

Unclassified

ENV/JM/MONO(2004)8/REV1



Organisation de Coopération et de Développement Économiques  
Organisation for Economic Co-operation and Development

09-Jul-2009

English - Or. English

**ENVIRONMENT DIRECTORATE  
JOINT MEETING OF THE CHEMICALS COMMITTEE AND  
THE WORKING PARTY ON CHEMICALS, PESTICIDES AND BIOTECHNOLOGY**

ENV/JM/MONO(2004)8/REV1  
Unclassified

**OECD SERIES ON EMISSION SCENARIO DOCUMENTS**

**Number 3**

**EMISSION SCENARIO DOCUMENT ON PLASTIC ADDITIVES**

**JT03267870**

Document complet disponible sur OLIS dans son format d'origine  
Complete document available on OLIS in its original format

English - Or. English

**OECD Environment Health and Safety Publications**

**Series on Emission Scenario Documents No. 3**

**EMISSION SCENARIO DOCUMENT ON  
PLASTICS ADDITIVES**

**IOMC**

**INTER-ORGANISATION PROGRAMME FOR THE  
SOUND MANAGEMENT OF CHEMICALS**

**A cooperative agreement among  
UNEP, ILO, FAO, WHO, UNIDO, UNITAR and OECD**

**Environment Directorate**

**Organisation for Economic Co-operation and Development**

**Paris 2009**

**Also published in the Series on Emission Scenario Documents:**

- No. 1, *Guidance Document on Emission Scenario Documents (2000)*
- No. 2, *Emission Scenario Document for Wood preservatives (2000)*
- No. 3, *Emission Scenario Document on Plastic Additives (2004; revised in 2009)*
- No. 4, *Emission Scenario Document on Water Treatment Chemicals (2004)*
- No. 5, *Emission Scenario Document on Photographic Industry (2004)*
- No. 6, *Emission Scenario Document on Rubber Additives (2004)*
- No. 7, *Emission Scenario Document on Textile Finishing (2004)*
- No. 8, *Emission Scenario Document on Leather Processing (2004)*
- No. 9, *Emission Scenario Document on Photoresist Use in Semiconductor Manufacturing (2004; revised in 2009)*
- No. 10, *Emission Scenario Document on Lubricants and Lubricant Additives (2004)*
- No. 11, *Emission Scenario Document on Automotive spray application (2004)*
- No. 12, *Emission Scenario Document on Metal finishing (2004)*
- No. 13, *Emission Scenario Document on Antifoulants main document (2005)*
- No. 14, *Emission Scenario Document on Insecticides for Stables and Manure Storage Systems (2006)*
- No. 15, *Emission Scenario Document on Kraft Pulp Mills (2006)*
- No. 16, *Emission Scenario Document on Non-Integrated Paper Mills (2006)*
- No. 17, *Emission Scenario Document on Recovered Paper Mills (2006)*
- No. 18, *Emission Scenario Document for Insecticides, Acaricides and Products to Control Other Arthropods for Household and Professional Uses (2008)*

- No. 19, *Complementing Guideline for Writing Emission Scenario Documents : The Life-Cycle Step “service-life”(2008)*
- No. 20, *Emission Scenario Document on Adhesive Formulation (2009)*
- No. 21, *Emission Scenario Document on the Formulation of Radiation Curable Coating, Inks, and Adhesives (2009)*
- No. 22, *Emission Scenario Document on Coating Industry (Paints, Lacquers and Varnishes) (2009)*
- No. 23, *Emission Scenario Document on Pulp, Paper and Board Industry (2009)*
- No. 24, *Emission Scenario Document on Transport and Storage of Chemicals (2009)*

## ABOUT THE OECD

The Organisation for Economic Co-operation and Development (OECD) is an intergovernmental organisation in which representatives of 30 industrialised countries in North America, Europe and the Pacific, as well as the European Commission, meet to co-ordinate and harmonize policies, discuss issues of mutual concern, and work together to respond to international problems. Most of the OECD's work is carried out by more than 200 specialised Committees and subsidiary groups composed of Member country delegates. Observers from several countries with special status at the OECD, and from interested international organisations, attend many of the OECD's Workshops and other meetings. Committees and subsidiary groups are served by the OECD Secretariat, located in Paris, France, which is organised into Directorates and Divisions.

The Environmental Health and Safety (EHS) Division publishes documents in eight different series: **Testing and Assessment; Good Laboratory Practice and Compliance Monitoring; Pesticides; Risk Management; Harmonization of Regulatory Oversight in Biotechnology; Chemical Accidents; Pollutant Release and Transfer Registers; and Emission Scenario Documents.**

The Environmental Health and Safety Programme co-operates closely with other international organisations. This document was produced within the framework of the Inter-Organization Programme for the Sound Management of Chemicals (IOMC).

**The Inter-Organization Programme for the Sound Management of Chemicals (IOMC) was established in 1995 by UNEP, ILO, FAO, WHO, UNIDO and the OECD (the Participating Organizations), following recommendations made by the 1992 UN Conference on Environment and Development to strengthen co-operation and increase international co-ordination in the field of chemical safety. UNITAR joined the IOMC in 1997 to become the seventh Participating Organization. The purpose of the IOMC is to promote co-ordination of the policies and activities pursued by the Participating Organizations, jointly or separately, to achieve the sound management of chemicals in relation to human health and the environment.**

**This publication is available electronically, at no charge.**

**For the complete text of this and many other Environmental Health and Safety publications, consult the OECD's World Wide Web site (<http://www.oecd.org/ehs/>)**

**or contact:**

**OECD Environment Directorate,  
Environmental Health and Safety Division**

**2 rue André-Pascal  
75775 Paris Cedex 16  
France**

**Fax: (33-1) 45 24 16 75**

**E-mail: [ehscont@oecd.org](mailto:ehscont@oecd.org)**

## EXPLANATORY NOTES

### Purpose and background

This OECD Emission Scenario Document (ESD) is intended to provide information on the sources, use patterns and release pathways of chemicals used as additives in plastics to assist in the estimation of releases of chemicals to the environment.

This ESD should be seen as a ‘living’ document, which provides the most updated information available. As such, an ESD can be updated to take account of changes and new information, and extended to cover the industry area in countries other than the lead (the United Kingdom). Users of the document are encouraged to submit comments, corrections, updates and new information to the OECD Environment, Health and Safety Division ([env.riskassessment@oecd.org](mailto:env.riskassessment@oecd.org)). The comments received will be forwarded to the OECD Task Force on Environmental Exposure Assessment, which will review the comments every two years so that the lead country can update the document. The submitted information will also be made available to users within the OECD web-site ([www.oecd.org/env/riskassessment](http://www.oecd.org/env/riskassessment)).

### How to use this document

The user of this ESD needs to consider how the information contained in the document covers the situation for which they wish to estimate releases of chemicals. The document could be used as a framework to identify the information needed, or the approaches in the document could be used together with the suggested default values to provide estimates. Where specific information is available it should be used in preference to the defaults. At all times, the values inputted and the results should be critically reviewed to assure their validity and appropriateness.

An alternative approach to estimating releases from service life based on surface area of products is described in this ESD, but no values for the area emission factors are included. In addition, it was pointed out that the nature of the product and its area of use will affect which of the emission routes from products in use will be relevant. For example, products used indoors will only be subject to leaching losses if they are washed regularly. The specific use pattern of the products containing the substance needs to be considered.

### Coverage

This ESD covers plastics processing (compounding and conversion) and also releases from plastics during their service life. The methods included mainly focus on wastewater emission but also provide emission factors to air for the processing steps and for service life. The industry categories, use categories and biocidal product types relevant to this document are as follows.

Industry category	Use Category	Biocidal product type
11 – polymers industry	7 – anti-static agents	7 – film preservatives

	10 – colouring agents 14 – corrosion inhibitors 20 – fillers 22 – flame retardants and fire preventing agents 25 – foaming agents 39 – biocides, non-agricultural 43 – process regulators 47 – softeners 49 – stabilisers 52 – viscosity adjusters	
--	-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------	--

### How this document was developed

The document is based on a report produced by the Building Research Establishment for the UK Department of the Environment entitled ‘Use Category Document – Plastic Additives’. The original report, produced in 1994, was developed to provide information to be used in risk assessments for new and existing substances in the EU. It should be noted that information such as that in Sections 2 to 5 was collected for this original document, relating to the UK unless indicated, and has not been updated subsequently.

For this ESD, RAPRA (formerly the Rubber and Plastics Research Association) developed release estimates for additives for the various steps in the life cycle of the plastic materials. These estimates were based on measurements, accepted estimation methods, or expert judgement. - The report makes it reasonably clear where a release estimate is based on industry measurements, or on calculations which relate to industry-specific values (such as sizes of vessels and quantities processed). Other values are largely from expert judgement. The emphasis in these cases was to have a reasonable worst case value, so that the estimates should be towards the high end of possible values. In addition, where emissions were expected to be negligible, but there were no available measurements to confirm this, a release of 0.01% was adopted as a minimum value.

Further discussions took place within the UK on this document, with representatives of the European Council for Plasticisers and Intermediates (ECPI, a Sector Group of CEFIC). This led to some changes in the estimates of emissions from the plastics processing sites, relating to the relative losses for low, medium and high volatility substances, and also to the effect of air treatment systems on emissions. These changes were included in the version of June 1998 (“Use Category Document – Plastic Additives, Revised draft for discussion”, produced for the Environment Agency).

The OECD Task Force on Environmental Exposure Assessment selected the June 1998 version of the document as a suitable basis for a pilot study for the development of OECD-wide emission scenario documents by revising it with additional information including some information from countries outside the EU. This ESD has since been updated considering comments from Canada, France, Germany, The Netherlands, Sweden, and United States, and from industry in Europe and in the US and Canada. A number asked for more details about the sources of information and the release of additives from products during their service life.

This ESD was published in June 2004 as an OECD Series on Emission Scenario Document No.3 [ENV/JM/MONO(2004)8]. Since the publication, the ESD has been updated to include a new model for estimating the emissions of additives from products during their service life. The method is presented as an alternative, for use alongside the original methodology. Guidance on the use of additional factors for small sites and for high temperature processing has been added. Further notes on



the use of the terms used to distinguish between volatile and non-volatile additives in relation to emissions have also been included. A draft for the revised ESD was circulated to the Task Force in May 2007 and discussed at the 15<sup>th</sup> meeting of the Task Force in December 2007, with a request for comments by the end of February 2008. No comments were received, and the draft was approved by the Task Force at its 16<sup>th</sup> meeting in October 2008.

## TABLE OF CONTENTS

EXPLANATORY NOTES.....	7
TABLE OF CONTENTS .....	10
1 INTRODUCTION.....	17
1.1 Overview of document.....	17
1.2 Using this document.....	18
2 THE PLASTICS INDUSTRY.....	19
2.1 Activities of the industry.....	19
2.2 General structure of the industry.....	20
2.3 Polymers.....	22
2.4 End uses for plastics.....	22
2.5 Plastics materials or compounds .....	23
2.5.1 General description.....	23
2.5.2 Additives used for performance enhancement.....	23
2.5.3 Additives used as processing aids.....	24
2.6 Masterbatches.....	24
2.7 The European dimension.....	25
2.7.1 Industry structure and uses of plastics .....	25
2.7.2 Uses and losses of additives .....	25
3 PLASTICS PROCESSING AND USE .....	26
3.1 Raw materials' handling .....	27
3.2 Compounding.....	27
3.2.1 Closed processes.....	27
3.2.2 Partially-open processes .....	30
3.3 Conversion Processes.....	31
3.3.1 Closed processes.....	31
3.3.1.1 Extrusion.....	31
3.3.1.2 Injection moulding.....	32
3.3.1.3 Compression moulding.....	32
3.3.1.4 Extrusion blow moulding .....	33
3.3.1.5 Injection blow moulding.....	34
3.3.2 Partially-open processes .....	35
3.3.2.1 Film extrusion.....	35
3.3.2.2 Paper and textile coating.....	35
3.3.3 Open processes .....	36
3.3.3.1 Thermoforming.....	36
3.3.3.2 Calendering.....	36
3.3.3.3 Fibre reinforced plastic fabrication.....	37
3.4 Use of processes.....	38

4	QUANTITIES AND APPLICATIONS OF POLYMERS .....	39	
4.1	Plastics usage by process.....	39	
4.2	Applications of plastics materials.....	39	
4.3	Life expectancy of plastics.....	40	
4.4	Waste disposal practices in the plastics processing industry.....	41	
4.4.1	Additives.....	41	
4.4.2	Polymer and plastics products.....	41	
4.5	Disposal and recycling of plastics products.....	41	
5	QUANTITIES OF ADDITIVES USED.....	44	
5.1	Estimates of quantities of polymer used on representative sites.....	44	
5.2	Quantities of additive used on site.....	46	
6	INTRODUCTION TO THE MODEL.....	48	
6.1	Release from manufacture of plastics materials.....	48	
6.1.1	Selection of emission factors.....	48	
6.1.2	Materials handling.....	49	
6.1.3	Compounding.....	49	
6.1.4	Conversion.....	49	
6.1.5	Overall emission factor for formulation (compounding) and processing (conversion).....	50	
6.1.6	Estimated emissions from formulation (compounding) and processing (conversion).....	50	
6.2	Release from use (service life) and disposal of plastics materials.....	52	
6.2.1	Service life.....	52	
6.2.2	Disposal.....	54	
6.2.3	Other sources of release.....	55	
6.3	Example calculations.....	55	
6.3.1	Example 1.....	55	
6.3.1.1	Emission factors.....	55	
6.3.1.2	Emission estimates.....	56	
6.3.2	Example 2.....	56	
6.3.2.1	Emission factors.....	57	
6.3.2.2	Emission estimates.....	57	
7	FILLERS.....	59	
7.1	General description.....	59	
7.1.1	Raw materials handling.....	59	
7.1.1.1	Particulate fillers.....	59	
7.1.1.2	Fibrous fillers.....	60	
7.1.2	Compounding.....	60	
7.1.2.1	Particulate fillers.....	60	
7.1.2.2	Fibrous fillers.....	60	
7.1.3	Conversion.....	61	
7.1.3.1	Particulate fillers.....	61	
7.1.3.2	Fibrous fillers.....	61	
7.1.4	Service life.....	61	
7.1.5	Disposal.....	61	
7.2	Estimating percentage (%) losses.....	61	
7.2.1	Raw materials' handling.....	62	
7.2.2	Compounding.....	62	
7.2.3	Conversion.....	62	

7.2.4	Small sites.....	63
7.2.5	Service life.....	63
7.2.6	Disposal.....	63
8	PLASTICISERS.....	64
8.1	General description.....	64
8.1.1	Raw materials handling.....	65
8.1.2	Compounding.....	65
8.1.2.1	Dry blending.....	66
8.1.2.2	Plastisol blending.....	66
8.1.2.3	Banbury mixing.....	66
8.1.3	Conversion.....	66
8.1.3.1	Calendering (open process).....	67
8.1.3.2	Extrusion (partly open or closed).....	67
8.1.3.3	Injection moulding (closed).....	67
8.1.3.4	Plastisol-spread coating (open).....	67
8.1.3.5	Other plastisol processes.....	68
8.1.4	Service life.....	68
8.1.4.1	Interior.....	68
8.1.4.2	Exterior.....	69
8.1.5	Disposal.....	69
8.2	Estimating percentage losses.....	70
8.2.1	Raw materials handling.....	70
8.2.2	Compounding.....	70
8.2.3	Conversion.....	70
8.2.4	Small sites.....	71
8.2.5	Service life.....	71
8.2.6	Disposal.....	72
9	ANTIOXIDANTS.....	73
9.1	General description.....	73
9.1.1	Raw materials' handling.....	73
9.1.2	Compounding.....	74
9.1.3	Conversion.....	74
9.1.4	Service life.....	76
9.1.5	Disposal.....	76
9.2	Estimating percentage (%) losses.....	76
9.2.1	Raw materials' handling.....	76
9.2.2	Compounding.....	76
9.2.3	Conversion.....	77
9.2.4	Small sites.....	77
9.2.5	Service life.....	78
9.2.6	Disposal.....	78
10	COUPLING AGENTS.....	79
10.1	General description.....	79
10.1.1	Raw materials' handling.....	79
10.1.2	Compounding.....	80
10.1.3	Fate after compounding.....	80
10.2	Estimating Percentage (%) Losses.....	80
10.2.1	Raw materials' handling.....	80

10.2.2	Compounding .....	80
10.2.3	Further stages (conversion, service life and disposal) .....	80
11	COLOURANTS.....	81
11.1	General description.....	81
11.2	Estimating percentage (%) losses .....	82
11.2.1	Raw materials' handling.....	82
11.2.2	Compounding .....	82
11.2.3	Conversion.....	83
11.2.3.1	Pigments .....	83
11.2.3.2	Dyes .....	83
11.2.4	Small sites.....	83
11.2.5	Service life.....	83
11.2.5.1	Pigments .....	83
11.2.5.2	Dyes .....	84
11.2.6	Disposal .....	84
12	UV AND OTHER WEATHERING STABILISERS .....	85
12.1	General description.....	85
12.2	Estimating percentage (%) losses .....	85
12.2.1	Raw materials' handling.....	85
12.2.2	Compounding .....	85
12.2.3	Conversion.....	86
12.2.4	Small sites.....	87
12.2.5	Service life.....	87
12.2.6	Disposal .....	87
13	POLYMERIC IMPACT MODIFIERS.....	88
13.1	General description.....	88
13.1.1	Raw materials' handling.....	88
13.1.2	Compounding .....	88
13.1.3	Conversion.....	89
13.1.4	Service life.....	89
13.1.5	Disposal .....	89
13.2	Estimating percentage (%) losses .....	89
13.2.1	Raw materials' handling.....	89
13.2.2	Compounding .....	90
13.2.3	Conversion.....	90
13.2.4	Service life.....	90
13.2.5	Disposal .....	90
14	ANTI-STATIC AGENTS.....	91
14.1	General description.....	91
14.2	Estimating percentage (%) losses .....	92
14.2.1	Raw materials' handling.....	92
14.2.2	Compounding .....	92
14.2.3	Conversion.....	93
14.2.3.1	Inorganic.....	93
14.2.3.2	Organic .....	93
14.2.4	Small sites.....	94
14.2.5	Service life.....	94

14.2.5.1	Inorganic .....	94
14.2.5.2	Organic .....	94
14.2.6	Disposal .....	95
15	FLAME RETARDANTS .....	96
15.1	General description .....	96
15.2	Estimating Percentage (%) Losses .....	97
15.2.1	Raw materials' handling .....	97
15.2.2	Compounding .....	97
15.2.3	Conversion .....	98
15.2.3.1	Inorganic .....	98
15.2.3.2	Organic .....	98
15.2.4	Small sites .....	99
15.2.5	Service life .....	99
15.2.5.1	Inorganic .....	99
15.2.5.2	Organic .....	99
15.2.6	Disposal .....	100
16	PRESERVATIVES (BIOCIDES) .....	101
16.1	General description .....	101
16.2	Estimating percentage (%) losses .....	102
16.2.1	Raw materials' handling .....	102
16.2.2	Compounding .....	102
16.2.3	Conversion .....	102
16.2.3.1	Inorganic .....	102
16.2.3.2	Organic .....	103
16.2.4	Small sites .....	103
16.2.5	Service life .....	104
16.2.5.1	Inorganic .....	104
16.2.5.2	Organic .....	104
16.2.6	Disposal .....	104
17	CURING AGENTS .....	105
17.1	General description .....	105
17.2	Estimating percentage (%) losses .....	105
17.2.1	Raw materials' handling .....	105
17.2.1.1	Solid curing agents .....	105
17.2.1.2	Liquid curing agents .....	106
17.2.2	Compounding .....	106
17.2.2.1	Solid curing agents .....	106
17.2.2.2	Liquid curing agents .....	106
17.2.3	Conversion, service life and disposal .....	106
18	BLOWING AGENTS .....	107
18.1	General description .....	107
18.2	Estimating percentage (%) losses .....	108
18.2.1	Raw materials' handling .....	108
18.2.1.1	Chemical blowing agents (solids) .....	108
18.2.1.2	Physical blowing agents (liquids and gases) .....	108
18.2.2	Compounding .....	108
18.2.2.1	Chemical blowing agents .....	108

18.2.2.2	Physical blowing agents .....	109
18.2.3	Conversion.....	109
18.2.3.1	Chemical blowing agents.....	109
18.2.3.2	Physical blowing agents .....	109
18.2.4	Service life.....	109
18.2.4.1	Chemical blowing agents.....	109
18.2.4.2	Physical blowing agents .....	109
18.2.5	Disposal .....	109
19	HEAT STABILISERS .....	110
19.1	General description.....	110
19.2	Estimating percentage (%) losses .....	111
19.2.1	Raw materials' handling.....	111
19.2.1.1	Solids .....	111
19.2.1.2	Liquids.....	111
19.2.2	Compounding .....	111
19.2.2.1	Non-volatile solids.....	111
19.2.2.2	Volatile solids.....	111
19.2.2.3	Liquids.....	112
19.2.3	Conversion.....	112
19.2.3.1	All solids.....	112
19.2.3.2	Volatiles.....	112
19.2.4	Small sites.....	113
19.2.5	Service life.....	114
19.2.5.1	Solids .....	114
19.2.5.2	Volatiles.....	114
19.2.6	Disposal .....	114
20	SLIP PROMOTERS .....	115
20.1	General description.....	115
20.2	Estimating percentage (%) losses .....	115
20.2.1	Raw materials' handling.....	115
20.2.2	Compounding .....	115
20.2.3	Conversion.....	116
20.2.3.1	Inorganic.....	116
20.2.3.2	Organic .....	116
20.2.4	Small sites.....	117
20.2.5	Service life.....	117
20.2.5.1	Inorganic.....	117
20.2.5.2	Organic .....	117
20.2.6	Disposal .....	117
21	VISCOSITY AIDS .....	119
21.1	General description.....	119
21.2	Estimating percentage (%) losses .....	119
21.2.1	Raw materials' handling.....	119
21.2.2	Compounding .....	119
21.2.3	Conversion.....	120
21.2.4	Service life.....	120
21.2.5	Disposal .....	120

22	REFERENCES .....	121
	APPENDIX I - ACRONYMS FOR POLYMERS .....	122
	APPENDIX II - VAPOUR PRESSURE AND VOLATILE LOSS .....	123
	APPENDIX III - PROCESSES AND ADDITIVES FOR SPECIFIC POLYMERS .....	126
	APPENDIX IV - DIFFUSION MODEL FOR PREDICTING SERVICE LIFE EMISSIONS TO AIR FROM POLYMERS .....	136



## 1 INTRODUCTION

### 1.1 Overview of document

1. The UK plastics manufacturing industry is large and complex. Numerous polymers provide the basis for these plastics; some are imported and some are manufactured in the UK. Polymer manufacture is not considered in this use category document.

