants, place the strips in the oven at 50° ± 2°C until the impregnated liquid has evaporated (approximately fifteen minutes). In the case of the oil simulant, allow the strips to cool.

1.5. *Assessment of visible migration*

Compare the strips that have been in contact with the sample with the blank strips; these should have remained colourless. The visual comparison of strips is undertaken in daylight (2). The plastic materials or articles meet the requirements if comparison of test strips and blank strips reveals no difference.

2. *Determination of metals and metalloids*

2.1. *Apparatus*

— agitation device having a rotary mechanical agitator, non-magnetic, with a speed sufficient to maintain the colourant in suspension but without causing air bubbles to be formed;

— membrane filter with 0.15 micrometre porosity.

2.2. *Reagent*

— hydrochloric acid 0.1M of analytical purity.

2.3. *Operating procedure* (3)

Place in suspension for fifteen minutes, at 23° ± 3°C, 10g of colourant in 150ml of 0.1M hydrochloric acid, using a mechanical agitator. Filter the acid solution, after sedimentation of the colourant for ten minutes, through the membrane filter. The filtrate is then analysed for elements mentioned under section III.1 in accordance with known methods, for example (4 to 6). Blank determination on reagents is essential.

3. *Determination of primary unsulphonated aromatic amines*

An extract containing the aromatic amines is prepared by treatment of the organic colourant with 1M hydrochloric acid as described in ETAD Method No. 212 (7). The quantitative determination of primary unsulphonated aromatic amines in this extract may be undertaken either according to this method or to specific methods (8-11).

4. *Analytical methods for the determination of aromatic aminosulphonic acids*

The pigments are extracted with a suitable solvent (for example acetic acid, diluted sodium hydroxide solution, methanolic ammonia or 1 N HCl, as described in ETAD Method No. 212) and the aminosulfonic acids in the extracts determined by thin layer chromatography. On the TC (toluene column), the compounds are identified by colour reaction (for example diazotation and coupling with N-(1-naphthyl)-ethylene-diamine or with R salt) and the quantity determined by comparison with standards of the compounds.

5. *Determination of the toluene-extractable fraction of carbon black*

5.1. *Principle* (12)

Carbon black is extracted in a Soxhlet apparatus with toluene. Thereafter, the solvent is evaporated and the residue weighed.

5.2. *Apparatus*

- Soxhlet extraction apparatus;
- extraction vessels of paper fibre, capable of containing 10g of carbon black;
- laboratory glassware;
- oven, adjustable up to 140° ± 5°C.

5.3. *Solvent*

Toluene.

5.4. *Operating procedure*

Dry a sufficiently large sample of carbon black for one hour at 105° ± 2°C. Place 10g of the dried carbon black (weighed with an accuracy of 0.1g) in an extraction vessel previously washed with toluene. Close the vessel with cotton previously washed with toluene and place the vessel in the Soxhlet apparatus.

Extract the carbon black for eight hours with 150ml toluene. Adjust the heating element of the apparatus in such a way that the extraction solvent in the extraction vessel is replenished approximately ten times per hour.

Allow to cool, remove the extraction vessel from the apparatus and concentrate the extract to a small volume by evaporation. Wash the residue with a little toluene into a weighed glass crucible (weight: a g) and remove the toluene by evaporation on a water bath. Place the crucible in an oven for two hours at 140°C; allow to cool in a desiccator and reweigh the crucible (weight: b g).

5.5. *Calculation*

Calculate the extractable fraction E of the carbon black using the following formula:

$E = 10\,(b - a)\%$

E shall not exceed 0.15%.

6. *Determination of extractable polychlorinated biphenyls (PCBs)*

Polychlorinated biphenyls (PCBs) are extracted from organic colourants and determined as specified in the various methods described in the literature (13). For the determination of very low levels of PCBs (<5 mg/kg), it is necessary to use methods (14, 15) based on gas chromatography/electron capture and capillary gas chromatography/electron impact mass spectrometry.

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Low-Temperature Decomposition of Epoxy Resin

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Abstract: We report a new method using a heating medium for the thermal decomposition of epoxy resin (EP) at temperatures ranging from 50 to 200 °C. EP decomposition also occurred below 50 °C during a 6-day period to generate bisphenol A (BPA) at concentrations as high as 5 ppm. When polyethylene glycol was used as a heating medium, we determined the kinetics of the EP decomposition at low temperature. We determined the apparent activation energy of the overall decomposition to be 40.8 kJ/mol and the frequency factor to be 2.3×10^3 by monitoring the rate of BPA formation. Thus, EP is clearly unstable upon the application of heat.

Keywords: epoxy resin, bisphenol A, endocrine disrupting chemical, low-temperature decomposition, plastic, landfill.