2. A wide range of different substances is added to polymers during their compounding and conversion to plastics materials. These additives include fillers, reinforcements and colours and other materials such as plasticisers which ensure the finished plastic has the required performance for its specific application. Other additives are used to aid the manufacturing process. The properties of the main classes of additives are described in this document, particularly in relation to their possible release during plastics manufacture and during the service and disposal of manufactured items.

3. The end use or application of a plastics material determines;

- the polymer from which it is made, and
- the form (pipe, sheet, film etc) of the finished plastic material.

4. These two factors determine;

- the substances added to the polymer to produce a plastics material of the expected performance for that end use and the additives used as processing aids,
- the properties and fractional content of the particular additives used, and
- the likely service life of the plastics material.

5. This use category document contains detailed descriptions of the commonly-used additives and the processes used in the compounding and conversion of plastics materials. It also contains detailed information, data and estimates which enable the calculation of estimated values for the quantity of an individual additive which may be released annually as a result of the manufacture of a particular plastics material and of its use and disposal. These estimates can be made once the following information is determined;

- the function of the additive,
- the polymer to which it is added,
- the type of process used in the conversion of the plastics material i.e. closed, open or partially-open, and

- possibly the industry sector or sectors in which the resulting product will be used.

## **1.2 Using this document**

6. For the purposes of estimating releases of new additives, it is likely that information on the polymer, the application for which it is formulated and the annual tonnage produced will be available from the notifier. In the absence of these data, sufficient information is provided in this document to estimate annual releases of particular classes of additives as a result of their incorporation into each of the polymers in which they are commonly used. An attempt has been made to classify the plastics processing industry based on the number of employees per site; this has been used as a basis for estimating the use of additives on individual processing sites.

7. In order to make estimates of releases of plastics additives, it is suggested that the Sections are used in the following order:

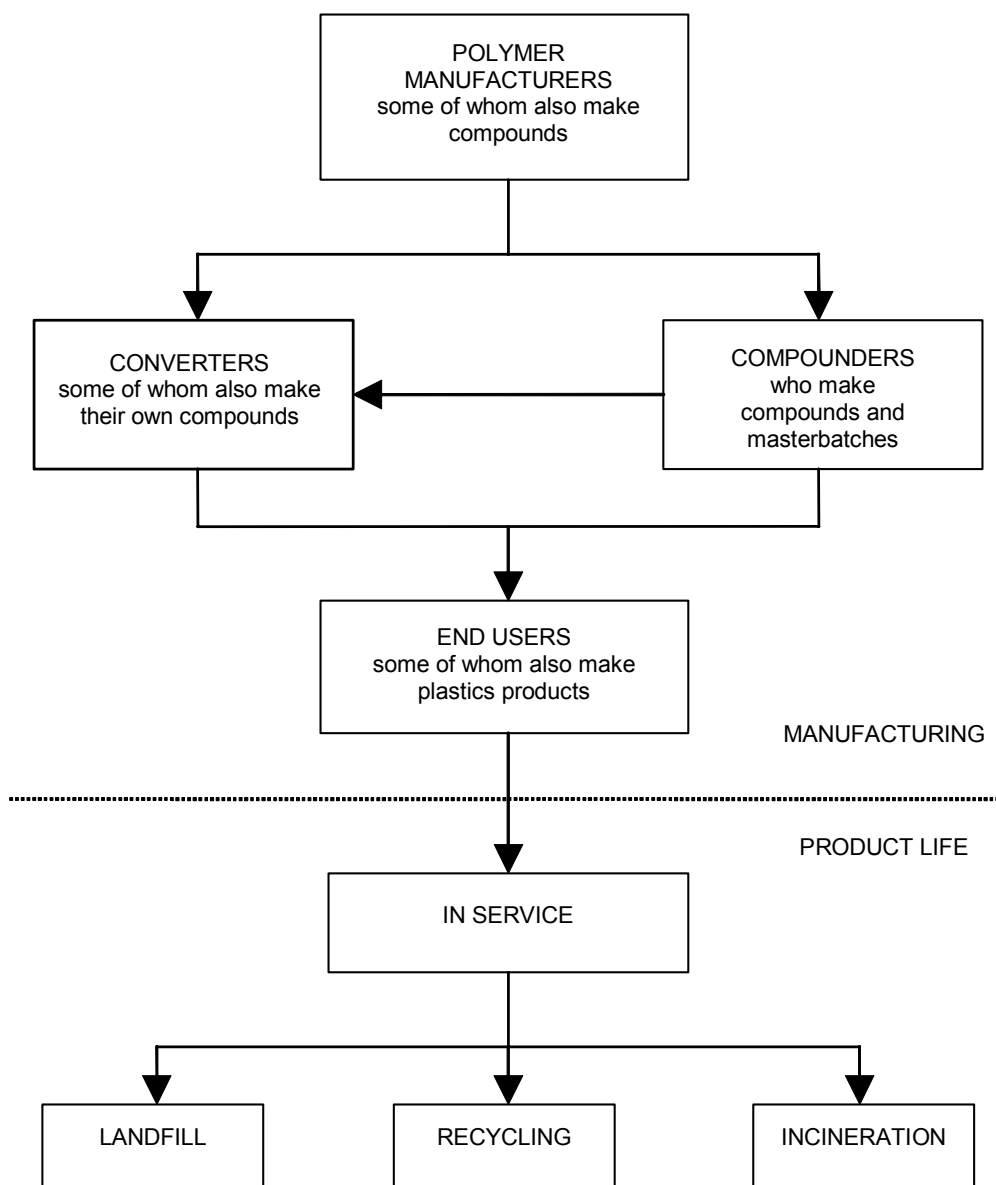
- a) Section 6 which sets out the calculations to be used and identifies the parameters for which values are required.
- b) Section 5 which contains information on the size distribution of plastics processors and estimates of the amount of polymer used on representative sites. This section also describes how the information in the tables in Appendix III can be used to estimate the amount of additive used.
- c) Sections 7 - 21 which provide values for loss factors for the individual additives during the manufacture of plastic materials, their use and their eventual disposal.
- d) Section 4 which gives information on the expected service life of plastics materials used for particular applications.

2 THE PLASTICS INDUSTRY

2.1 Activities of the industry

8. Four distinct activities fall under the general heading of the plastics industry - polymer manufacture, compounding, conversion and "in-house" manufacture. The relationship between these activities is illustrated in Figure 2.1.

Figure 2.1 Manufacturing stages of the plastics industry



9. In keeping with general practice, this document distinguishes between polymers and plastics materials as follows.

- **Polymers** are the virgin products of the chemical/petrochemical industry and have undergone no significant post-reactor treatments. In this document, this group includes those polymers which may have been modified within the reactor as part of a subsequent chemical process.
- **Plastics materials** are polymers which have been modified in some way, such as the addition of additives and processing under pressure and/or heat. They are then ready to be converted into plastics artifacts.

10. **Polymer manufacture** is usually undertaken by chemical and petrochemical companies. The processes used include continuous and batch polymerisation as well as the manufacture of resins by condensation etc. The resulting materials take the form of either thermoplastics polymers or thermosetting resins.

11. **Compounding** involves the blending into the polymers of various types of additives, including fillers, reinforcements and colours to meet the requirements of specific applications for plastics materials. There are companies which specialise in this field, but many polymer makers and converters also undertake this work.

12. **Conversion** of compounds into finished artefacts is carried out using a diversity of processes. In the case of thermoplastics, the materials are shaped by heat and pressure using moulding, extrusion and other processes. Thermosetting resins are similarly cured under heat and pressure, although some resins are capable of being cured at ambient temperatures. Thermosetting processes are irreversible.

13. **"In house" manufacture** is undertaken in other industry sectors by companies who wish to manufacture their own plastics components and have the required facilities for conversion and, to a modest degree, compounding.

## 2.2 General structure of the industry

14. There are some 20 chemical and petrochemical companies manufacturing polymers in the United Kingdom. These include UK based multinational operations, such as ICI and BP Chemicals, manufacturing sites of overseas multinational companies, such as Elf Atochem and Dow, as well as smaller national companies.

15. Some 50 UK companies specialise in the compounding of plastics and it is estimated that there are over 3,000 companies carrying out plastics conversion. Many of these companies are very small and there is little information on the precise structure of the industry. There are few industrial estates or regions within the UK, or indeed in most industrialised countries, which do not have one or more companies manufacturing plastics.

16. **Table 2.1** sets out the last data published (in 1989) by the now defunct Plastics Processing Industry Training Board (PPITB). These figures only account for some 1,100 establishments.

**Table 2.1 Structure of the industry by processing activity**

Conversion process	Number of companies	
	PPITB Data	RAPRA Estimates
<b>CLOSED PROCESSES</b>		
<b>Moulding</b>		
Blow moulding	73	50
Injection moulding	469	2,000
Compression moulding	43	100
Rotational moulding	18	25
In House operations		50
<b>Total Moulding</b>	603	2225
<b>Extrusion</b>	86	125
<b>Foams</b>	50	50
<b>TOTAL CLOSED</b>	739	2,400
<b>PARTIALLY OPEN PROCESSES</b>		
Sheet, foil and extrusion coating	32	150
Film	34	70
<b>TOTAL PARTIALLY OPEN</b>	66	220
<b>OPEN</b>		
Calendering	3	5
Fabric coating	28	30
Casting	3	10
Thermoset hand fabrication	127	250
Thermoset - mechanised fabrication	12	100
Thermoforming	92	300
<b>TOTAL OPEN</b>	265	700
<b>TOTAL INDUSTRY</b>	1,070	3,300

17. The balance of some 2,000 is believed by RAPRA to be made up of the following.

- Small companies scattered throughout the UK about which little is known. For example, a study undertaken by RAPRA in 1984/85 indicated there were at least 2,000 injection moulding operations which is considerably more than the figure of 469 given by PPITB.
- A significant number of "in house" plastics processing operations which would not have been registered with the PPITB.
- At least 200 fabricators who cut, shape, weld and otherwise operate on moulded and extruded artefacts.
- Between 50 and 100 companies engaged in the compounding, reprocessing and colouring of plastics materials.

18. The second column in **Table 2.1** gives figures based on this information, on 'conventional wisdom' within the industry and hearsay views. They are considered by RAPRA to represent the situation in the industry today. The operations in the industry range from plants dedicated to the production of a discreet range of products (bottles, film or pipe etc.) to sites which essentially offer a jobbing service to other industries. Their activities are dependent on the requirements of their customers.

### 2.3 Polymers

19. Polymers fall into two categories defined by their chemical structure.

- **Thermoplastic polymers** are melted or softened in order to be formed under pressure into the required shape which is established on cooling the product. The process is reversible and the plastics materials can be reshaped and reused.
- **Thermosetting resins** are converted into finished products with the application of heat and pressure. Chemical cross-linking takes place and the process is not reversible. The materials cannot readily be recovered and reused.

20. The most common thermoplastics materials and thermosetting resins in current use are listed below.

#### Thermoplastics

Low density polyethylene (LDPE)  
 High density polyethylene (HDPE)  
 Polypropylene (PP)  
 Rigid polyvinyl chloride (Rigid PVC)  
 Flexible polyvinyl chloride (Flexible PVC)  
 Polystyrene (PS)  
 Expanded polystyrene (EPS)  
 Acrylonitrile-butadiene-styrene copolymers (ABS)  
 Polyethene terephthalate (PET)  
 Polyamides (nylons)  
 Acrylics  
 Acetals  
 Polycarbonate

#### Thermosetting resins

Polyurethanes  
 Unsaturated polyester resins  
 Phenolic resins  
 Amino resins  
 Epoxy resins

21. The most commonly used of these polymers are polyethylenes, PVC and polystyrene. Although all of the polymers are used in the United Kingdom in varying quantities, not all of them are manufactured in the UK. Most polymers and the plastics materials made from them are referred to by acronyms. These are listed above and in Appendix I.

### 2.4 End uses for plastics

22. Plastics are used in a wide variety of applications as shown in **Table 2.2**.

**Table 2.2 Plastics consumption by end use sector**

End use area	Plastics material used (tonnes x 10 <sup>3</sup> )
Packaging	1,200
Building and construction	840
Electrical and electronic	350
Automotive and transport	180
Agriculture	70
Other - housewares, toys, mechanical engineering etc.	860
Total	3,500

## 2.5 Plastics materials or compounds

### 2.5.1 General description

23. Plastics materials have to satisfy a variety of performance criteria requiring specific physical and chemical properties. Frequently, the polymer itself does not possess the full range of required properties and the majority of plastics will have undergone some form of compounding process before their conversion into finished artefacts.

### 2.5.2 Additives used for performance enhancement

24. The main functions of additives used for performance enhancement are listed below.

Type	Description
Fillers	Fillers are inert materials which reduce polymer costs, improve processability and can be used to improve the mechanical properties of the resulting plastics material. They are solids, which are incorporated into polymers but which remain as a separate phase. In general terms, fillers are either powders or fibres.
Plasticisers	Liquids or waxy (i.e. low melting) solids which fall into two general classes:  <u>Permanent plasticisers</u> enhance the flexibility of a plastics material and/or inhibit the embrittlement of the material at low temperatures; these substances are expected to survive the service life of the product in which they have been incorporated and so require a low propensity to migration.  <u>Latent plasticisers</u> improve the processability of plastics material during compounding and melt fabrication. They are subsequently removed during post-fabrication oven drying.
Antioxidants	A range of chemicals such as amines, phenols, phosphates etc. are used to inhibit degradation of polymers such as polyethylenes, polypropylenes and styrenic materials during the life of the product.
Coupling agents	Silane and titanate compounds are used to improve the bond between polymer matrices and mineral fillers and fibre reinforcements.
Colourants	A wide range of dyes and pigments are used throughout the industry.
UV & other weathering stabilisers	Generally these are benzo derivatives. However, polymers with good weathering properties such as PVC are sometimes blended into other polymers. They are mainly incorporated into plastics for applications requiring long life, such as building products, automotive and other engineering components. As in the case of permanent plasticisers, the stabilisers are required to function throughout the life of the product.

<b>Type</b>	<b>Description</b>
Polymeric impact modifiers	These are often elastomers or elastomer/polymer blends, used to retard or inhibit brittle fracture by absorbing the crack-initiating energy. By definition, the elastomers and the matrix polymers may not be fully compatible.
Anti-static agents	The purpose of these substances is to inhibit the development of static. In general, these are conductive powders and metal flakes but intrinsically conductive polymers may also be used in certain circumstances.
Flame retardants	Key application areas include packaging, the electrical and the electronic industries. Compounds based on halogens, boron and phosphorous are used to reduce the risk of ignition and retard combustion.
Preservatives	Fungicides and bacteriostatics are occasionally used in plastics which may be expected to be exposed in service for long durations.

### **2.5.3 Additives used as processing aids**

25. The main functions of additives used as processing aids are listed below.

<b>Type</b>	<b>Description</b>
Curing agents	Peroxides, amines and organotin compounds are used to assist in the curing of thermosetting materials. In some cases there is a need to retard curing and amines may be used for this purpose.
Blowing agents	Plastics materials are often used in a cellular form. The cells may be formed either by direct gassing or, more commonly, by the use of chemicals or solvents which release copious quantities of gas on heating.  Cellular plastics are used as lightweight foams for packaging and thermal insulation; in higher densities the cellular structure enhances the rigidity of polymers.
Heat stabilisers	Organic or organometallic compounds used to reduce the degradation of PVC and other vinyl materials subject to degradation during processing and conversion into finished products.
Slip promoters or Lubricants	Improve surface lubrication during processing and use
Viscosity aids	Materials which are used to regulate the viscosity of PVC- plasticiser-solvent mixtures during processing. They are themselves polymers.

### **2.6 Masterbatches**

26. Masterbatches are compounds which are made up to contain high concentrations of specific additives. These are then supplied to processors who disperse them into the main polymer matrix by



simple mixing. There is a growing trend towards the use of masterbatches, especially where the additive requires careful handling for reasons of cleanliness or health.

## **2.7 The European dimension**

27. The information presented in this document relates to the United Kingdom. To a large degree, the models are applicable to other Member States of the European Union. However, there are some significant differences in the values contained within the tables given in Appendix III and these will need to be estimated for each country.

### **2.7.1 *Industry structure and uses of plastics***

28. The general structure of the industry described in the above Sections applies throughout Europe. Similarly, the descriptions of the processing activities given in Chapter 3 and the applications for plastics products and additives set out in Chapter 4 and Appendix III are applicable to most developed countries.

29. Nevertheless, the extent to which a particular polymer or plastics material is used can differ substantially from one country to another. The actual quantities used are determined by a country's industrial structure, technical practices within individual end use sectors and, more recently, approach to environmental issues.

### **2.7.2 *Uses and losses of additives***

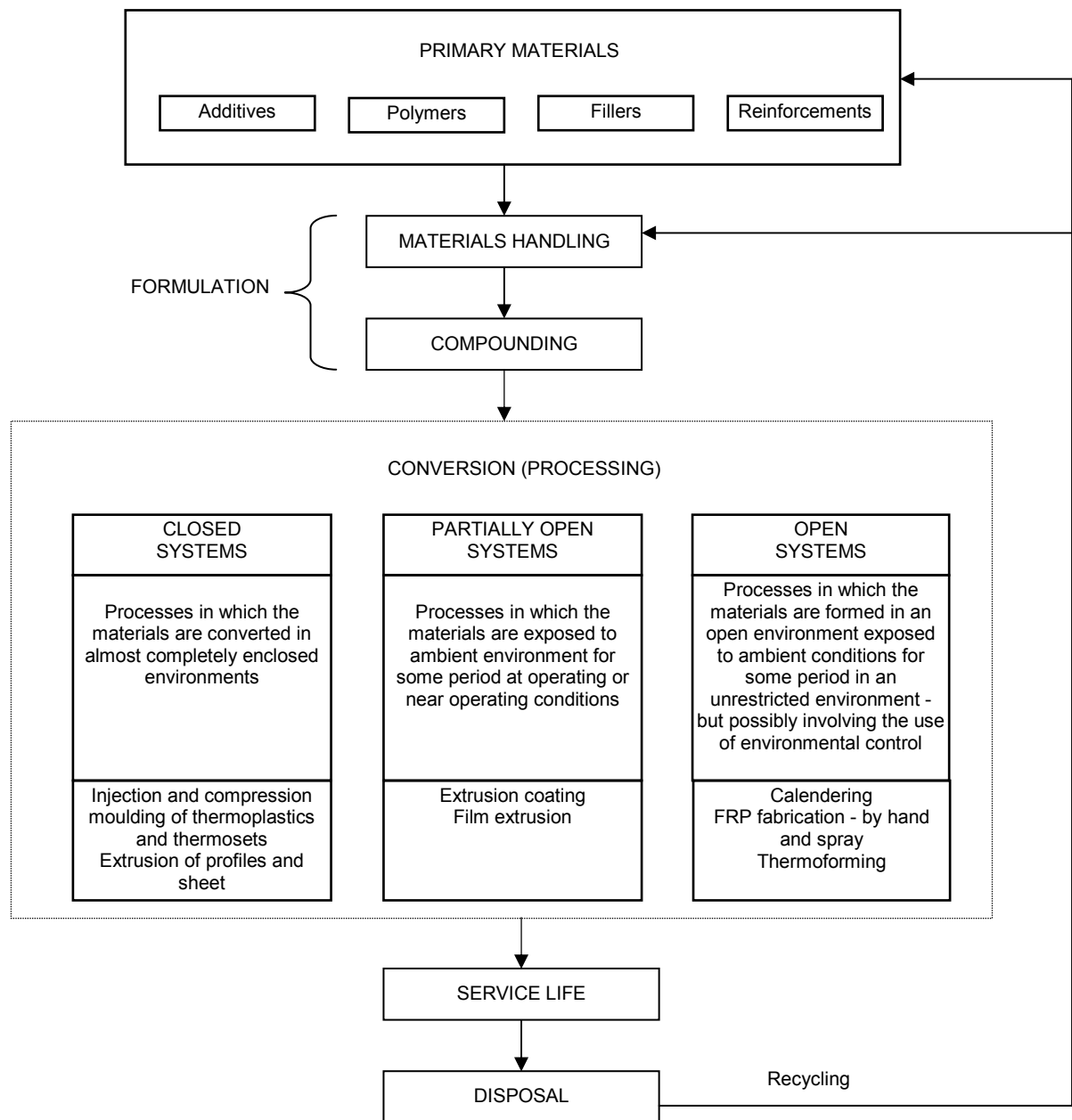
30. The fractional quantities of generic additives set out in Appendix III are technologically determined and are applicable throughout Europe. In some cases there are some differences in the *sub types* of additives which may be used in different countries. The general structure of the industry is similar in most European countries. Therefore, it is reasonable to assume that the loss factors set out in the following chapters are applicable throughout Europe in so far as the life span of the plastic artefacts are concerned.

31. Care needs to be exercised in estimating the losses on individual sites. The distribution of size of companies may differ and this may impact on estimates of quantities lost on a given site as a proportion of the total consumption of an additive in a given country. Care must also be taken in addressing the losses during ultimate disposal. Disposal practices differ from country to country and the proportions described above may not apply throughout the European Union.

3 PLASTICS PROCESSING AND USE

32. In this section the basic processes used by the plastics industry are described. In essence the activities are characterised in **Figure 3.1**. This figure maps the progress of the materials from their sources - manufacturers of polymers, additives, reinforcements etc. - through materials handling, compounding, processes which convert the materials into artefacts, their life and eventual disposal which may involve some degree of recycling.

**Figure 3.1** Plastics processing and use



33. The individual processes are described in the following sections. The processing of plastics materials involves the use of heat and pressure to melt or soften and/or cure them. In the case of some resins e.g. polyester resins, curing is carried out at ambient temperatures.

### 3.1 Raw materials' handling

34. The handling of raw materials from their arrival on site to their addition to polymers is undertaken by a variety of means. These include manual handling of bags and sacks, conveyor belts and pneumatic or pumped transfer from bulk storage vessels.

### 3.2 Compounding

35. The process of compounding during which additives are incorporated into plastics can take place either during:

- a) polymer production,
- b) a secondary process with the specific function of compounding which, as indicated above, is often undertaken by specialist companies,
- c) the final conversion process.

36. It is the second of these which dominates the compounding activity in the plastics industry.

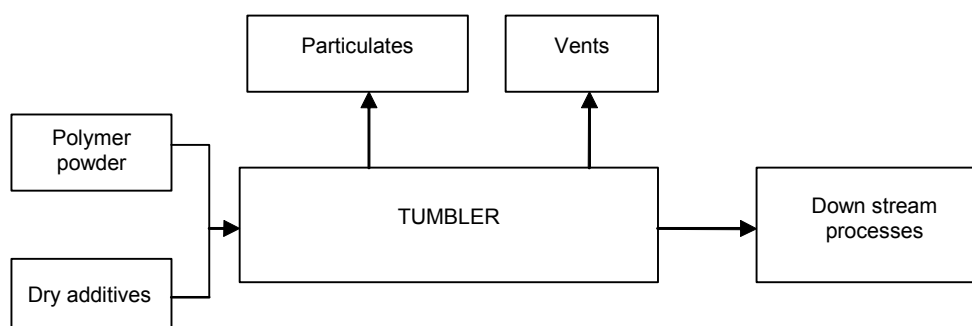
37. There are several processes for the incorporation of additives into polymers. These may be classed as closed or partially-open processes.

#### 3.2.1 Closed processes

38. **Tumbling** is used for the preblending of solids of similar particle size. In essence a closed container is rotated/tumbled.

39. This form of mixing can produce particulate and volatile emissions.

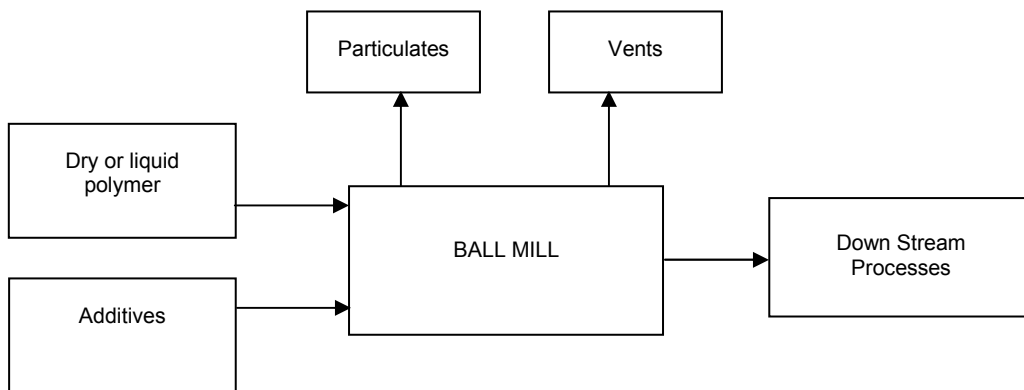
### Tumbling



40. **Ball blenders** are essentially tumble blenders with mills to enhance fine dispersion. They may be used for dry or liquid polymer systems.

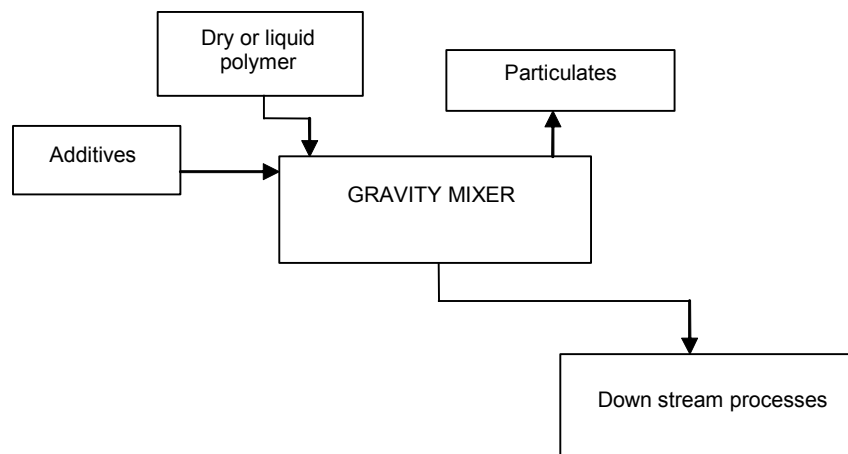
41. This form of mixing can produce particulate and volatile emissions.

**Ball Blending**



42. In **Gravity mixers** the materials are cascaded downwards through a series of baffles. Several passes are made possible by use of an elevator or auger. Particulate emissions can occur during this process.

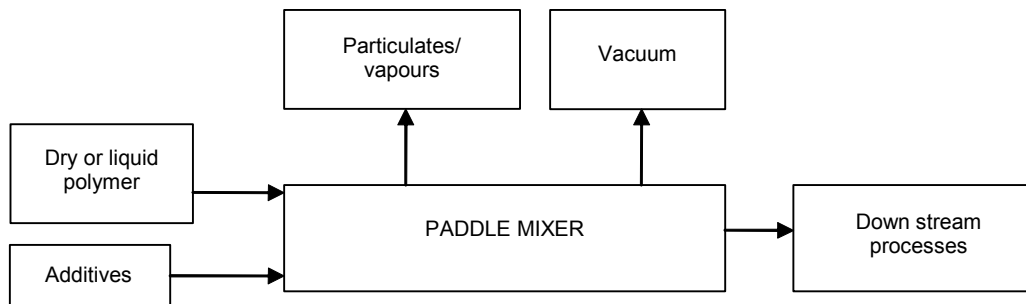
**Gravity mixer**



43. **Paddle/double arm mixers** involve the use of contra-rotating blades to give a kneading and folding action. The mixers are useful for high viscosity mastics, pastes, elastomers and dough moulding compounds based on thermosetting materials. Materials with a high filler content are often mixed by this method.

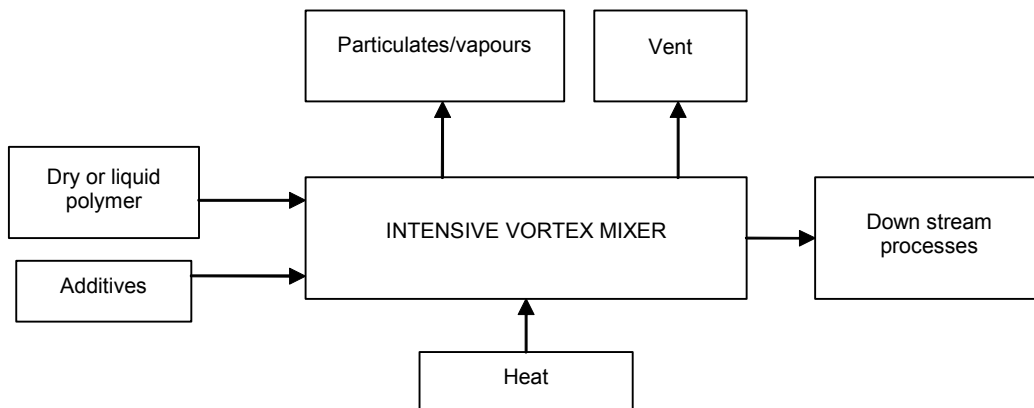
44. The process is usually enclosed but some emissions are possible at opening and closing.

### Paddle mixer



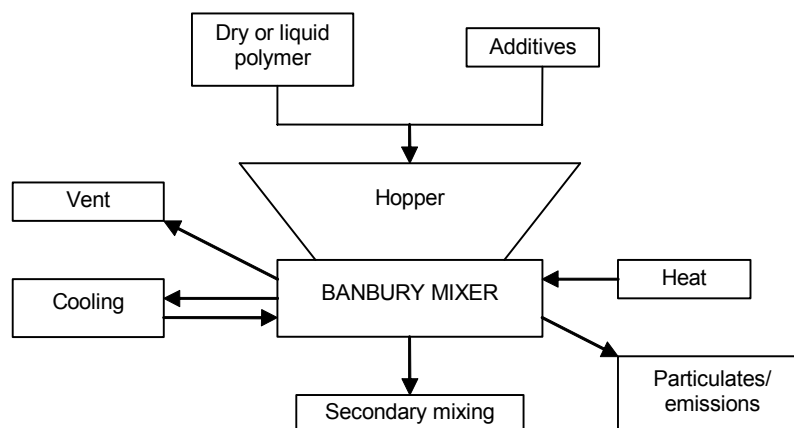
45. **Intensive vortex action mixers** use high speed stirrers to mix preheated polymers. Some emissions may arise through vents.

### Intensive vortex mixer



46. In **Banbury (type) internal mixers**, a ram presses the polymer and additives against rotor blades revolving within an enclosed chamber. This batch process is used to mix a wide range of plastics materials and is one of the basic tools for rubber compounding. Intensive shear heating is generated and can lead to degradation of materials if not controlled. Internal mixers are often used for the first of two or more compounding stages and may feed two roll mills, extruders or other internal mixers.

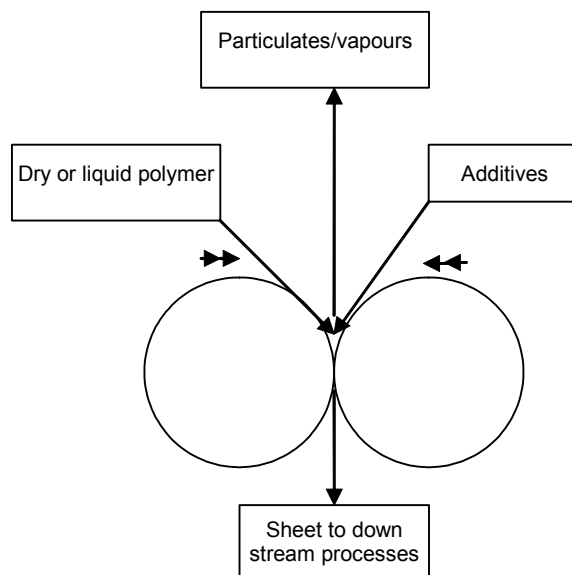
### Banbury mixer



### 3.2.2 Partially-open processes

47. In **Two roll mills**, two rollers contra-rotate at different speeds to generate a shearing action which kneads the compound. This is an open process with emissions of particulates and the shear heating can give rise to volatile additives being released.

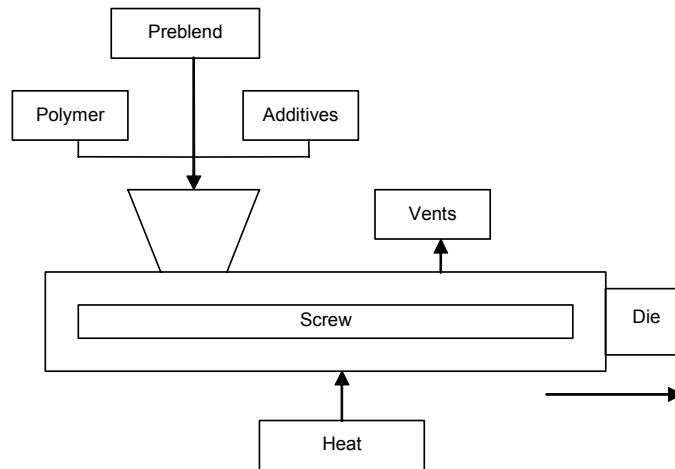
### Two roll mill



48. **Extruders.** Blends of polymer, additives and/or masterbatch are mixed either in the hopper or in tumblers and then fed into an extruder comprising one or two screws. These both shear the material and transport it through a heating regime.

49. Volatile emissions may be produced and these are vented at various points in the extruder barrel. A very wide range of polymers is compounded by this method and the resultant compound can be converted directly into an extrudate such as profile, pipe, sheet or film (see Section 3.3.1).

### Extruder mixing



## 3.3 Conversion Processes

50. There are some significant differences between the processes used to convert thermosetting and thermoplastics materials.

51. **Thermoplastics.** All thermoplastics processes involve the melting of the plastics material, forming it into a new shape and then cooling it. In several cases, melting is undertaken using the extrusion process which delivers a hot melt into a forming process which may be periodic or continuous. The individual processes may be described as closed, partially-open or open.

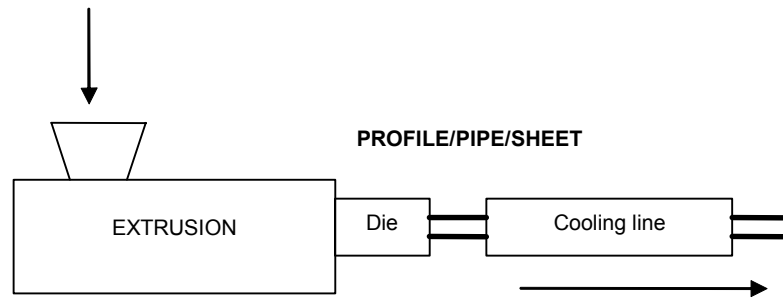
52. **Thermosetting resins.** There are fewer processes used for the conversion of thermosetting resins. After compounding, the processes are dedicated to the promotion of curing (generally by cross-linking) using heat and pressure and these are generally closed processes. However, fibre reinforced plastics products are made using open or partially-open processes such as hand lay up, spray moulding and filament winding.

### 3.3.1 Closed processes

#### 3.3.1.1 Extrusion

53. Extrusion as an extension of the compounding process (see above) may be regarded as a closed process. It is used to manufacture products such as pipe, profiles, sheet and wire coating. In these circumstances, the extrudate is quenched almost immediately after egress from the die. In other cases the process may be considered to be partially-open (see below).

**Extrusion**

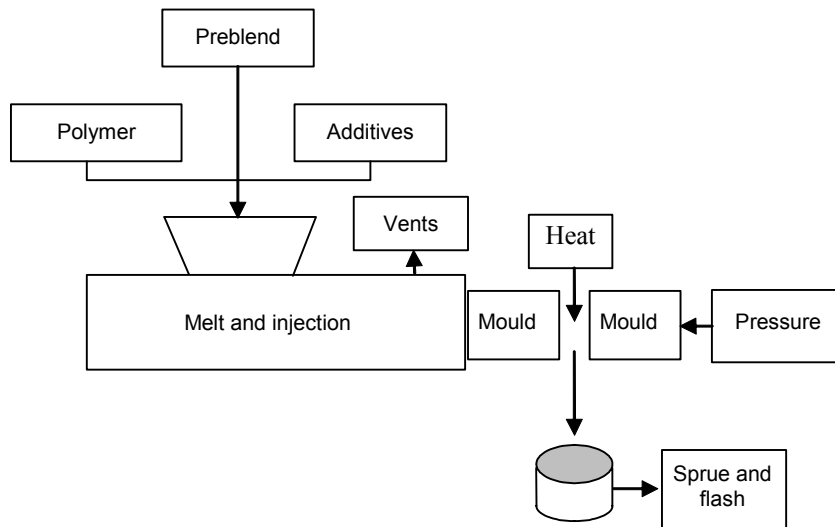


*3.3.1.2 Injection moulding*

54. Materials (polymer plus additives or masterbatch or compound) are melt plasticised - usually by extrusion; the melt is then projected into a mould where it is cooled. The product may undergo subsequent trimming for the removal of a sprue and/or flash.

55. Approximately 30% of all thermoplastics are processed by injection moulding.

**Injection moulding**

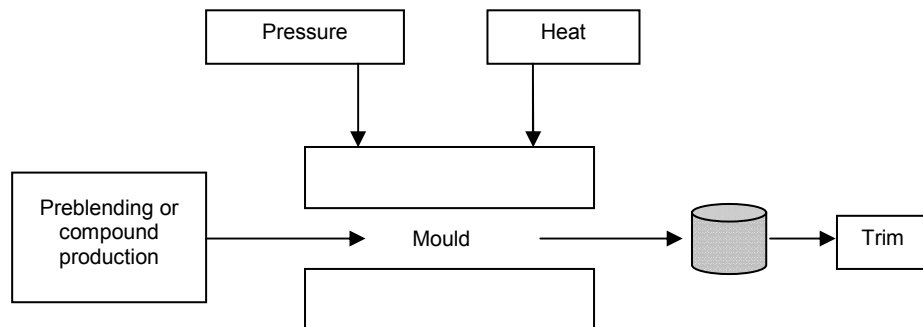


*3.3.1.3 Compression moulding*

56. Compression moulding is rarely used in the processing of thermoplastics but is the main process used for thermosetting materials. Prepared compound is inserted into a mould which is then closed and maintained under pressure during a heating cycle.

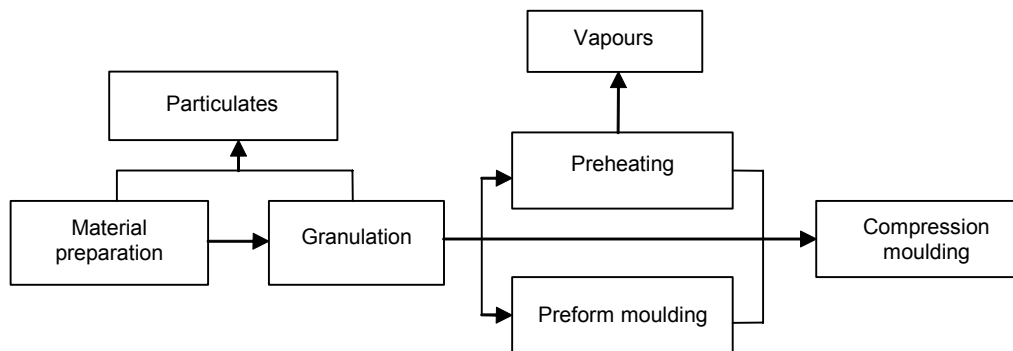


### Compression moulding for thermoplastics



57. For thermosetting materials, moulding resins, various types of compounds and composites of resins and reinforcements are used. In certain cases, preforms are prepared and preheated before being inserted into the mould. The resultant flash may be ground up and used as a filler, although the potential for this is small since thermosetting resins are not readily recyclable. The preparation of material may give rise to particulates and the preheating and moulding cycles produce emissions of volatiles.