Introduction

Plastic is cheaply and is easy to be produced of large quantities, because the stable property is shown at the living environment. Plastic is disposed in landfill as not recycle, since it generates dioxin, etc. by reacting with the chlorine in the incomplete combustion.[1] Wide area is necessary for landfill, and there are the many problems that the hazardous compounds migrate to water and that it contributes to living organisms.[2]

Cured epoxy resin is a typical heat-resistant engineering plastic produced with bisphenol A (BPA) as a starting material. Epoxy resin is used to prepare electric and electronic equipment and widely used for paints and household goods. Waste plastic constitutes an environmental pollutant itself[3] and the more serious problem is certain chemicals derived from plastics which may seep out from waste plastics in landfill. Recent researches demonstrate that plastics disposed in the nature cause the environmental pollution. Especially the pollutants are usually low-molecular-weight compounds such as styrene oligomer,[4] nonylphenol,[5] BPA,[6] and phthalate esters (PAE).[7] BPA has been shown to have adverse effect on reproductive and immunologic functions at lower concentrations under ppm in living organisms.[8-10] We have little knowledge on the kinetics of the low-temperature decomposition of plastic products in a diary use situations and after being disposed.

The present paper demonstrates that at low temperature, the decomposition of uncured epoxy resin (EP) gives rise to BPA, and thus may be presented even in canned food and water discharged from a landfill.

Experimental

Materials. Uncured epoxy resin (average M_n *ca.* 4,000) was purchased from Aldrich Chemical Company, Inc. This uncured EP contained 200 μg/g 2,2-bis(4-glycidyloxyphenyl)-propane (BADGE) and trace BPA, which was removed at the concentration less than 0.2 μg/g by reprecipitation with tetrahydrofuran and diethyl ether in three times. The heating medium (polyethylene glycol 1,540, PEG, reagent grade) was used without purification (WAKO, Tokyo Japan). The detailed experimental procedures[11] and apparatuses were described previously.[12]

For GC/MS column was CP-Sil 8CB (Chrompack, 30-m

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length×0.32 mm I.D., 0.25 m film thick) and for GPC column was Polymer Laboratory Inc., two Mixed-E columns (300×7.5 mm) + 50 A-column (300×7.5 mm), column oven 40 °C) were used in this study.

Calibration Curve. Due to a strong adsorption property of BPA, a GC column was washed with acetone before and after quantitative analysis although the trimethylsilylation of BPA is a typical treatment for GC/MS samples. Possible amounts of BPA adsorption were at 0.01 ppm or less in the analysis. In this study, calibration curve was made by internal standard method, in which diphenyl was added at a constant amount and a coefficient of variation of calibration curve was 0.9994.

Results and Discussion

Temperature Effect on EP Decomposition. Average molecular weight of EP was estimated as 4,000, and molecular weight of BPA is 228. One cannot distinguish the low molecular weight products in the large amounts of polymers. We newly constructed the method in order to solve these problems. It is possible of this newly constructed method that there is no elevated temperature process by using PEG as heating medium, in respect of the thermal decomposition of EP and that it does under the softening point and in use of the living life or after being disposed of EP.

The minute quantity under ppm can determine BPA only in the simple treatment of liquid/ liquid distribution by water. Therefore, this study is regarded as the initial stage of EP decomposition well. The details of method was shown in another report.[12] The EP showed the thermal decomposition at 50 °C, and 5 ppm BPA was formed. The result was shown in Figure 1.

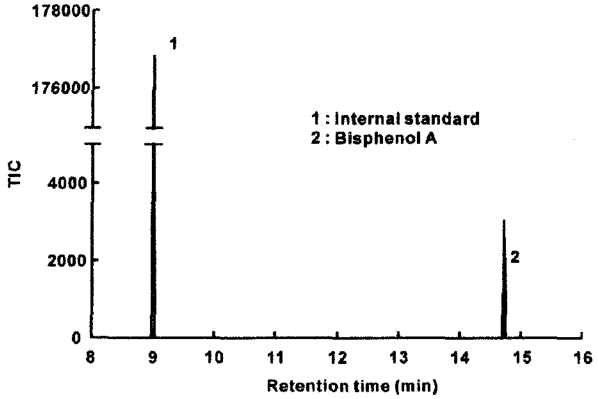

Figure 1. TIC chromatogram of thermal decomposed epoxy resin at 50 °C, 6 days [Selected ion at m/z: 75, 135, 150, 154, 213, 228, 325, 340].

Apparatus: GC/ HP6890. Column, DB-5; 30 m; I.D. 0.32 mm; 0.25 mm. He, 1.5 mL/min. Splitless injection. Injection temperature, 280 °C.
Column temperature, 50 °C (2 min hold) to 290 °C (15 °C/min) and 2 min hold.
MS/ Jeol JMS-AMII. Interface temperature, 255 °C.
Ion source temperature, 210 °C. Electron accelerating voltage, 70 eV.

It was shown that the decomposition product in this study was simple unlike the result of other EP thermal decomposition at high temperature.[13,14] In Japan, canned drinks coated with cured epoxy resin keep 60-65 °C, 7~10 days warm in the vending machine and are sold.[15] The canned food is being heat-treated by the necessity for the sterilization at 121 or 175 °C for several minutes.[16] The result showed that the EP receives the thermal decomposition at the life utilization, and formed endocrine disrupting chemical, BPA.

Figure 2 showed the emitted BPA content according to the heating temperature under the fixed time (3 hrs). It was recognized that the decomposition product was only BPA and it was increased for the rise in the reaction temperature rectilinear. Thermally stable plastic cured EP that it does not decompose in 250 °C or less[17] but uncured EP was decomposed even in the low temperature of 50 °C.

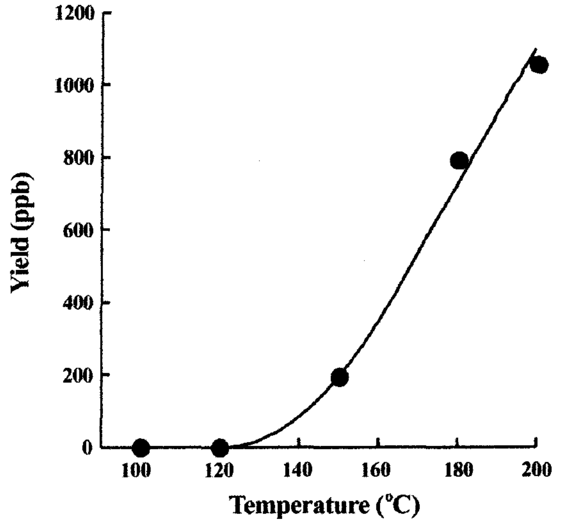

Figure 2. Relationship between the yield of bisphenol A and the temperature on the thermal decomposition of epoxy resin under the fixed time (3 hrs).

BPA Formation with the Reaction Time. Plastics have been considered to be thermally stable, especially at the ordinary temperatures. Waste plastic was disposed in landfill sites, and the elution of biologically-active compounds to the environment could not be expected until the studies on the pollutants like nonylphenol, BPA, and PAE. At the wide temperature range of 50-200 °C, EP was decomposed in PEG. The formation of BPA was monitored with the exposing time. The result was shown in Figure 3.

In Figure 3, the content of emitted BPA was increased with the reaction time at each temperature.

Figure 4 shows the Arrhenius plot of EP decomposition, and the good linearity of the kinetic results was confirmed. The apparent kinetic parameters of the Arrhenius equation were obtained based on the rate constants of BPA formation

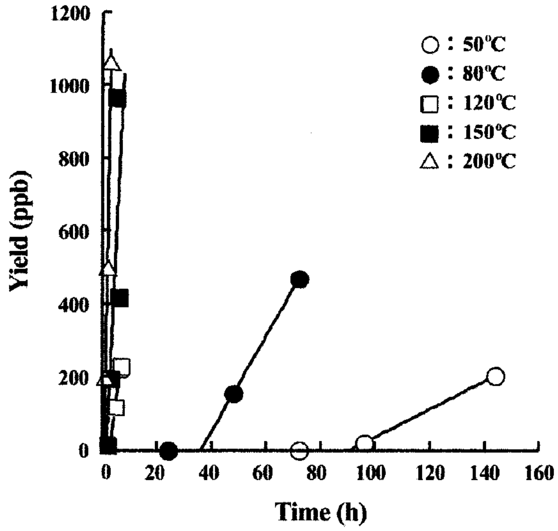

Figure 3. Effect of reaction time on the thermal decomposition of epoxy resin.

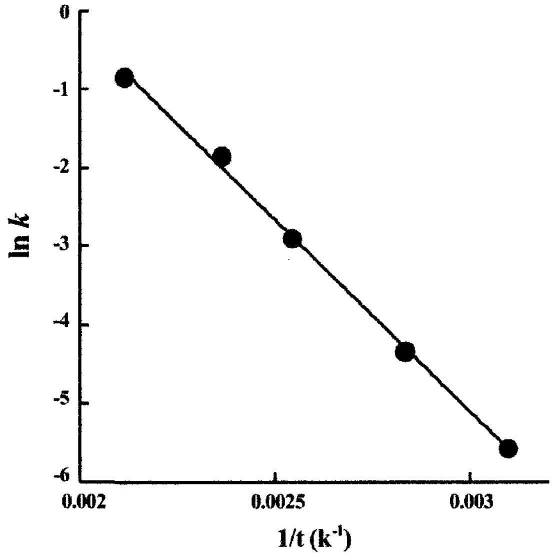

Figure 4. Arrhenius plots of bisphenol A.

at each temperature. The activation energy of the EP decomposition was given as 40.8 kJ/mol and the frequency factor was 2.3×10^3.

In this study, the uncured EP was powdered in 40-80 mesh, and the resulting sample was dispersed in PEG with stirring (500 rpm). This procedure is the enhanced conditions for the accelerated thermal decomposition. The activation energy of the decomposition was less than that of PAE,[18] thus decomposes more easily than the latter. In the landfills where EP or polycarbonate have been discarded, there is the possibility of long-term pollution by BPA which is generated via the decomposition of those materials since landfill temperature may remain at 50 °C or more for many years.[19]

Conclusions

The apparent activation energy of the overall decomposition of EP was calculated as 40.8 kJ/mol, based on the rate of the formation of BPA. In the thermal treatment such as the sterilization of canned food, the similar decomposition of EP may proceed to lead the formation of BPA. There would be several pathways of BPA emission to the environment, and one of the pathway can be a thermal decomposition of BPA-containing plastics like polycarbonate and EP.

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