### Compression moulding for thermosetting



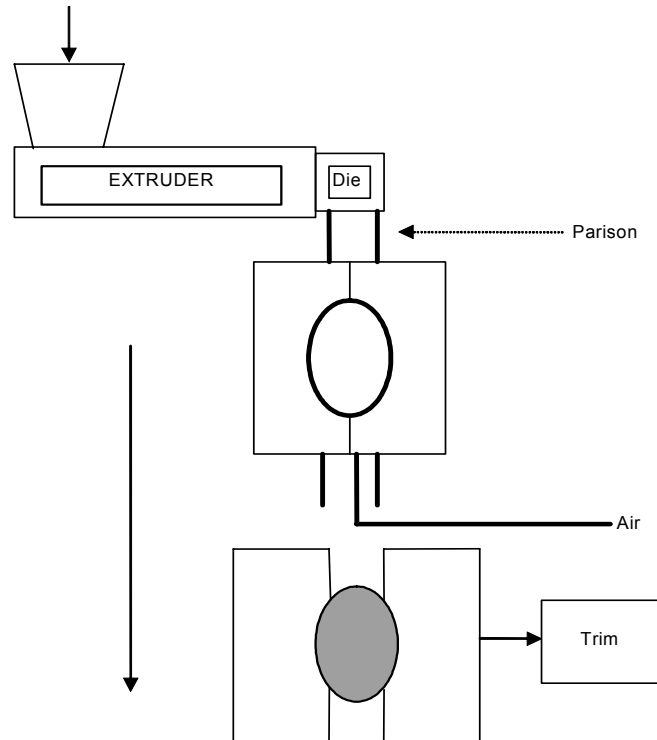
#### 3.3.1.4 Extrusion blow moulding

58. In extrusion blow moulding, an extruder delivers a tubular extrudate (parison) between two halves of a mould which are brought together around the hot extrudate, closing its top and bottom. Air is blown into the parison, forcing the polymer melt against the sides of the mould. During this stage the mould is removed from the line of extrusion to permit the extrudate to continue to flow. Once cooled the moulding is released and the mould is repositioned around the extrudate for the next cycle.

59. This is a high speed process used to manufacture a wide range of packaging bottles, containers such as petrol tanks and other thin walled articles such as vehicle air ducts.

60. Top and bottom trimmings, where the parison has been pinched by the mould, are reground.

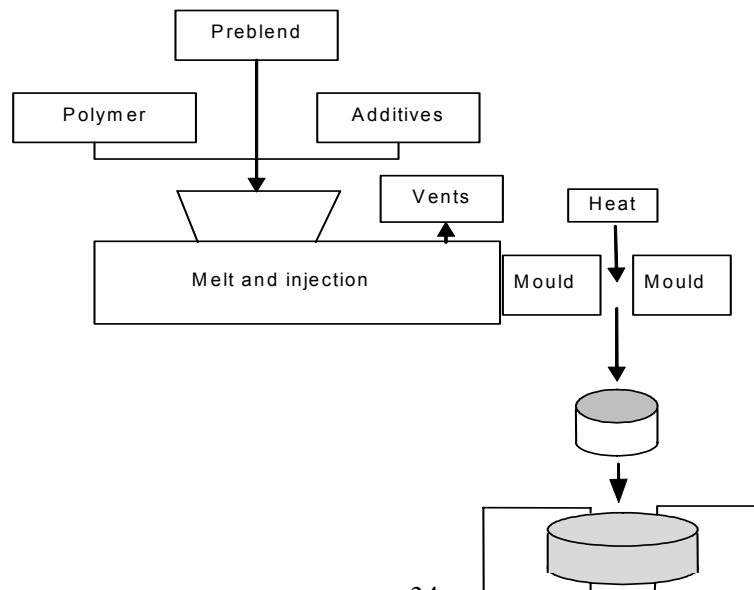
**Extrusion blow moulding**



**3.3.1.5 Injection blow moulding**

61. The parison, usually in a preform shape, is formed by injection moulding. The parison is normally transferred directly to a blow moulding unit or it may be cooled and stored as a preform. This process produces no trimmings.

**Injection blow moulding**

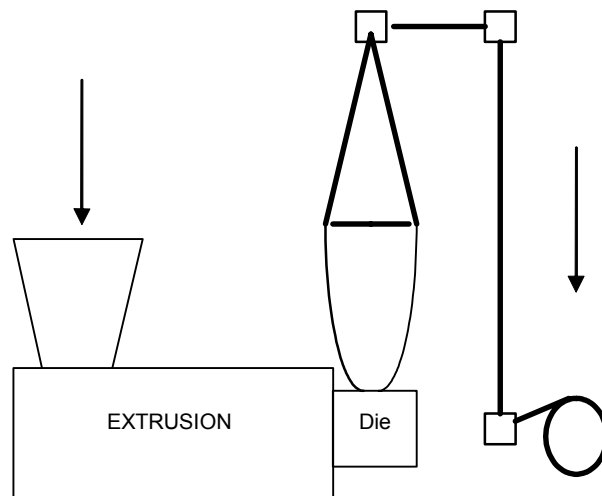


### 3.3.2 *Partially-open processes*

#### 3.3.2.1 *Film extrusion*

62. When film is cooled by travelling upwards over a vertical bubble of air before being taken up onto reels, it is known as Blown Film. Film may also be extruded through a slit die; this approaches a closed process since the extrudate is quenched immediately after it leaves the die.

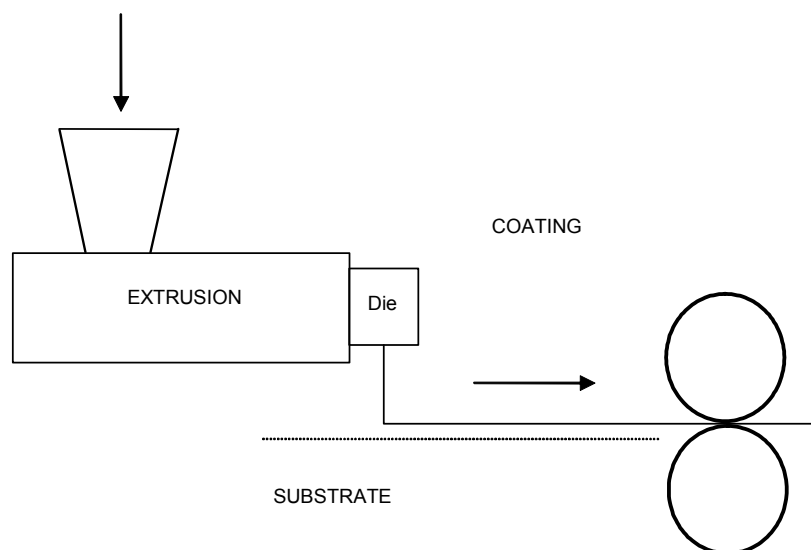
#### **Film extrusion**



#### 3.3.2.2 *Paper and textile coating*

63. In extrusion coating, a layer of film is deposited onto a substrate and the resultant composite is passed through cooling rolls.

#### **Extrusion coating**



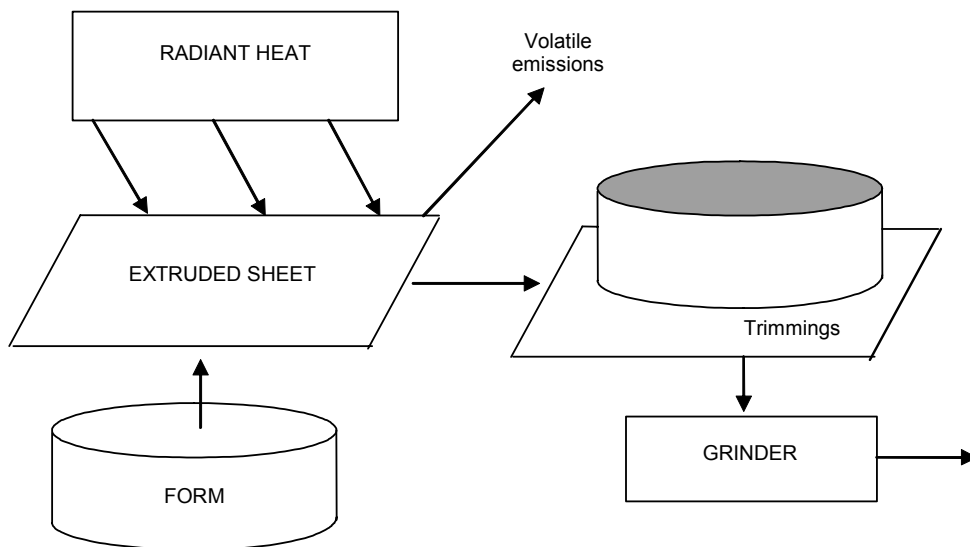
### 3.3.3 *Open processes*

#### 3.3.3.1 *Thermoforming*

64. Thermoforming involves the use of a sheet which will have been extruded on the same site or bought in. In the case of on-site extrusion the process may be continuous.

65. Plastics sheet is locked in a frame and is heated to the forming temperature when it is brought into contact with a mould whose shape it assumes. In some cases, the process is assisted by drawing the sheet on to the form using vacuum, in others, pressure is applied. Matched moulds may also be used.

#### **Thermoforming**

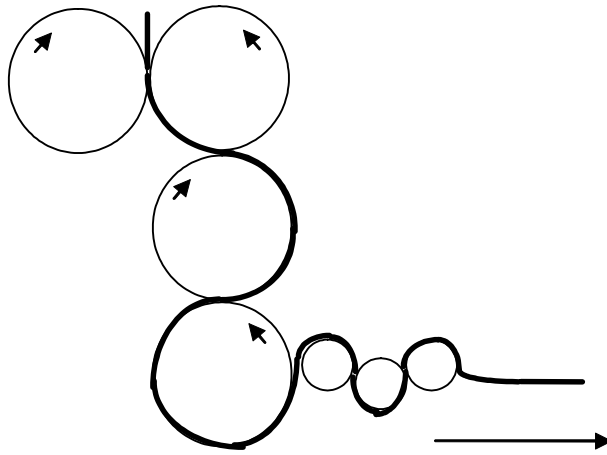


#### 3.3.3.2 *Calendering*

66. Calendering is the most complex of the operations used for the manufacture of plastics products. It commences with preblending and mixing using one of the processes described above. The resulting preheated compound is fed onto a calender which comprises a number of rolls which compress the melt into a thin layer. This may take the form of a sheet of film or may be used to coat a fabric.

67. The process is primarily used for the production of finely gauged flexible film. Releases of volatile additives and particulates may occur.

**Inverted L calender** (other configurations used)

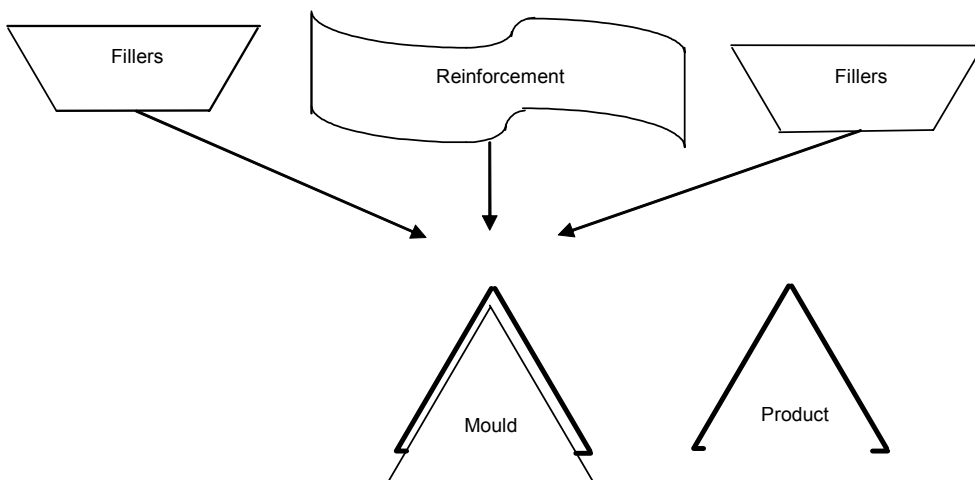


3.3.3.3 *Fibre reinforced plastic fabrication*

*Hand lay up*

68. Unsaturated polyester resins can be readily cured at ambient temperatures or with the assistance of small amounts of heat. This property enables the fabrication of large shapes (e.g. boat hulls) by depositing resin, glass and other reinforcements onto a mould and curing these in an ambient atmosphere in the presence of heat.

**Hand lay up**



*Spray techniques*

69. Spray techniques exploit the same properties but in this case the reinforcements and resin are mixed in a sprayer which then delivers the blend onto a mould - this permits a high degree of automation.

*Filament winding*

70. In filament winding the resin and reinforcements are deposited onto a rotating mandrel; the mould is subsequently introduced into an oven for heating.

**3.4 Use of processes**

71. Closed processes predominate in the plastics industry. **Table 3.1** shows that some 55% of the plastics materials converted by the industry and considered in this document are converted by closed processes; of these the dominant process is injection moulding. The majority of the materials not covered by this document are also converted by closed processes. Partially- (or semi-) open processes are the next important, converting some 35% of total consumption.

**Table 3.1 Processes by categories**

<b>Conversion process</b>	<b>Process category (%)</b>	<b>Polymer consumption (%)</b>
<b>Closed</b>		
Blow moulding	20	11
Injection moulding	37	21
Compression moulding	8	4
Rotational	2	1
Pipes	13	7
Profiles and other extrusions	10	6
Foams	10	5
<b>Total closed</b>	<b>100</b>	<b>55</b>
<b>Partially open</b>		
Wire and cable	10	3
Fibres	14	5
Extrusion coating	5	2
Film	72	26
<b>Total partially open</b>	<b>100</b>	<b>36</b>
<b>Open</b>		
Calendered	15	1
Coated fabrics	10	1
Casting	7	1
FRP fabrication	12	1
Thermoforming	52	4
Filament winding/pultrusion	5	0
<b>Total open</b>	<b>100</b>	<b>9</b>

## 4 QUANTITIES AND APPLICATIONS OF POLYMERS

### 4.1 Plastics usage by process

72. The United Kingdom plastics industry consumes some 3.5 million tonnes of polymers per annum. A breakdown of this consumption is given in Table 4.1 together with an analysis of the quantities converted by each of the process categories described in the previous Section.

**Table 4.1 Estimates of UK consumption of polymers (1994) together with breakdown by conversion processes – tonnes**

Polymer	Tonnage	Conversion Process Used		
		Closed	Partially- open	Open
<b>THERMOPLASTICS</b>				
LDPE	710,000	85,000	625,000	0
HDPE	395,000	325,000	70,000	0
PP	500,000	260,000	240,000	0
Rigid PVC	365,000	294,000	0	71,000
Flexible PVC	220,000	55,000	108,000	57,000
PS	190,000	118,000	14,000	58,000
EPS	40,000	40,000	0	0
ABS	75,000	71,000	0	4,000
PET	72,000	65,000	7,000	0
Polyamides	38,000	34,000	0	4,000
Acrylics	30,000	17,000	0	13,000
Acetals	14,000	14,000	0	0
Polycarbonate	12,000	10,000	2,000	0
Other Polymers	300,000	no data	no data	no data
<b>Total Thermoplastics</b>	<b>2,961,000</b>	<b>1,388,000</b>	<b>1,066,000</b>	<b>207,000</b>
<b>THERMOSETS</b>				
Polyurethanes	120,000	120,000	0	0
Unsat Polyesters	75,000	31,000	0	44,000
Phenolics	28,000	28,000	0	0
Aminos	70,000	70,000	0	0
Epoxy Resins	12,000	12,000	0	0
<b>Total Thermosets</b>	<b>305,000</b>	<b>261,000</b>	<b>0</b>	<b>44,000</b>
<b>TOTAL POLYMER</b>	<b>3,266,000</b>	<b>1,649,000</b>	<b>1,066,000</b>	<b>251,000</b>

Source - Industry data plus RAPRA estimates

73. The industry is expected to grow at an overall rate of one or two percentage points above GDP, although some sections of the industry will grow faster and others more slowly.

### 4.2 Applications of plastics materials

74. The polymer consumption by end use is summarised in **Table 4.2**. In general, the end use to which a plastics material is put determines the polymer used, the process by which it is converted and the type and quantity of additives used. For the majority of applications, a plastics material may be used in more than one form and this leads to the use of different additives in varying proportions as well as the use of different conversion processes. For simplicity, this document has restricted information to the main classes of polymers and the most common applications for each one.

**Table 4.2 Polymer consumption by end use**

<b>Application</b>	<b>Polymer used (%)</b>
Agriculture	9
Building and construction	14
Domestic appliances or `white goods' i.e. washing machines, fridges etc.	5
Domestic equipment or `brown goods' i.e. TVs, videos etc.	2
Electrical	5
Electronic	3
Furniture	1
Housewares	4
Marine	<1
Miscellaneous	15
Packaging	30
Sports	<1
Transport and automotive	13
<b>TOTAL</b>	<b>100</b>

75. Clearly, packaging is the dominant use of polymer, with building a second major use. It should be noted that the market for building products is highly sensitive to the state of the economy and that the current low level of consumption in the UK is attributable to the poor health of this sector of British industry. The large miscellaneous category encompasses a great number of different applications ranging from plastics coat hangers to a wide diversity of small engineering components.

76. It should also be noted that the spread of applications varies from polymer to polymer. Thus packaging accounts for some 80% of total PET use.

#### **4.3 Life expectancy of plastics**

77. In view of the diversity of applications for polymers, not all plastics products will come into the waste stream at the same stage of their lives. In **Table 4.3** estimates are given of the range of life times expected for plastics materials used for different purposes. There are currently few data on which to base more precise information.

78. The calculation for the prediction of emissions set out in Section 6 assumes an average life expectancy; where no range is given in this table, the quoted number should be used.

79. It must be stressed that these life expectancies are for products manufactured now and do not necessarily represent the life time of plastics materials produced in the past.



**Table 4.3 Life expectancy of plastics**

<b>Applications</b>	<b>Service Life (years)</b>
Agriculture	2
Building and construction	>10
Domestic appliances i.e. white goods <sup>a</sup>	5 to 10
Domestic appliances i.e. brown goods <sup>b</sup>	5 to 10
Electrical	10 to 20
Electronic	0 to 5
Furniture	5 to 10
Housewares	0 to 5
Marine	>10
Miscellaneous	0 to 10
Packaging	2
Sports	0 to 5
Transport and automotive	10 to 20

Notes: a) Examples of white goods include washing machines, fridges etc.

b) Examples of brown goods include TVs, videos etc.

Source: RAPRA estimates based on figures produced by the Association of European Polymer Makers (APME) for the life expectancy of the materials.

#### **4.4 Waste disposal practices in the plastics processing industry**

80. The industry uses little, if any, process water. Its use is predominantly for cooling equipment when it is used in closed water systems, recirculating between chillers and the processing equipment. The only other use of water, of significance in this context, is for washdown of plant surfaces.

##### **4.4.1 Additives**

81. A large proportion of the additives used in the plastics industry are expensive; many several times more than the matrix polymers. Users of such additives are therefore very careful to minimise any waste. Residues in the delivery containers generally join the general waste stream and are most likely disposed of to landfill.

82. Materials known to constitute any form of hazard are handled and disposed of in an appropriate manner. Similarly, any condensates in ducts etc. are cleaned out and disposed of professionally.

##### **4.4.2 Polymer and plastics products**

83. Wherever possible, internally generated scrap/waste is reground and reused on site in the conversion process. The regrinding process does generate some waste but this is in the form of large particles which are landfilled. Where regrinding is not possible, the scrap appears as industry waste and is usually landfilled. There are a few instances where scrap plastics materials are used on site as a fuel but this is very rare.

#### **4.5 Disposal and recycling of plastics products**

84. The situation regarding the disposal and recycling of plastics is currently in a state of flux. New legislation with respect to plastics recycling is proposed throughout the European Union which

has particular, but not exclusive, reference to plastics packaging. Consequently, the current waste streams do not necessarily reflect the future situation.

85. **Table 4.4** presents the best estimates of the main mechanisms in use for the ultimate disposal of some groups of plastics waste. Only 8% of plastics waste is recycled as plastics material. A proportion of municipal and distribution waste is burnt to generate heat, accounting for about 17% of total waste plastic. The remainder is disposed of to landfill or is incinerated. The main area for recycling of plastics waste is that generated by the plastics industry itself and from the packaging used by large distributors, e.g. supermarkets, where 50% is mechanically recovered by recycling into the plastics stream.

**Table 4.4 Mechanisms for disposal of plastics waste in the UK in the mid-1990s**

Source	% of total arising	Not recycled or recovered	Thermal recovery <sup>a</sup>	Mechanical recovery <sup>b</sup>
Municipal solid waste	72%	79%	20%	1%
Agricultural	5%	71%	0%	29%
Automotive	6%	97%	0%	3%
Construction/demolition	5%	90%	0%	10%
Large distribution and industry waste	12%	35%	20%	45%
<b>TOTAL</b>	100%	75%	17%	8%

Notes: a) Incineration to recover and use the heat generated.

b) All other forms of product recycling.

Source - Based on APME data

86. Mechanical recovery may take one of several forms but this is an evolving situation which is likely to change in the future as follows.

- a) The articles may be sold to specialist companies which clean, grind and market them as clean low grade plastics material. The material may be classified into polymer type and, at the highest level, the materials may be compounded into other polymers/plastics materials and sold as well specified materials which compete against virgin plastics.
- b) The articles may be collected by a specialist manufacturer of plastics products who, after cleaning and compounding, processes them into a particular product. Examples of this include the conversion of some waste from large distributors into plastic film and the use of spent PET bottles to produce polyester staple fibre for use as an insulating filler for clothing, duvets and pillows etc.
- c) Certain industries, notably the automotive sector, are being encouraged to take back their post consumer waste and reuse the materials within the same industry.

87. In many of these processes the thermoplastic material is essentially melted and reused. The release of additives would be expected to be similar to that which results from the conversion of plastics compounds made from virgin polymers. It is not known whether extra additives are used when recovered plastics articles are used as the feedstock for particular products.

88. In later sections, estimates are made of the possible releases of an additive during disposal by incineration and through the leaching effects of contact with water in a landfill. It is possible that, ultimately, degradation of the plastic material leads to the release of the remaining additives contained within it. A prediction whether or not this breakdown will occur cannot be made because it must

depend on the conditions in the landfill as well as the properties of the plastics material. As a result, this is not considered further in the document.

## 5 QUANTITIES OF ADDITIVES USED

89. If specific information on the amounts of additives used on representative sites is not available, then the information in this section can be used to provide an estimate.

### 5.1 Estimates of quantities of polymer used on representative sites

90. As indicated in Section 2, the industry operates on more than 4,000 sites throughout the UK. It is not possible to anticipate on which site an additive may be used or on what size of site it might be used. In order to derive some measure of the distribution of an additive's use throughout the industry, it is necessary to make the following assumptions.

- The quantity of additive used is distributed uniformly throughout the relevant processing sector. Thus, a company's use of an additive will be directly related to its size.
- The size of an individual company is directly proportional to its level of employment which is the only readily accessible index of its scale of activity.
- Notional company sizes are defined as the mid-points of the size ranges obtained from published information. This will depend on the processing sector.
- Although a company may well operate on more than one site, the available data give no indication of this. Therefore it has to be assumed that all the additives are used on one site employing all the staff in that company.

91. **Table 5.1** provides size ranges and a breakdown of the numbers of companies in each size range.

92. It must be stated here again that there is considerable uncertainty as to the scale of the industry and the distribution of processing activities within it. The estimates given in **Table 5.1** should therefore be treated as *notional*.

The values in **Table 5.1** are derived as follows.

Manpower = no of companies × middle of size range

% Total activity =  $\frac{\text{manpower for each size range within process type}}{\text{total manpower for process type}}$

Average % activity/company =  $\frac{\% \text{ total activity for size range}}{\text{no of companies in size range}}$

**Table 5.1 Distribution by size of plastics processing operations**

Number of employees	Number of companies (N)	Manpower	% Total "activity" (T) = Manpower/total manpower	Average % activity per company $T_s = T/N$
<b>Closed</b>				
0 to 50	1,500	45,000	37	0.02
51-100	700	28,000	23	0.03
101 to 250	150	21,000	17	0.12
251 to 500	50	19,000	16	0.32
501 to 1,000	10	7,500	6	0.62
<b>TOTAL</b>	<b>2,410</b>	<b>120,500</b>	<b>100</b>	
<b>Partially Open</b>				
0 to 50	139	5,200	48	0.35
51 - 100	65	3,100	29	0.44
101 to 250	15	2,100	19	1.30
251 to 500	1	400	4	3.70
<b>TOTAL</b>	<b>220</b>	<b>10,800</b>	<b>100</b>	
<b>Open</b>				
0 to 50	450	12,000	47	0.10
51-100	210	7,000	27	0.13
101 to 250	24	3,000	12	0.49
251 to 500	10	2,600	10	1.02
501 to 1,000	3	1,000	4	1.30
<b>TOTAL</b>	<b>700</b>	<b>25,600</b>	<b>100</b>	

93. For each process type the largest size range accounts for the highest percentage of the activity, and these values can be taken as the realistic worst case estimates. Thus the values are 0.62% for closed processes, 3.7% for partially open processes and 1.3% for open processes. The assumption in these calculations is that the use of each polymer is spread out over all companies, but is weighted towards the larger companies. It is not the same as the average, e.g. for closed processing the average over companies is 0.04% as against 0.62% by this method (for partially open, 0.45% vs. 3.7% and for open 0.14% vs. 1.3%). It is also assumed that all companies deal with all types of polymer. It is not clear if companies operate more than one type of process, or perhaps use both open and say partially open on the same site. For polymers where more than one type of process can be used (and the same additive used in each case) then the emissions could be combined.

94. To estimate the amount of polymer used on the site ( $Q_{\text{polymer}}$ ) using this method (Method 1):

$$Q_{\text{polymer}} = \text{tonnage of polymer} \times \text{fraction by process type} \times \text{average \% activity per company}$$

95. For example, for LDPE in closed systems:

tonnage of polymer = 710 kT (from **Table 4.1**)

fraction processed in closed system = 12% (derived from **Table 4.1**)

% activity per company for closed process = 0.62% (**Table 5.1**)

So tonnage of LDPE on a site is  $710,000 \times 0.12 \times 0.0062 = 528$  tonnes.

96. Values for the fraction of each polymer processed by each process type, derived from the values in **Table 4.1**, and the resulting tonnages of polymer used on a site are given in **Table 5.2**.

**Table 5.2 Polymer usage (by process type) in the UK and estimate usage on a site ( $Q_{\text{polymer}}$ ) by Method 1**

Polymer	Tonnage (kT)	Percentage by process type			Usage on site ( $Q_{\text{polymer}}$ ) (tonnes year <sup>-1</sup> )		
		open	partially open	closed	open	partially open	closed
LDPE	710		88	12		23,100	528
HDPE	400		14	86		2,070	2,130
Polypropylene	500		48	52		8,880	1,610
Rigid PVC	400			81	988		2,010
Flexible PVC	220	26	49	25	744	3,990	341
Polystyrene	150	31	7	62	605	389	623
Expanded polystyrene	450			100			2,790
ABS	75	8		92	78		428
PET	135	10		90	176		814
Polyamides	30	10		90	39		181
Acrylics	14	30	40	30	55	207	28
Acetals	14		10	90		52	84
Polycarbonates	12		14	86		62	69
Polyurethanes	120			100			804
Unsaturated polyesters	75	59		41	575		206
Phenolic resins	18			100			121
Amino resins	70			100			469
Epoxy resins	12			100			80

97. An alternative estimate (Method 2) of the tonnage of polymer used on a site can be made by dividing the total polymer tonnage (for all types of polymer) for each type of process by the total manpower for that process. This gives a tonnage per person (worker) per year. Multiplying this by the mid-point of the largest range for each process type gives the tonnage on a large site. These are: 10,260 tonnes year<sup>-1</sup> for closed processing, 39,250 tonnes year<sup>-1</sup> for partially open processing and 7,350 tonnes year<sup>-1</sup> for open processing (one value for all types of polymer). The assumption inherent in these estimates is that each site effectively deals with only one type of polymer. This gives much larger values than Method 1. However, some of the polymers are not used in tonnages of this scale and so this method may not be appropriate for all polymer types. Therefore Method 1 is recommended as a first stage estimate in the absence of any specific information.

98. A further factor which may be considered is the area in which the plastic containing the additive is to be used. The tables in Appendix III include a breakdown of where the plastics made from each major polymer type are used (e.g. packaging, building, white goods etc.). If the particular additive being considered is only used in plastics for a specific purpose, then the total amount of polymer used for that purpose can be estimated using the appropriate factor. This value could then be used with the value for activity to give the amount used on a site.

## 5.2 Quantities of additive used on site

99. In the previous Section, the amounts of polymer processed on representative sites were estimated. If specific information on the content of the additive in the plastic is available then this should be used to estimate the amount of additive likely to be used on one site. If specific information is not available, then Appendix III contains details of reasonable worst case values for the percentage content by weight of different additive types for each major polymer type. Appendix III also has

indications of the realistic range of additive contents. Each polymer type has a separate table in Appendix III, broken down by the process type (open, partially open, closed) and also by the areas in which the products are used relevant to the polymer (e.g. packaging, construction etc.). This latter may influence the use and content of the additive.

100. The quantity of an additive used at a site ( $Q_{\text{additive}}$ ) can be estimated as follows.

$$Q_{\text{additive}} = Q_{\text{polymer}} \times \frac{F_{\text{polymer}}}{100} \quad -1$$

Explanation of symbols:

$Q_{\text{additive}}$	= amount of additive used at a site	[tonnes.yr <sup>-1</sup> ]	
$Q_{\text{polymer}}$	= amount of polymer processed at a site	[tonnes.yr <sup>-1</sup> ]	see Table 5.2
$F_{\text{polymer}}$	= additive content of polymer by weight	[%]	see Appendix III

101. As an example, colourants are used in LDPE at 3% of polymer ( $F_{\text{polymer}} = 3\%$ ) in closed processes (**Table AIII.1**). From above (example in Section 5.1), the tonnage of LDPE on a site is 528 tonnes. Hence the amount of colourant used at a site ( $Q_{\text{additive}}$ ) is  $528 \times 3\%$ , or 16 tonnes per year.

102. It should be noted that although Appendix III gives details of reasonable worst case amounts of additives that may be used in polymers, it does not necessarily follow that all of the possible additive types indicated for a given polymer will be present in all polymers of that type. The actual amounts and combination of additive types that will be used in a given type of plastic will depend to a large extent on the final application or required properties of the final polymer. For example, not all LDPE (from the above example) will contain colourant.

## 6 INTRODUCTION TO THE MODEL

103. This Section sets out methods to predict the quantity of a particular additive which may be released during its use in the production of a plastics material, during its service life and, at the end of its life, as a result of its disposal. Some of the information required to make these predictions has already been set out in previous sections of this document.

104. Specific information about particular types of additive is given in the sections which follow. In these the operations of the industry and the fates of the materials concerned have been discussed in terms of five generic stages each of which has a generic emission factor as follows.

- Raw materials' handling  $F_{\text{handling}}$
- Compounding  $F_{\text{compounding}}$
- Conversion  $F_{\text{conversion}}$
- Service life  $F_{\text{service life}}$
- Disposal  $F_{\text{disposal}}$

105. All the emission factors relate to worst case scenarios. This is a consequence of the wide ranges in type of plastics material, the processing conditions used, the form of the product and the service conditions. Because of these variations, the concept of 'average' in this industry is meaningless.

### 6.1 Release from manufacture of plastics materials

#### 6.1.1 Selection of emission factors

106. The emission or loss factors (as a percentage of the amount of additive used) are presented in Sections 7 to 21 for the various types of additives that may be used during the manufacture of plastics. In some cases the emission factor depends on the properties of the substance. Where possible, the actual properties should be used directly, but if this is not possible, examples are given to allow the substances to be classified into groups for which a common factor can be used. The major properties considered are particle size and volatility. The particle size affects the loss of solids, and the threshold value is 40  $\mu\text{m}$ . Volatile losses can be related to the vapour pressure, ideally that at the temperature of the operation being considered. A rough classification into high, medium and low groups is given in **Table 6.1**, based on the vapour pressures at various temperatures for some additives. This classification can then be applied to other types of additives (by comparison of the vapour pressure for the additive with those given in **Table 6.1** for the various volatility groupings) and is used to select the appropriate emission factor from the following Sections. The divisions between the classes are somewhat arbitrary, and ideally each substance should be assessed individually. The basic emission factors are largely based on the behaviour of DEHP and, if possible, data on the substance of interest should be compared with that for DEHP. Further details of the basis behind the emission factors for particulates and DEHP are given in Sections 7 and 8 respectively.



**Table 6.1: Vapour pressure (VP) of plasticisers and volatility groupings used in this guidance**

Temperature (°C)	VP (hPa; 1 hPa = 0.75 mm Hg)			
	DEHA	BBP	DEHP	DIDP
20	$6.3 \times 10^{-7}$	$6.5 \times 10^{-6}$	$2.2 \times 10^{-7}$	$3.3 \times 10^{-8}$
50	$2.7 \times 10^{-5}$	$1.5 \times 10^{-4}$	$1.0 \times 10^{-5}$	$1.8 \times 10^{-6}$
100	$3.7 \times 10^{-3}$	$9.1 \times 10^{-3}$	$1.6 \times 10^{-3}$	$3.4 \times 10^{-4}$
150	0.16	0.21	0.076	0.019
200	3.1	2.5	1.6	0.46
<i>Volatility grouping</i>	<i>high</i>	<i>high</i>	<i>medium</i>	<i>low</i>

In some sections of this document a broad distinction is made between “inorganic” and “organic” additives for the purposes of estimating releases. This distinction is related to the properties of the additive in relation to the polymer. Additives which are notionally soluble in the polymer and potentially volatile are referred to as "organic" and those which are insoluble in the polymer and non-volatile are referred to as "inorganic". These descriptions are not intended to reflect the chemical composition of the additive as organic or inorganic in the classical sense. The decision as to which description is the more appropriate should be made on the basis of the properties of the specific additive and the polymer concerned.

### 6.1.2 Materials handling

107. The emission factors for materials handling ( $F_{\text{handling}}$ ) are given in Sections 7 to 21 for the various additive types. Some of the losses are of powders. In this case some of the loss is likely to be initially to the atmosphere (as dust), but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Therefore, as a worst case it could be assumed that all this loss will eventually be released to waste water. Material remaining in sacks can be assumed to go to solid waste, presumably landfill.

### 6.1.3 Compounding

108. The emission factors for compounding ( $F_{\text{compounding}}$ ) are shown in Sections 7 to 21 for the various additive types. Some of the losses are of powders. As was the case with materials handling, some of the loss is likely to be initially to the atmosphere (as dust), but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Therefore, as a worst case it could be assumed that all this loss will eventually be released to waste water.

109. Volatile losses are initially to the atmosphere. However, the processes involve elevated temperatures and subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This approach has been used to give the suggested values for  $F_{\text{compounding, air}}$  and  $F_{\text{compounding, water}}$  in Sections 7 to 21.

### 6.1.4 Conversion

110. The emission factors for conversion ( $F_{\text{conversion}}$ ) are shown in Sections 7 to 21. Some of the losses are of particulates. As was the case with materials handling, some of the loss is likely to be initially to the atmosphere (as dust), but ultimately all particulates will be removed or settle and losses

will be to solid waste or to waste water as a result of wash down. Therefore, as a worst case it could be assumed that all this loss will eventually be released to waste water.

111. Volatile losses are initially losses to the atmosphere. However, the processes involve elevated temperatures and subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This approach has been used to give the suggested values for  $F_{\text{conversion, air}}$  and  $F_{\text{conversion, water}}$  reported in Sections 7 to 21.

### 6.1.5 Overall emission factor for formulation (compounding) and processing (conversion)

112. As indicated earlier there are some companies that specialise in the compounding (formulation) of plastic and some companies that specialise in the conversion (processing) of plastic, whereas other companies undertake both compounding and conversion (combined formulation/processing) of polymers at the same site. Therefore, it is necessary to consider these three possibilities in the emission scenarios as follows.

Formulation (compounding) only site:

$$F_{\text{formulation, air}} = F_{\text{handling, air}} + F_{\text{compounding, air}} \quad -2$$

$$F_{\text{formulation, water}} = F_{\text{handling, water}} + F_{\text{compounding, water}} \quad -3$$

Processing (conversion) only site:

$$F_{\text{processing, air}} = F_{\text{conversion, air}} \quad -4$$

$$F_{\text{processing, water}} = F_{\text{conversion, water}} \quad -5$$

Combined formulation/processing site:

$$F_{\text{form/proc, air}} = F_{\text{handling, air}} + F_{\text{compounding, air}} + F_{\text{conversion, air}} \quad -6$$

$$F_{\text{form/proc, water}} = F_{\text{handling, water}} + F_{\text{compounding, water}} + F_{\text{conversion, water}} \quad -7$$

Explanation of symbols:

$F_{\text{handling, air}}$	= emission factor to air for materials handling	[%]	see Section 7-21
$F_{\text{handling, water}}$	= emission factor to water for materials handling	[%]	see Section 7-21
$F_{\text{compounding, air}}$	= emission factor to air for compounding	[%]	see Section 7-21
$F_{\text{compounding, water}}$	= emission factor to water for compounding	[%]	see Section 7-21
$F_{\text{conversion, air}}$	= emission factor to air for conversion	[%]	see Section 7-21
$F_{\text{conversion, water}}$	= emission factor to water for conversion	[%]	see Section 7-21
$F_{\text{formulation, air}}$	= emission factor to air for formulation	[%]	
$F_{\text{formulation, water}}$	= emission factor to water for formulation	[%]	
$F_{\text{processing, air}}$	= emission factor to air for processing	[%]	
$F_{\text{processing, water}}$	= emission factor to water for processing	[%]	
$F_{\text{form/proc, air}}$	= emission factor to air for combined formulation and processing	[%]	
$F_{\text{form/proc, water}}$	= emission factor to water for combined formulation and processing	[%]	

### 6.1.6 Estimated emissions from formulation (compounding) and processing (conversion)

113. The emission on an annual basis resulting from manufacture (E<sub>local</sub>) for each lifecycle stage can be obtained from these emission factors using the following equations.

$$E_{\text{local}, i, \text{air}} = \frac{F_{i, \text{air}}}{100} \times Q_{\text{additive}} \times 1000 \quad -8$$

$$E_{\text{local}, i, \text{water}} = \frac{F_{i, \text{water}}}{100} \times Q_{\text{additive}} \times 1000 \quad -9$$

Explanation of symbols:

$E_{\text{local}, i, \text{air}}$	= local emission to air from lifecycle stage i	[kg.yr <sup>-1</sup> ]	
$E_{\text{local}, i, \text{water}}$	= local emission to water from lifecycle stage i	[kg.yr <sup>-1</sup> ]	
$F_{i, \text{air}}$	= emission factor to air for lifecycle stage i	[%]	equation 2,4 or 6
$F_{i, \text{water}}$	= emission factor to water for lifecycle stage i	[%]	equation 3, 5 or 7
$i$	= formulation, processing or formulation/processing		
$Q_{\text{additive}}$	= amount of additive used at a site	[tonnes.yr <sup>-1</sup> ]	equation 1

114. If the number of days of emission (T<sub>emission</sub>) for the process are known, the local emissions can also be estimated on a daily basis. Alternatively, Table B3.9 of Appendix I of the TGD can be used to estimate T<sub>emission</sub> for this purpose. The local emission can also be estimated separately for each stage of materials handling, compounding and conversion. This is shown in the examples in Section 6.3.

115. For new substances, the notifier will be able to provide information on the polymer, the application of the resulting plastics material and the type of conversion process which is likely to be used. For existing substances, similar information may be available. If not, Appendix III includes detailed tables which identify values to use for all the classes of polymer, applications and the main groups of conversion processes set out in this document. Information on the identity of the polymer, application and process is also required in order to choose the appropriate emission factors (F<sub>i, water</sub> and F<sub>i, air</sub>) for the additive from the following Sections 7 - 21.

116. The total EU wide emission from formulation (compounding) and processing (conversion) lifecycle stages can be estimated from:

$$\text{RELEASE}_{\text{tot polymer, form/proc, air}} = \frac{F_{\text{form/proc, air}}}{100} \times Q_{\text{tot polymer}} \times 1000 \quad -10$$

$$\text{RELEASE}_{\text{tot polymer, form/proc, water}} = \frac{F_{\text{form/proc, water}}}{100} \times Q_{\text{tot polymer}} \times 1000 \quad -11$$

Explanation of symbols:

$\text{RELEASE}_{\text{tot polymer, form/proc, air}}$	= total emission to air from the formulation and processing lifecycle stages of a polymer	[kg.yr <sup>-1</sup> ]	
$\text{RELEASE}_{\text{tot polymer, form/proc, water}}$	= total emission to water from the formulation and processing lifecycle stages of a polymer	[kg.yr <sup>-1</sup> ]	
$F_{\text{form/proc, air}}$	= emission factor to air for the formulation and processing lifecycle stages	[%]	equation 6
$F_{\text{form/proc, water}}$	= emission factor to water for formulation and processing lifecycle stages	[%]	equation 7
$Q_{\text{tot polymer}}$	= total amount of additive used in a polymer type in the EU each year	[tonnes.yr <sup>-1</sup> ]	

## 6.2 Release from use (service life) and disposal of plastics materials

### 6.2.1 Service life

117. Some additives are destroyed or entirely released during the manufacturing process. For those which are not, estimates can be made of the quantities of the additive which will be released to the environment over the service life of the polymer product. Unlike the emissions from manufacture, these are likely to be diffuse emissions, and so need to be calculated for an appropriate scale.

118. Loss of additives over the service life of polymers can be considered to occur through volatilisation to air and leaching to water. The use of polymers is widely dispersed and so the service life emissions are considered on a regional level rather than a local level. The emission factors over the service life ( $F_{\text{service life}}$ ) are given in Section 7 to 21 for the various additive types. Some of the emission factors also include particulates caused by abrasion/degradation of the plastic. Ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Therefore, as a worst case it could be assumed that all this loss will eventually be released to water. Some of the emission factors also depend on the service life of the plastic. Table 4.3 gives values for the service lives of plastics for various applications.

119. The yearly emissions of additives during the service life of polymers can be estimated from the following equations:

$$\text{RELEASE}_{\text{tot\_STST}}_{\text{polymer, air}} = \frac{F_{\text{servicelife,air}}}{100} \times Q_{\text{tot}}_{\text{polymer}} \times 1000 \quad -12$$

$$\text{RELEASE}_{\text{tot\_STST}}_{\text{polymer, water}} = \frac{F_{\text{servicelife,water}}}{100} \times Q_{\text{tot}}_{\text{polymer}} \times 1000 \quad -13$$

#### Explanation of symbols:

$\text{RELEASE}_{\text{tot\_STST}}_{\text{polymer, air}}$	= annual total release of the substance to air over the service life of the product at steady state	[kg.yr <sup>-1</sup> ]	
$\text{RELEASE}_{\text{tot\_STST}}_{\text{polymer, water}}$	= annual total release of the substance to water over the service life of the product at steady state	[kg.yr <sup>-1</sup> ]	
$F_{\text{service life, air}}$	= emission factor to air over service life of the polymer product	[%]	Section 7-21 or Appendix IV
$F_{\text{service life, water}}$	= emission factor to water over service life of the polymer product	[%]	Section 7-21
$Q_{\text{tot}}_{\text{polymer}}$	= annual total input of the substance into the polymer product	[tonnes.yr <sup>-1</sup> ]	

120. An alternative method of estimating the emission from articles over their service life is to assume that the emission is directly proportional to the surface area of the product exposed to water (leaching) or air (volatilisation). Such an approach was taken in the risk assessment of several “phthalate” plasticisers for PVC. **Table 6.2** outlines the annual surface area (i.e. the surface area for the PVC products produced each year) for various plasticised PVC products. These figures formed the basis of the approach taken with the phthalate plasticisers. Such an approach needs area emission

factors ( $Emission_{area}$ ) to be available on a  $mg\ m^{-2}\ year^{-1}$  basis. If such an emission factor is known for the substance of interest then the annual emissions of the substance, taking into account the service life of the product, can be estimated as follows.

$$RELEASE_{tot\_STST\_polymer,air} = \frac{Emission_{area,air} \times Area_{polymer} \times T_{service\ polymer}}{1 \times 10^6} \quad -14$$

$$RELEASE_{tot\_STST\_polymer,water} = \frac{Emission_{area,water} \times Area_{polymer} \times T_{service\ polymer}}{1 \times 10^6} \quad -15$$

#### Explanation of symbols:

$RELEASE_{tot\_STST\_polymer,air}$	= annual total release to air of the substance over the service life of the product at steady state	[kg.yr <sup>-1</sup> ]	
$RELEASE_{tot\_STST\_polymer,water}$	= annual total release to water of the substance over the service life of the product at steady state	[kg.yr <sup>-1</sup> ] [mg.m <sup>-2</sup> .yr <sup>-1</sup> ]	
$Emission_{area,air}$	= annual emission factor to air on an area basis	[mg.m <sup>-2</sup> .yr <sup>-1</sup> ]	Table 6.2
$Emission_{area,water}$	= annual emission factor to water on an area basis	[m <sup>2</sup> .yr <sup>-1</sup> ]	Table 4.3 and 6.2
AREA	= annual emitting surface area	[yr]	
$T_{service\ polymer}$	= service life of product		

121. The above equations assume that the quantities of additive lost during manufacture are negligible. If this is not so, then the losses in use need to be corrected for the earlier losses.

122. It should be noted that if an additive is used in more than one type of polymer product then a total release at steady state should be estimated for each product type.

**Table 6.2: Estimated annual emitting surface areas of plasticised PVC**

PVC Application	Estimated annual emitting surface area (Area)	Service life ( $T_{service}$ )
Indoor applications		
PVC flooring	$2.3 \times 10^8\ m^2\ year^{-1}$	20 years
Vinyl wall covering	$4 \times 10^8\ m^2\ year^{-1}$	7 years
Coated products, film and sheet		7 years
Cable		30 years
Hose and profile		
Outdoor applications		
Car undercoating	$7,262,200\ m^2\ year^{-1}$	12 years
Roofing material	$1,037,500\ m^2\ year^{-1}$	20 years
Coal coating	$51,872,500\ m^2\ year^{-1}$	10 years
Fabric coating	$43,572,900\ m^2\ year^{-1}$	10 years
Cable and wires (above ground)	$4,149,800\ m^2\ year^{-1}$	30 years
Cable and wires (buried)	$16,599,200\ m^2\ year^{-1}$	30 years
Hoses and profiles	$3,112,400\ m^2\ year^{-1}$	10 years
Shoe soles	$6,171,800\ m^2\ year^{-1}$	5 years

Source: draft ESR risk assessment for diethylhexyl phthalate, available from <http://ecb.jrc.it/esis/>

123. The methods given in equations 12, 13, 14 and 15 take into account that for any given year, the total amount of additive present in plastic products that have service lives >1 year will be related to the actual service life, and will be greater than the total annual input of the additive into new polymeric products. Thus, using an emission factor based on the total release over the service life of the plastic with the annual tonnage of the additive used in the plastic, gives an annual “steady state” release figure from this source.

### 6.2.2 Disposal

124. Losses from polymers at disposal can be considered as widely dispersed and so are considered on a regional level rather than a local level. The emission factors at disposal are shown given in Sections 7 to 21.

125. The situation regarding the disposal and recycling of plastics is currently in a state of flux. New legislation with respect to plastics recycling is proposed throughout the European Union which has particular, but not exclusive, reference to plastics packaging. Consequently the current waste streams do not necessarily reflect the future situation. **Table 4.4** presents the current estimates for the main mechanisms used for ultimate disposal of some groups of plastics waste in the United Kingdom and shows that the majority of used and discarded plastics materials are currently disposed of to landfill. A small proportion is incinerated, either in municipal facilities or on sites operated by the plastics industry. Information on the fate of each additive under these conditions is given in Sections 7 to 21 together with loss factors where appropriate.

126. The emissions of an additive from disposal of a polymer product can be estimated from the following equations:

$$Q_{\text{remain}}_{\text{polymer}} = (Q_{\text{tot}}_{\text{polymer}} \times 1000) - (RELEASE_{\text{tot}}_{\text{polymer, form/proc, air}} + RELEASE_{\text{tot}}_{\text{polymer, form/proc, water}}) - (RELEASE_{\text{tot\_STST}}_{\text{polymer, air}} + RELEASE_{\text{tot\_STST}}_{\text{polymer, water}}) \quad -16$$

$$RELEASE_{\text{disposal}}_{\text{polymer, air}} = F_{\text{disposal, air}} \times Q_{\text{remain}}_{\text{polymer}} \quad -17$$

$$RELEASE_{\text{disposal}}_{\text{polymer, water}} = F_{\text{disposal, water}} \times Q_{\text{remain}}_{\text{polymer}} \quad -18$$

#### Explanation of symbols:

$RELEASE_{\text{disposal}}_{\text{polymer, air}}$	= annual release to air of the substance at disposal of the polymer	[kg.yr <sup>-1</sup> ]	
$RELEASE_{\text{disposal}}_{\text{polymer, water}}$	= annual release to water of the substance at disposal of the polymer	[kg.yr <sup>-1</sup> ]	
$RELEASE_{\text{tot\_STST}}_{\text{polymer, air}}$	= annual total release to air of the substance over the service life of the product at steady state	[kg.yr <sup>-1</sup> ]	equation 12 or 14
$RELEASE_{\text{tot\_STST}}_{\text{polymer, water}}$	= annual total release to water of the substance over the service life of the product at steady state	[kg.yr <sup>-1</sup> ]	equation 13 or 15
$RELEASE_{\text{tot}}_{\text{polymer, form/proc, air}}$	= total emission to air from the formulation and processing lifecycle stages of a polymer	[kg.yr <sup>-1</sup> ]	equation 10
$RELEASE_{\text{tot}}_{\text{polymer, form/proc, water}}$	= total emission to water from the formulation and processing lifecycle stages of a polymer	[kg.yr <sup>-1</sup> ]	equation 11
	= emission factor for release to air at disposal	[%]	Section 7-21
		[%]	Section 7-21

---

$F_{\text{disposal, air}}$	= emission factor for release to water at disposal	
$F_{\text{disposal, water}}$	= annual total input of the substance into the polymer product	[tonnes.yr <sup>-1</sup> ]
$Q_{\text{tot polymer}}$	= annual amount of additive disposed of in polymer	
$Q_{\text{remain polymer}}$		[tonnes.yr <sup>-1</sup> ]

---

127. It should be noted that if an additive is used in more than one type of polymer product then a total release at steady state should be estimated for each product type.

### 6.2.3 Other sources of release

128. Releases to the environment of additive in polymeric particulates caused by wear/weathering of polymers could also occur over the service life and at disposal of a product. These releases are not considered further here.

## 6.3 Example calculations

### 6.3.1 Example 1

129. An inorganic anti-static agent has been developed to be used in HDPE in the packaging sector. The additive has a particle size <40 µm, is converted in closed processes and the total amount used in EU ( $Q_{\text{tot polymer}} = 100$  tonnes/year. What are the worst case losses to the environment?

#### 6.3.1.1 Emission factors

130. The following emission factors are appropriate for this substance.

$F_{\text{handling, water}}$	= 0.6% to solid waste/water (assume all goes to water)	
	(+ 1% to solid waste (residue in bags)) - Section 14.2.1	
$F_{\text{compounding, water}}$	= 0.05% to solid waste/water (assume all goes to water)	-
Section 14.2.2		
$F_{\text{conversion, water}}$	= 2.5% to solid waste/water for grinding/machining or 0.01%	
	to solid waste/water for other operations (assume all goes to water) – Section 14.2.3	
$F_{\text{service life, water}}$	= 0.01% to solid waste/water (assume all goes to water)	
- Section 14.2.4		
$F_{\text{disposal, air}}$	= 0% from incineration – Section 14.2.5	
$F_{\text{disposal, water}}$	= not known	

6.3.1.2 *Emission estimates*

*Local emissions (emissions from a plastics' processing site)*

131. From **Table 5.2**, the amount of HDPE processed at a site ( $Q_{\text{polymer}}$ ) using closed systems is 2,130 tonnes/year. From **Table III.2** in the Appendix III, the amount of anti-static agent used ( $F_{\text{polymer}}$ ) in HDPE is 0.3% by weight.

132. Amount of anti-static agent used at the site ( $Q_{\text{additive}}$ ) =  $0.3 \times 2,130 = 6.39$  tonnes/year

133. Losses at the site can occur from materials handling, compounding and conversion. Applying the above emission factors for these stages to the amount of anti-static agent used at the site ( $Q_{\text{additive}} = 6.39$  tonnes/year), the following emission estimates can be obtained.

Materials handling = 38.3 kg/year to water and 63.9 kg/year to solid waste  
 Compounding = 3.2 kg/year to water  
 Conversion = 159.8 kg/year or 0.64 kg/year to water

134. The total loss of the anti-static agent from the site is therefore 201.3 kg/year to water and 63.9 kg/year to solid waste assuming that the conversion stage involves grinding/machining or 42.1 kg/year to water and 63.9 kg/year to solid waste assuming the conversion stage involves operations other than grinding/machining.

*Total EU and regional emission*

135. The total EU emission is derived from the sum of the emissions from the various lifecycle stages based on the total amount of the anti-static agent used in the EU. The regional emission is taken as 10% of this total EU emission. In this example, the total amount of the anti-static agent used in the EU ( $Q_{\text{tot polymer}}$ ) is taken as 100 tonnes/year. The following emission estimates are obtained using the above emission factors.

		<u>Total EU emission</u>	<u>Regional emission</u>	
Formulation	{	Materials handling	600 kg/year to water 1,000 kg/year to solid waste	60 kg/year to waste 100 kg/year to solid waste
		Compounding	50 kg/year to water	5 kg/year to water
Processing	{	Conversion	2,500 kg/year or 10 kg year to water	250 kg/year or 1 kg/year to water
		Service life	10 kg/year to water	1 kg/year to water
		Disposal	amount in leachate not known	amount in leachate not known

136. The estimate for disposal could assume that all the HDPE containing the additive is disposed of to landfill. From **Table 4.4**, an average of 75% of all plastics used in the applications listed is disposed of by either landfill or incineration, but the actual split between the two modes of disposal for packaging is unknown.

6.3.2 *Example 2*

137. Plasticiser X is widely used in flexible PVC applications for indoor use. The additive is a liquid with a vapour pressure of  $1 \times 10^{-4}$  hPa at 100°C, is dry blended, is converted to form profiles by



extrusion and the total amount used in the EU ( $Q_{\text{tot,polymer}} = 10,000$  tonnes/year). What are worst case losses to the environment?

#### 6.3.2.1 Emission factors

138. Comparing the vapour pressure with that given in **Table 6.1**, the substance can be considered to be in the low volatility grouping.

139. The following emission factors are appropriate for this substance.

$F_{\text{handling, water}}$	= 0.01% to liquid waste (water) – Section 8.2.1
$F_{\text{compounding,air}}$	= 0.001% volatile loss – Section 8.2.2
$F_{\text{compounding, water}}$	= 0.001% - Section 8.2.2
$F_{\text{conversion, air}}$	= 0.001% volatile loss – Section 8.2.3
$F_{\text{conversion, water}}$	= 0.001% - Section 8.2.3
$F_{\text{service life, air}}$	= 0.05% - Section 8.2.4
$F_{\text{service life, water}}$	= 0.05% - Section 8.2.4
$F_{\text{disposal, air}}$	= 0% from incineration – Section 8.2.5
$F_{\text{disposal, water}}$	= not known

#### 6.3.2.2 Emission estimates

##### *Local emissions (emissions from a plastics' processing site)*

140. From **Table 5.2**, the amount of flexible PVC processed at a site ( $Q_{\text{polymer}}$ ) using closed systems (e.g. extrusion of profiles: see Figure 1) is 744 tonnes/year. From **Table AIII.5** in the Appendix III, the amount of plasticiser used in flexible PVC is 30-50% by weight. In this example, a figure of 40% is used.

$$\text{Amount of anti-static agent used at the site } (Q_{\text{additive}}) = \frac{40 \times 744}{100} = 298 \text{ tonnes/year}$$

141. Losses at the site can occur from materials handling, compounding and conversion. Applying the above values for the emission factors for these stages to the amount of plasticiser used at the site ( $Q_{\text{additive}} = 298$  tonnes/year), the following emission estimates can be obtained.

Materials handling	= 29.8 kg/year to water
Compounding	= 2.98 kg/year to water and 2.98 kg/year to air
Conversion	= 2.98 kg/year to water and 2.98 kg/year to air

142. The total loss of the plasticiser from the site is therefore 35.76 kg/year to water and 5.96 kg/year to air.

##### *Total EU and regional emission*

143. The total EU emission is derived from the sum of the emissions from the various lifecycle stages based on the total amount of the plasticiser used in the EU. The regional emission is taken as 10% of this total EU emission. In this example, the total amount of the plasticiser used in the EU ( $Q_{\text{tot,polymer}}$ ) is taken as 10,000 tonnes/year. The following emission estimates are obtained using the above emission factors.

		<u>Total EU emission</u>	<u>Regional emission</u>	
Formulation	{	Materials handling	1,000 kg/year to water	100 kg/year to waste
		Compounding	100 kg/year to water 100 kg/year to air	10 kg/year to water 10 kg/year to air
Processing	{	Conversion	100 kg/year to water 100 kg year to air	10 kg/year to water 10 kg/year to air
		Service life	5,000 kg/year to water 5,000 kg/year to air	500 kg/year to water 500 kg/year to air
		Disposal	amount in leachate not known	amount in leachate not known

144. The estimate for disposal could assume that all the flexible PVC containing the additive is disposed of to landfill. PVC will be disposed of by either landfill or incineration, but the actual split between the two modes of disposal is unknown.

## 7 FILLERS

### 7.1 General description

145. Fillers are solids which are incorporated into polymers but which remain as a separate phase within the mix. In general terms, there are essentially two types of filler - powders and fibres.

146. Powdered fillers for plastics may be expected to be of high surface area (small particle size) if gross differences in surface polarity are not to impair interfacial wetting properties. Special surface treatments may help to offset such problems but some dimensional constraints will always remain. Thus in particulate terms, coarse materials are unlikely to be satisfactory as fillers, and untreated powders may have particle sizes of one micron or less.

147. Continuous fibres can be woven into mats which are then cut to size, impregnated with a thermosetting resin and subsequently moulded at ambient or slightly elevated temperatures. Recognising the distinctions between powders and fibres helps to define emission behaviour, although the distinctions are not mutually exclusive. In the case of particulate fillers, the primary factor determining emissions is particle size. In the case of discontinuous fibres the determining factor is the shape of the fibre.

#### 7.1.1 Raw materials handling

##### 7.1.1.1 Particulate fillers

148. The fact that particulate fillers are ideally solids of high surface area governs their characteristics on handling. Firstly, they are likely to be handled in sacks or bags and some losses due to wear and tear are always possible. No figures are available but the loss here is estimated as 0.1%. This loss is independent of the size of the particle.

149. Secondly, there are problems of flow due to the presence of attractive forces between the individual particles. Such forces may have several origins (mechanical interlocking, interfacial and capillary forces between adsorbed layers, etc) and for the finest particles, even van der Waals forces can cause significant interaction.

150. Stanley-Wood **(1)** has presented theoretical data to show that such attractive forces become significant for particles associated with adsorbed water when diameters are less than 50 microns ( $\mu\text{m}$ ) and for dry particles which are about two orders of magnitude smaller. Adsorbed mono-layers of water are present on many particles and the practical situation is that agglomeration effects are particularly bad for particles of sizes less than 40  $\mu\text{m}$  **(2)**. Such particles will not empty cleanly from the bag. Filler left in the bag may be a significant route of environmental release. An opinion here is that a worst case scenario is perhaps as much as 1% loss. For particles  $>40 \mu\text{m}$ , retention in the bag does not occur to a significant extent. Losses will be minimal i.e. 0.01%.

151. The material remaining in the packaging may be lost to the environment at the factory site, presumably into landfill via solid waste. It is also possible that such loss may take place away from the

production site. If the packaging is sent away for recycling (e.g. for paper sacks), the release could occur in the process water of the recyclers. However there are unlikely to be releases to water from this route at the plastic production site.

152. Another route to release on handling is through dust generation. The terminal velocity for falling particles of 10 µm diameter is less than 1 cm/s and, once disturbed and projected into the air, such fine particles will display very slow settlement rates **(3)**. Thus, in addition to the bag emptying problem, one should expect slight additional losses throughout the raw material handling operations of weighing, transporting, etc. No comparative data have yet been seen, although discussions with the industry suggest that bag emptying remains the biggest overall loss of powder. A worst case scenario for dust generation would be 0.5% for particle sizes less than 40 µm and 0.1% for particle sizes greater than 40 µm.

153. One change to handling which may help reduce emissions is the pelletisation of powders to increase particle size. Some carbon blacks are already available in this form. Some of the new fillers offered for registration may be compacted materials of this type.

#### *7.1.1.2 Fibrous fillers*

154. Discontinuous fibres have diameters that range from 1 µm to 100 µm with length to diameter ratios from 10 to 1 up to 2,500 to 1. Given this wide range of physical dimensions a worst case scenario would result in emissions of 1.6% as in the case of particulate fillers with diameters of <40 µm.

155. The nature of the production process for continuous fibre fillers is such that in a worst case scenario releases are unlikely to exceed 0.01%.

### **7.1.2 Compounding**

#### *7.1.2.1 Particulate fillers*

156. The process of mixing fine particles into plastics also has a susceptibility to dust generation but losses are not thought to approach those of the previous handling stages. Any losses would occur early in the mixing cycle and localised containment may be sufficient to ensure that recovered material can be returned to the compound. Notionally, losses will be at least an order of magnitude down on the original handling: representative values, for a worst case scenario, may be 0.05% for fine (<40 µm) particles and 0.01% for coarser (>40 µm) particles. Losses again will be to solid waste (from vacuum cleaner bags, filters, etc).

#### *7.1.2.2 Fibrous fillers*

157. For discontinuous fibre fillers a worst case scenario would result in emissions of 0.05% as in the case of particulate fillers with diameters of <40 µm. For continuous fibre strands a worst case scenario would result in emissions of 0.01% as in the case of particulate fillers with diameters of >40 µm.

### **7.1.3 Conversion**

#### **7.1.3.1 Particulate fillers**

158. Once mixed into the compound, filler is unlikely to be removed during normal conversion operations. Nevertheless, wear of compound at metal surfaces (e.g. in dies) is conceptually possible and losses, albeit minimal, could be put at the 0.01% level.

159. One potentially significant source of emission is grinding where, for example, some thermosetting composites may be reshaped after cure. The waste grindings, which are very likely to be fragments of filler bound to plastic, are usually taken off into local exhaust ventilation (LEV). The worst case scenario is where the filler is fully released, i.e. as a mixed dust in proportions representative of the original filler loading. Such losses may be significant, but seem unlikely to exceed 2.5% of filler.

#### **7.1.3.2 Fibrous fillers**

160. Longer fibres, including chopped glass, are more easy to handle without loss owing to their larger size. There is a possible problem of the generation of smaller fragments through wear, although quantities lost would be very small (0.01% at worst).

161. Woven substrates, such as fibre mats, present minimal opportunity for accidental loss but may give significant losses through off-cuts. This may be in the region of 10%. Of course such off-cuts are not necessarily a single component as the fibres may be coated with both an interfacial aid (e.g. "size") and coupling agents for the fabric (see Section 10).

162. All these losses of fillers from any of the above processes in the factory will end up in solid waste. These will appear as contaminated bags, dusts from filters (LEV), vacuum cleaners, etc and sediments from settlement tanks (floor washings).

### **7.1.4 Service life**

163. Minimal losses of filler are envisaged in service. Any loss through abrasion would be expected to be of adhering filler/polymer fragments (i.e. not filler alone), although some loss of free filler might occur following degradation of the plastic. Such effects would most likely be confined to plastics surfaces and are put at the minimal level (0.01%) over the service life of the plastic.

### **7.1.5 Disposal**

164. No losses of filler are anticipated when disposal is by landfill. Of course, this assumption takes no account of geological time scales. Ultimately it may be possible for the plastic to degrade to the extent that physical separation of its components can occur but this outcome is not considered here.

165. For incineration, organic materials will be completely destroyed. There may be residues of inorganic materials left in the ash, which will be disposed of as solid waste.

## **7.2 Estimating percentage (%) losses**

166. Emission control to prevent particulate atmospheric release (e.g. bag filters) have an efficiency in excess of 99% provided they are regularly maintained. If emission control measures are employed there is no significant likelihood of atmospheric release.

167. The emission factors for fillers can be estimated as follows.

### 7.2.1 *Raw materials' handling*

168. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The loss factors, for a worst case scenario, are as follows.

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags

For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

For discontinuous fibre strands,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags

For continuous fibres and fibre mats,  $F_{\text{handling, water}} = 0\%$   
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

### 7.2.2 *Compounding*

169. Initially some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water. On the basis of susceptibility to dust generation the loss factors are as follows.

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{compounding, water}} = 0.05\%$  to solid waste/water  
 $F_{\text{compounding, air}} = 0\%$

For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{compounding, water}} = 0.01\%$  to solid waste/water  
 $F_{\text{compounding, air}} = 0\%$

For discontinuous fibre strands,  $F_{\text{compounding, water}} = 0.05\%$  to solid waste/water  
 $F_{\text{compounding, air}} = 0\%$

For continuous fibre and mats,  $F_{\text{compounding, water}} = 0.01\%$  to solid waste/water  
 $F_{\text{compounding, air}} = 0\%$

### 7.2.3 *Conversion*

170. Ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water. On the basis of wear of plastic material the loss factors are as follows.

For all forms other than woven mats  $F_{\text{conversion, water}} = 0.01\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

For grinding/machining  $F_{\text{conversion, water}} = 2.5\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

For woven mats,  $F_{\text{conversion, water}} = 0\%$   
 $F_{\text{conversion, air}} = 0\%$   
 $F_{\text{conversion, waste}} = 10\%$  (to solid waste, as off-cuts)

#### 7.2.4 *Small sites*

For smaller sites (<750 tonnes of plastic per year) an increase in the emissions factors up to 10x may be considered on a case-by-case basis, based on the likelihood of smaller sites not having emission control equipment and procedures as effective as those at larger sites.

#### 7.2.5 *Service life*

171. Ultimately all particulates will settle and losses will be to solid waste or to water. On the basis of degradation and wear the loss factors are as follows.

For all types,  $F_{\text{service life, water}} = 0.01\%$  over the service life of the plastic  
 $F_{\text{service life, air}} = 0\%$

#### 7.2.6 *Disposal*

172. Emissions from incineration are considered to be negligible, so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0$  for incineration. Fillers are not expected to volatilise or leach from plastics to any significant extent in landfills, and so  $F_{\text{disposal, air}}$  and  $F_{\text{disposal, water}}$  for landfills can also be considered to be zero.

## 8 PLASTICISERS

### 8.1 General description

173. Plasticisers are additives which improve the flexibility, processability and softness of the polymer material. In essence they reduce the glass transition temperature. They are normally high boiling, organic liquids, a few are waxy solids. They are not chemically bound to the polymer and are therefore able to migrate to the surface of the polymer matrix where they may be lost by a variety of physical processes.

174. The bulk of plasticisers used in plastics materials, over 98%, are used in PVC, with a small quantity of specialised materials being used in polyamides (nylon). Whilst plasticiser-like materials may be used in low concentrations in other polymers their function is to act as processing aids, mould release agents or some other specialised function.

175. Retention in the polymer is one of the main factors in considering which plasticiser to use. The plasticiser must be sufficiently involatile to remain in the compound during its mixing and formation stages. During service in the final product the compound may be subjected to extremes of temperature, extraction by water or attack by sunlight, and these factors also need to be taken into account.

176. The main development in the industry in recent years has been the development of a range of high molecular weight plasticisers, mainly branched and linear phthalates and trimellites, which have satisfied most demands for improved permanence. Plasticisers of molecular weight lower than diheptyl phthalate are not often used alone because of volatility considerations.

177. Since virtually all plasticisers are used in PVC, it is relevant to consider the factors that dictate selection for a particular application. These are functionality and economics of use. Over 95% of all plasticisers used are dialkyl phthalates; this is because they combine together qualities such as compatibility, permanence, efficiency, processability etc., while also having economic advantages. Compatibility problems preclude the use of esters of molecular weight lower than dibutyl- or higher than ditridecyl.

178. In Western Europe, DBP is only used in isolated cases in conjunction with heavier plasticisers that reduce overall volatility, while C5 phthalate simply is not available in significant commercial quantity.

179. Both linear and branched dialkyl phthalates are used. The more costly linear esters give superior low temperature properties to the finished PVC products and also have lower volatilities. The C8-C13-dialkyl phthalates are the dominant plasticisers with di-2-ethylhexyl phthalate predominant. The relatively low volume butylbenzyl phthalate is mostly used in flooring.

180. Other plasticisers for PVC worth mentioning are di-2-ethylhexyl adipate (mostly used in food wrap), alkyl/aryl phosphates (used as fire retardant components, mostly in cables), trialkyl trimellitates (mostly used in high-temperature cable because of their low volatility) and polymeric plasticisers (polyester type) for high permanence. These latter plasticisers are "specialities" and their total use is less than about five percent of the total plasticiser use in PVC.



181. The main factor affecting losses of plasticiser during the manufacture of plastics is the vapour pressure. **Table 8.1** gives vapour pressure data (4) for a representative range of plasticisers.

**Table 8.1: Vapour pressure of plasticisers (in hPa, 1 hPa = 0.75 mm Hg)**

	<b>DEHA</b>	<b>BBP</b>	<b>DEHP</b>	<b>DIDP</b>
<i>Volatility class</i>	<i>high</i>	<i>high</i>	<i>medium</i>	<i>low</i>
Temperature ( <sup>0</sup> C)				
20	$6.3 \times 10^{-7}$	$6.5 \times 10^{-6}$	$2.2 \times 10^{-7}$	$3.3 \times 10^{-8}$
50	$2.7 \times 10^{-5}$	$1.5 \times 10^{-4}$	$1.0 \times 10^{-5}$	$1.8 \times 10^{-6}$
100	$3.7 \times 10^{-3}$	$9.1 \times 10^{-3}$	$1.6 \times 10^{-3}$	$3.4 \times 10^{-4}$
150	0.16	0.21	0.076	0.019
200	3.1	2.5	1.6	0.46

182. The divisions between the classes of high, medium and low volatility are to some degree arbitrary and each substance should if possible be assessed individually. The DEHP data represent the industry volatility standard for present purposes, a conservative assumption, because it is the most volatile of the general purpose plasticisers. In all the following emission estimates it is assumed that DEHP is used. DIDP data are representative of the less volatile plasticisers which include some linear alkyl chain phthalates and DTDP. The DEHA/BBP data are representative of the somewhat more volatile specialities. The two major applications where significant volumes of more volatile plasticisers are used are in flooring, (BBP), and car undercoating, (C<sub>7</sub> phthalate). It is important to understand that for both these applications treatment of air to remove fumes is standard.

183. Appendix II contains calculations of the rate of loss of plasticiser through volatilisation. From these calculations the approximate ratio between losses for the high, medium and low volatility groups is 5:1:0.2, taking medium volatility as the standard. These ratios can be applied to air losses to convert the medium volatility losses described in the following sections. If specific information on a substance is available to allow losses to be related to those for DEHP, then this should be used in preference.

#### **8.1.1 Raw materials handling**

184. Plasticisers are not volatile at normal ambient temperatures and loss by volatilisation is not expected. Liquid plasticisers are usually transported and handled in bulk through enclosed storage systems and minimal loss by spillage can be assumed. A figure of 0.01% is proposed.

#### **8.1.2 Compounding**

185. Two general methods are used to prepare blends for the convenient processing of PVC. Dryblending, a process unique to PVC technology is used to prepare blends for extrusion, injection moulding and sometimes calendaring. Plastisol blending is used to prepare plastisols (approximately 30-35% of all plasticiser in PVC is applied in plastisol applications). A third method, rather obsolete but occasionally associated with calendaring, is Banbury blending or mixing.

186. The emission figures given represent the total loss by volatilisation during the compounding step. The losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere.

#### 8.1.2.1 *Dry blending*

187. This method is based on suspension or mass grade PVC and typically consists of mixing all ingredients with a high speed rotating agitator which heats the material by friction. Temperatures of 100-120°C (max.) are reached and the liquid plasticiser is completely absorbed by the fine PVC powder grain. Gelling is carefully avoided by keeping the temperature at this level, so that a free flowing powder results. Residence times in the lidded blender are in the order of fifteen minutes and the hot blend is dropped in a cooling blender (also lidded) for rapid cooling to avoid lumping. During the last minutes the temperature rises fairly rapidly so that the period of temperatures over 100°C only covers a short time span, carefully controlled to conserve a free flowing sandy dry-blend. During dryblending the exposure of hot material to open air is small. On a total charge of typically 150 kg including, say, 50 kg of plasticiser and free air space in the blender of 100 litres, at 100°C the saturation concentration of general purpose plasticiser is 20 mg/m<sup>3</sup> or a total of 100 x 20 mg = 2 grams. Assuming one air exchange per run, the amount of emitted plasticiser vapour is very small (~0.01%).

#### 8.1.2.2 *Plastisol blending*

188. Plastisol blending takes place in stirred vessels at ambient temperatures. To avoid the development of high viscosities by swelling of the PVC particles due to plasticiser uptake, the vessels may be cooled to remove the heat of friction. Examination of **Table 8.1** shows that any significant emissions of plasticiser at ambient temperatures is excluded.

#### 8.1.2.3 *Banbury mixing*

189. Banbury mixers are lidded vessels with a small open vent to the air. The mixing process is a batch process, starting with the raw materials at ambient temperatures and going up to maximum temperatures of 120-140°C. Emissions are comparable to those in dry blending.

### 8.1.3 *Conversion*

190. PVC is processed in a number of ways: calendaring; extrusion; injection moulding; several plastisol applications including spread coating (with oven fusion/gelation), rotational moulding (typically closed mould gelation), dip coating (oven gelation), slush moulding and spray coating (with closed tunnel ovens); and miscellaneous small to very small applications.

191. As is noted specifically for some of the processes, fume elimination equipment is commonly used to reduce emissions. Such equipment is considered to reduce emissions by one order of magnitude. However it is less likely to be found on smaller sites. As a rule of thumb, plants using more than 250 tonnes of plasticiser per year can be considered to have such equipment, while those using 250 tonnes or less per year do not. Unless specifically stated, release factors in this section refer to plants *with* fume elimination equipment, so emissions for smaller plants should be increased by a factor of 10.

192. The emission figures given represent the total loss by volatilisation from the process. The losses will initially be to air at elevated temperature. However subsequent condensation could result in

losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere.

#### 8.1.3.1 *Calendering (open process)*

193. The output of a typical calendering line is 1000 kg/hr. The majority of calendered products are relatively inflexible, (e.g. stationery products, furniture veneer), consequently the average plasticiser content is relatively low, say 25%. The rate of air extraction for such a line is typically 25,000 m<sup>3</sup>/hr. Assuming that this extracted air contains a mixture of air from the area over the hot calender bowls containing 20 mg/m<sup>3</sup> of plasticiser and that from the general atmosphere containing the regulated maximum of 5 mg/m<sup>3</sup> of plasticiser, (a legal requirement in most EU countries), this results in an emission of plasticiser of 0.2%. However, it is more and more common (and in certain countries obligatory) to have air purification equipment in place. For calendering this is mostly incineration, reducing the concentration to approximately zero. As reasonable worst case, an emission of 0.05% is suggested.

#### 8.1.3.2 *Extrusion (partly open or closed)*

194. The major different product types of plasticised PVC extrusion are "profiles" such as wire, cable and hose, and blow moulded film. Profiles are the largest outlet of the two types and at the same time give rise to the least emission. There is no exposure in the extruder itself; it is only for moments after leaving the die that a short exposure of hot material takes place. In addition the surface to volume factor is much lower than in calendering. An emission factor of 0.01% is proposed.

195. For blown film there is somewhat more evaporation potential since the film bubble has a fairly large surface area and is subject to air currents. The situation is comparable to calendering (at worst) and the same estimate of 0.05% is justified.

#### 8.1.3.3 *Injection moulding (closed)*

196. Injection moulding is comparable to extrusion except that even the cooling process takes place in a closed space (mould). It appears that there is practically no potential for evaporation but a similar factor to that for extrusion (0.01%) could be used.

#### 8.1.3.4 *Plastisol-spread coating (open)*

197. Spread coated products like cushioned flooring, wall covering, tarpaulins etc., are "fused" (gelled) in tunnel ovens heated with hot air at about 180°C. It can be shown that the amount of air used, (and purged to the environment), is 15-25 m<sup>3</sup>/kg of plasticiser consumed **(5)**. This figure is remarkably constant and is independent of the type of product being manufactured. It provides therefore a useful means of calculating the total emission of plasticiser to the environment from the whole range of spread coating activities. The extracted air contains typically 200-1,000 mg/m<sup>3</sup> (average 500 mg/m<sup>3</sup>) of plasticiser. Taking the average air consumption to be 20 m<sup>3</sup>/kg plasticiser, the total loss from the process is 20×500 mg/kg plasticiser used or 10 grams (1%). This figure is in close agreement with data based on laboratory experiments **(6)**.

198. Even if there were no treatment of the purged air, not all of this would reach the environment since abundant condensation would take place in cooler pipes, ducts and stacks.

199. Already by 1989, 75% of all plasticiser in spread coating applications was used in production lines with air treatment (53% with filters, 25% with incineration) **(5)**. This proportion has certainly

increased since then and is probably approaching 100% under the influence of national and European regulations. Air filtration removes at least 95% of the fumes (plasticiser concentration  $\sim 20 \text{ mg/m}^3$ ), whilst incineration leaves no plasticiser behind. The conclusion is that, depending on the presence of air treatment equipment ( $\sim 75\%$  of all consumption, presently approaching 100%), the emission may fluctuate between 0-0.05% (majority of sites), and 0.5% (plant without air treatment).

#### 8.1.3.5 *Other plastisol processes*

200. The processes concerned are car underbody coating and sealing, rotational coating, dipping and slush moulding. Of these, car underbody coating and sealing is by far the largest volume application. In this process the sprayed coating is "dried" in long air-heated tunnel ovens at relatively low temperatures (130-160°C). The ovens in this industry invariably have integrated air incinerators since at the same time paint coats containing solvents are dried. The result is practically zero organic output to the environment.

201. Of the other processes mentioned above, dip coating and slush moulding (both small volume) are comparable to spread coating in terms of process loss; the presence or absence of air treatment really defines the emission of plasticiser (0.05% or 0.5% respectively). In rotational moulding, final fusion takes place in closed moulds with practically no loss of plasticiser.

### 8.1.4 *Service life*

#### 8.1.4.1 *Interior*

##### *Vapour losses*

202. Vapour losses in service may present less of a localised hazard than for processing, but the loss may be greater overall. Losses to air may be at such a slow rate that condensation need not be expected, the vapour released remaining as an airborne contaminant.

203. The migration and volatilisation of plasticiser from PVC has been the subject of extensive study. Worst case releases are seen when sample thicknesses are small, as for example with thin films. Quackenboss (7) derived an expression for loss in terms of the time to lose 10% of the plasticiser for thin films:

$$T = 0.080/P$$

where T = time to lose 10% plasticiser in hours and  
P = vapour pressure in mmHg.

204. The figures given by Quackenboss are tabulated below, where  $T_{98}$  and  $T_{25}$  are the times to 10% loss at 98 and 25°C respectively.

Plasticiser	P at 98°C (mmHg)	$T_{98}$ (hr)	P at 25°C (mmHg)	$T_{25}$ (years)
Di-n-butyl phthalate		$3.0 \times 10^{-2}$	2.9	$3.5 \times 10^{-5}$
Di-2-ethylhexyl phthalate		$9.6 \times 10^{-4}$	88	$3.4 \times 10^{-7}$
Dioctyl sebacate	$2.3 \times 10^{-4}$	350	$2.0 \times 10^{-8}$	450

Assuming a linear rate loss then the above expression becomes:

$$\begin{aligned} \text{Rate} &= \frac{P}{0.008} \text{ \% per hour} \\ &= 1.1 \times 10^6 P \text{ \% per year} \end{aligned}$$

205. Thus for the medium volatility plasticiser DEHP, the rate loss will be 0.1% per hour at 98°C and 0.4% per year at 25°C. For the high volatility plasticiser DBP, the equivalent values are 4% per hour at 98°C and 40% per year at 25°C.

206. More recent measurements and calculations (**8, 9, 10**) estimate indoor vaporisation losses at around 140 tonnes per year for the whole of Western Europe. Taking flooring, wallcovering and wire/cable into account (**5**), the result is 0.05% of the annual consumption in these applications. This figure will be used as a general release factor to cover the range of applications and types of product. The more specific approach above could be used when the substance being assessed is known to be used in thin film applications. An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

#### *Leaching*

207. Calculations have been made for losses from flooring due to leaching during cleaning, based on general soapy water extraction data (**7**). The overall release for Western Europe obtained from this work was 500 tonnes per year. Recently new data became available, based on work done by/for Forbo Forshaga in Sweden, (**11**), using actual washing tests. For the whole of Sweden, a maximum emission of 6.25 tonnes per year results. Approximately one eighth of all vinyl flooring in W. Europe is used in Sweden. Using this data the emission for the whole of Europe would be 50 tonnes per year. It may be concluded that the emission via leaching from interior-based products is of the order of 0.05%.

#### *8.1.4.2 Exterior*

208. Actual data on emissions from products used outside are scarce. One source, (**12**) relates to roofing, where an annual loss of average 0.75% was found for PVC roofing material exposed for several years. Leaching was believed to be the main route of loss. The losses were not however purely emissions of plasticiser to the environment since degradation products were found in the vicinity. These findings can be generalised to include other applications, e.g. car undercoating. The average loss rate/year in the study was around 0.16%/year for open air exposures (a higher figure of around 0.35%/year was obtained for a surface covered with gravel). This factor should be applied to the actual amount of additive present in products, taking into account the products lifetime. It should also be noted that the derived emission factor will also include contributions from loss of particulates, degradation etc. from the material due to weathering or erosion and so is likely to overestimate the actual leaching loss of the plasticiser.

#### **8.1.5 Disposal**

209. At some stage, depending on their use, products will be discarded. Most will still contain a substantial proportion of the original plasticiser content. Incineration under normal conditions should lead to complete destruction and thus no loss of volatilised plasticiser to the environment. There is no evidence in the literature suggesting significant loss by this route.

210. In landfills, water ingress is possible and as a consequence extraction of plasticiser is a possibility. However, normal landfill practice should minimise water penetration and there is a body of evidence which indicates that while groundwater does contain plasticisers the concentrations are very

small (5). The maximum possible release would be the amount of plasticiser remaining in the plastic at disposal. This would be a very much worst case assumption, depending on the solubility of the additive. Such releases should be considered on a regional scale.

## 8.2 Estimating percentage losses

211. All losses quoted so far are for medium volatility plasticisers which represent the bulk of those used. As noted above, losses from high, medium and low volatility plasticisers are expected to be in the ratio 5:1:0.2.

### 8.2.1 Raw materials handling

212. For liquids  $F_{\text{handling, water}} = 0.01\%$  (to liquid waste for all volatility groups)  
 $F_{\text{handling, air}} = 0\%$  (all volatility groups)

### 8.2.2 Compounding

213. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

For dry blending and Banbury blending,  $F_{\text{compounding, water}} = 0.001\%$  (low volatility group)  
 $F_{\text{compounding, water}} = 0.005\%$  (medium volatility group)  
 $F_{\text{compounding, water}} = 0.025\%$  (high volatility group)  
 $F_{\text{compounding, air}} = 0.001\%$  (low volatility group)  
 $F_{\text{compounding, air}} = 0.005\%$  (medium volatility group)  
 $F_{\text{compounding, air}} = 0.025\%$  (high volatility group)

For plastisol compounding  $F_{\text{compounding, water}} = 0$  (all volatility groups)  
 $F_{\text{compounding, air}} = 0$  (all volatility groups)

### 8.2.3 Conversion

214. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

For calendaring  $F_{\text{conversion, water}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.125\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.125\%$  (high volatility group)

For extrusion  $F_{\text{conversion, water}} = 0.001\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.005\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (high volatility group)

$F_{\text{conversion, air}} = 0.001\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.025\%$  (high volatility group)

For blown film

$F_{\text{conversion, water}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.125\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.125\%$  (high volatility group)

For injection moulding

$F_{\text{conversion, water}} = 0.001\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.005\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.001\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.025\%$  (high volatility group)

For spread coating

$F_{\text{conversion, water}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.125\%$  (high volatility group)

215. If information on the specific process being used is not available, then the following factors are suggested for a medium volatility substance.

Default (for a medium volatility Substance)

$F_{\text{conversion, water}} = 0.005\%$  (closed processes)  
 $F_{\text{conversion, water}} = 0.015\%$  (partially open processes)  
 $F_{\text{conversion, water}} = 0.025\%$  (open processes)  
 $F_{\text{conversion, air}} = 0.005\%$  (closed processes)  
 $F_{\text{conversion, air}} = 0.015\%$  (partially open processes)  
 $F_{\text{conversion, air}} = 0.025\%$  (open processes)

#### 8.2.4 *Small sites*

216. All the above values relate to situations where fume elimination equipment is in operation, i.e. larger sites. For smaller sites (<250 tonnes plasticiser per year, which corresponds to ~ 750 tonnes of plastic) the emission factors should be increased by a factor of 10.

#### 8.2.5 *Service life*

Indoor service, leaching to liquid waste	$F_{\text{service life, water}} = 0.05\%$ over lifetime
Indoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\%$ over lifetime
Outdoor service, leaching to environment	$F_{\text{service life, water}} = 0.16\% \times T_{\text{service}}$ (where $T_{\text{service}}$ = service life of product in years; see <b>Table 4.3</b> )
Outdoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\%$ over lifetime

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

### **8.2.6 Disposal**

217. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

218. Emissions from incineration are considered to be negligible, so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0\%$  for incineration.



## 9 ANTIOXIDANTS

### 9.1 General description

219. Plastics are organic materials which suffer deterioration as a result of air oxidation. Oxidative degradation can result in loss of tensile strength, discolouration and other property changes which can shorten service life.

220. Antioxidants for plastics are characteristically aromatic compounds with a suitable functionality for participation in radical chain breaking reactions. Such functionality may be amino, phenolic or phosphite and species containing only one aromatic ring are known. For example, 2,6-di-tert-butyl-4-methylphenol, although a solid, has a normal boiling point of 265°C, which is lower than most plasticisers and therefore is relatively volatile. These types are more likely to be introduced during polymerisation rather than by compounding, when they protect the polymer during final work-up after polymerisation. This is a widely used antioxidant for this purpose, although species of such volatility would not be recommended for long-term use.

221. In general, most antioxidants for plastics are two-ring compounds (many phenolic types and some amines) or three-ring compounds (phenyl-p-phenylenediamine or triaryl phosphites). Whilst volatilities are sufficiently low to allow conventional compounding into plastic melts they are still not necessarily lower than for many plasticisers. **Table 9.1** below gives vapour pressures at 150°C for several antioxidants (**13**), together with values for three plasticisers for comparison. The data are included for comparison only: compounding and conversion of antioxidants may take place at temperatures higher than 150°C.

**Table 9.1: Vapour Pressures at 150°C**

Compound	Vapour Pressure at 150°C (hPa)
Diphenylamine	10.0
Di-n-butyl phthalate (plasticiser)	1.1
Phenyl-β-naphthylamine	0.39
Di-isodecyl adipate (plasticiser)	0.27
2,2'-methylenebis (4-methyl-6-tert-butylphenol)	0.23
N,N'-diphenyl-p-phenylenediamine	0.043
Di-isodecyl phthalate (plasticiser)	0.019

222. Thus antioxidants have measurable volatility at processing temperatures even though the raw materials are solids and conventionally handled in powder or flake form. To estimate releases, antioxidants are analogous to fillers with respect to handling, but analogous to plasticisers with respect to their volatility characteristics. This distinction is covered in more detail below.

#### 9.1.1 Raw materials' handling

223. As with fillers (Section 7.1.1), antioxidants are solids likely to be encountered as powders or pellets and conventionally supplied in sacks or bags. The problems of bag emptying will apply as before, with the pellet forms offering less risk of unwanted retention in the bag through agglomeration

effects. However, such risks are not entirely eliminated as attrition effects can still generate fine powder from pelletised forms. Agitation associated with bag handling (on transportation to the factory, or transfers within the factory) can change the particle size distribution from that as originally dispatched by the supplier. Thus handling problems should be assessed in terms of the nature of the material at the point of mixing and not necessarily as originally specified. Consequently, both powdered and pelletised forms will be potentially susceptible to agglomeration-induced losses and the 40 µm cut-off can be applied as for fillers. The model for loss is taken as the same as in Section 7.2.1.

### **9.1.2 Compounding**

224. The process of mixing fine particles into plastics has a susceptibility to dust generation, although losses will be expected to be low as for fillers at this stage in the processing. The loss factor for dust generation is therefore taken as 0.05% or 0.01% depending on particle size.

225. Such compounding will inevitably involve the input of heat, and volatile losses must also be considered. High temperatures are necessary to overcome vitrification or crystallisation effects which inhibit flow in unplasticised polymers. Conventionally, compounding (in twin-screw extruders) may be operated at 200°C or possibly higher. Such operations are normally carried out with the exclusion (as far as is practical) of air. The risk of volatile loss therefore approximates to that of conversion in closed operations as described in Section 8.1.3. The volatility of antioxidants is taken to be similar to that of plasticisers already considered (see **Table 9.1** above – and further discussion below), and the average loss factor for volatilisation (medium volatility substance) is taken as 0.01%.

226. This emission figure given for volatilisation loss represents the total loss by volatilisation during the compounding step. The loss will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere.

### **9.1.3 Conversion**

227. Antioxidants are widely used, and conversion may be carried out using any of the processes described in Section 3.2. As with the discussion in that Section, and as previously considered for plasticiser conversion (Section 8.1.3), it is convenient to break these operations down into open, partially-open and closed operations. Little has been published on antioxidant loss under these separate conversion operations, and the relevance or otherwise of the plasticiser models needs to be considered.

228. It has already been shown in **Table 9.1** that the vapour pressures of antioxidants are not dissimilar to those of plasticisers. Temperature is another area of similarity. Many conversion processes operate at around the temperature (200°C) already considered for plasticised-PVC conversion, with perhaps only a relatively small proportion of production operating at temperatures significantly higher than this. However, that proportion is not negligible and will include virtually all the engineering plastics such as the polycarbonates, polyamides and PET. Such higher temperature operations could include the oven post-cure of polyamide (open), the extrusion of polyester film (partially-open) or various materials in injection moulding (closed). An upper limit for all these might reasonably be 300°C.

229. In their function, antioxidants must be at least partially soluble in the plastic which provides another similarity with plasticisers. As a result, opportunities for migration must follow. Rates of permeation will be a function of the character of the permeant itself but the nature of the plastic itself may also be a variable. Antioxidants are used in both crystalline and amorphous plastics and the level of crystallinity is a key factor. Even, for example, with commodity polyolefins, there is considered to

be a two order of magnitude difference in the diffusion constants for typical antioxidants in either low density polyethylene or the more crystalline polypropylene (14).

230. Whilst a number of variables make this situation quite complex, a simplified treatment may allow some estimate of a worst case scenario. In the case of antioxidant loss by evaporation, this might conceivably occur with those geometries (thin films) where diffusion is sufficiently fast to allow evaporative loss from the surface to be the controlling factor, and where the concentration of antioxidant is never in excess of its solubility limit, so that ideal solution character may be assumed. In such a case, rate of loss of antioxidant from the polymer is proportional to that from the pure antioxidant under the same conditions and is controlled by volatility. A situation closely analogous to plasticisers results. As a result of all these similarities, and in the absence of information to the contrary, it is suggested therefore that the same model as in Section 8 be used for compounding, conversion, service and disposal losses. The criteria for distinction in most cases can be the vapour pressures (preferably at operating temperatures, e.g. 200°C) to distinguish between high, medium or low volatility antioxidants.

231. Notionally a worst case scenario should correspond to the highest temperatures involved, which may be 300°C rather than 200°C. Such conditions are likely to be encountered with the more crystalline (less permeable) high performance polymers such as polyesters and polyamides. It may be that opportunities for antioxidant loss may be no greater at these higher processing temperatures than for less crystalline commodity polymers such as low-density polyethylene at 200°C. However, some amorphous polymers such as polystyrene or ABS are processed at temperatures up to 250°C and, as a precaution, some allowance for higher temperature volatility may be appropriate.

232. In the absence of any simple model (assumptions of evaporation control may no longer hold), it may be prudent to increase loss factors by one order of magnitude for all plastics converted at temperatures substantially in excess of 200°C.

233. Thus for medium volatility antioxidants, processed at these higher temperatures, the total volatilisation loss would be 0.5% for open conversion, 0.3% for partially open conversion and 0.1% for closed conversion.

234. In tonnage terms, these may still represent a small proportion of the total of all plastics processing and therefore for the majority of situations the 200°C upper limit represents the worst case scenario. In order to apply the appropriate loss factor, the type of polymer in which a particular antioxidant may be used will need to be determined using the criteria described above.

235. In the majority of cases, the loss factors revert to those in Section 8.1.3 (i.e. as for plasticisers) and these are the loss factors used here. A further process, not considered for PVC processing in the previous section, is the production of foamed articles. This is estimated to give losses double those from the production of solid articles.

236. Section 8.1.3 described how fume reduction equipment was expected to be in use at all larger sites. The threshold suggested, below which sites may not have such equipment, was the use of 250 tonnes of plasticiser. This equates to ~750 tonnes of plastic. Applying a similar rationale here, for sites handling less than 750 tonnes of plastic the release factors should be increased by a factor of 10.

237. The emission figures given in Section 8.1.3 represent the total loss by volatilisation from the process. The losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere.

### 9.1.4 *Service life*

238. Antioxidant may be lost in service in the same manner as for plasticiser loss from PVC. Whether this is by volatile loss or by leaching will depend on the conditions of service. In view of the existence of models for plasticiser loss and the similarities in volatility between plasticisers and antioxidants, it is proposed that the same models be used here. Thus the loss factors used are as in Section 8.1.4 or can be estimated as in Appendix IV. These factors do not include an adjustment for the fact that antioxidants are used up through reaction in performing their function, hence there will be some overestimation of the release. If specific information on the degradation or reaction during the service life is available this could be used to modify the estimates.

### 9.1.5 *Disposal*

239. Antioxidants are organic chemicals and similar conditions as for plasticisers apply. The loss factors for antioxidants are therefore the same as in Section 8.1.5.

## 9.2 **Estimating percentage (%) losses**

### 9.2.1 *Raw materials' handling*

240. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The emission factors, for a worst case scenario, are as follows:

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags  
 For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

### 9.2.2 *Compounding*

241. Initial losses will be to atmosphere, but ultimately particulates will be removed or will settle, and vapours will condense, resulting in losses to both solid waste and aqueous washings. It will be assumed here that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

For powders of low volatility group  $F_{\text{compounding, water}} = 0.051\%$   
 particle size  $<40 \mu\text{m}$   $F_{\text{compounding, air}} = 0.001\%$   
 medium volatility group  $F_{\text{compounding, water}} = 0.055\%$   
 $F_{\text{compounding, air}} = 0.005\%$   
 high volatility group  $F_{\text{compounding, water}} = 0.075\%$   
 $F_{\text{compounding, air}} = 0.025\%$

For powders of low volatility group  $F_{\text{compounding, water}} = 0.011\%$

particle size >40 $\mu\text{m}$	$F_{\text{compounding, air}} = 0.001\%$
medium volatility group	$F_{\text{compounding, water}} = 0.015\%$
	$F_{\text{compounding, air}} = 0.005\%$
high volatility group	$F_{\text{compounding, water}} = 0.035\%$
	$F_{\text{compounding, air}} = 0.025\%$

### 9.2.3 Conversion

242. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

Open processes solid articles	$F_{\text{conversion, water}} = 0.005\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.025\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.125\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.005\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.025\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.125\%$ (high volatility group)

Open processes foamed articles	$F_{\text{conversion, water}} = 0.01\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.05\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.25\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.01\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.05\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.25\%$ (high volatility group)

Partially open processes	$F_{\text{conversion, water}} = 0.003\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.015\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.075\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.003\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.015\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.075\%$ (high volatility group)

Closed processes	$F_{\text{conversion, water}} = 0.001\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.005\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.025\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.001\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.005\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.025\%$ (high volatility group)

243. For processing significantly in excess of 200°C (see Section 9.1.3), the above emission factors should be increased by 10x.

### 9.2.4 Small sites

244. For smaller sites (<750 tonnes plastic per year) emission factors related to volatile emissions should be increased by 10x. (If higher temperature processing is involved, the need for this further increase of 10x in addition to that in the section above should be considered on a case-by-case basis.)

A similar increase in emission factors related to dust emissions should also be considered on a case-by-case basis.

### 9.2.5 *Service life*

Indoor service, leaching to liquid waste	$F_{\text{service life, water}} = 0.05\%$ over lifetime
Indoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\%$ over lifetime
Outdoor service, leaching to environment	$F_{\text{service life, water}} = 0.16\% \times T_{\text{service}}$ (where $T_{\text{service}}$ = service life of product in years; see <b>Table 4.3</b> )
Outdoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\%$ over lifetime

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

### 9.2.6 *Disposal*

245. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

246. Emissions from incineration are considered to be negligible, so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0\%$  for incineration.

## 10 COUPLING AGENTS

### 10.1 General description

247. Coupling agents act at the interface between filler and plastic: if possible, bonding with both phases in order to improve interfacial adhesion between the filler and the polymer. Generally, coupling agents possess an inorganic functional group and an organic functional group, the inorganic functional group being attracted to the filler surface and the organic functional group being attracted to the polymer. Commonly, they are applied to the filler's surface prior to its incorporation into the plastic, a sequence which requires that the coupling agent be accessible in a low viscosity form. Coupling agents are characteristically low viscosity liquids, or capable of becoming such by melting or dissolution in a suitable solvent.

248. A combination of low viscosity and low surface tension implies that coupling agents will include materials of significant volatility. Thus for example, mercaptopropyl- trimethoxysilane  $[\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3]$  has a molecular weight of 196 which is similar to dimethyl phthalate (see Appendix II), but a boiling point (213-215°C) some 110°C lower. Coupling agents such as vinyltrimethoxysilane (MW 148) or aminopropyltrimethoxysilane (MW 179) have even lower boiling points.

249. These relatively volatile silane coupling agents are not normally compounded directly into polymers as are other additives. Conventionally, they are introduced via a lower temperature mixing process, as a treatment stage in the manufacture of filler. This is not therefore a process carried out within the plastics industry and the estimation of environmental releases does not fall within the scope of the model discussed here.

250. Recent developments have seen the emergence of less volatile coupling agents based on the Group VIa tetravalent elements, such as titanium and zirconium. These are organometallic compounds consisting of a metal atom, a hydrolysable group or groups and an organofunctional group. These types of coupling agents can be used in both thermoplastic and thermosetting systems, although most work to date has been with thermosetting materials. The lower volatility of these materials allows their direct introduction into polymers by conventional compounding techniques. It is these types of coupling agents which are likely to be the subject of notifications as new substances and so will be considered here.

#### 10.1.1 Raw materials' handling

251. Those coupling agents which are suitable for direct compounding into molten plastics will not be expected to have notable ambient temperature volatility. The general situation is analogous to that of plasticisers (see Section 8.1.1) and handling considerations will be similar with minimal loss (0.01%). As coupling agents hydrolyse in water they would have a limited life after any spillage.

**10.1.2 Compounding**

252. No data are available on titanate or zirconate volatilities, or on latent heats, etc. In the absence of such information, the corresponding losses will be assumed to be minimal (0.01%). Coupling agents are intended to react within the polymer/filler mix and the opportunity for losses must decrease as mixing continues.

253. The reactive nature of coupling agents has an implication on releases, as the presence of atmospheric moisture will ultimately destroy these species once airborne. The worst case scenario must therefore include a dry atmosphere and even then, because of the nature of these compounds, presents only a temporary problem.

**10.1.3 Fate after compounding**

254. Coupling agents are intended to react within the compounded plastic and thus are expected to change chemically during the processes of compounding. Once changed, none of the original coupling agent is available for loss; nor is there any simple mechanism by which such agents could be regenerated.

**10.2 Estimating Percentage (%) Losses****10.2.1 Raw materials' handling**

255. Losses will be to liquid waste. On the basis of incidental losses,

$$F_{\text{handling, water}} = 0.01\% \text{ (for all volatility groups)}$$

$$F_{\text{handling, air}} = 0\% \text{ (for all volatility groups)}$$

**10.2.2 Compounding**

256. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

Low volatility group	$F_{\text{compounding, water}} = 0.001\%$
	$F_{\text{compounding, air}} = 0.001\%$

Medium volatility group	$F_{\text{compounding, water}} = 0.005\%$
	$F_{\text{compounding, air}} = 0.005\%$

High volatility group	$F_{\text{compounding, water}} = 0.025\%$
	$F_{\text{compounding, air}} = 0.025\%$

**10.2.3 Further stages (conversion, service life and disposal)**

Assume  $F_{\text{conversion}} = F_{\text{service life}} = F_{\text{disposal}} = \text{zero}$  for both water and air (material destroyed during processing).



## 11 COLOURANTS

### 11.1 General description

257. Colourants used in plastics are of two types; pigments and dyes. They are distinguished by the phase in which they act; dyes dissolve in the plastic whereas pigments form a separate dispersed phase. Thus to be effective, pigments must be of fine particle size and well dispersed within the plastic. The situation for pigments is analogous to that of fillers, and indeed some fillers (carbon black) have notable pigment action.

258. Pigments may be organic or inorganic compounds and are normally solids: the latter include metal oxides ( $\text{TiO}_2$ ), metal chromates ( $\text{ZnCrO}_4$ ) etc. Organic pigments include various substituted aromatic azo compounds, some complexed to metals such as nickel or copper. They are typically large multi-ring molecules such as: copper phthalocyanine ( $\text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}$ , MW 576), carbazole dioxazine violet ( $\text{C}_{34}\text{H}_{22}\text{N}_{402}\text{Cu}_{12}$ , MW 589) or benzidine yellow AAMX ( $\text{C}_{36}\text{H}_{34}\text{N}_{604}\text{Cu}_{12}$ , MW 685). Molecules of such size are essentially non-volatile. Hence the majority will be considered as “inorganic”, as described in Section 6.1.1. If a pigment is considered to have significant volatility under the relevant conditions, then it should be assessed using the approach for dyes as described in the following paragraphs.

259. Dyes for plastics are organic materials containing some of the structural features of the organic pigments but typically of lower molecular weight. Examples include thioindigo ( $\text{C}_{16}\text{H}_{80}\text{S}_2$ , MW 296), hydroxybis(phenylazo)benzene ( $\text{C}_{18}\text{H}_{14}\text{N}_4$ , MW 302) or Rhodamine B ( $\text{C}_{28}\text{H}_{31}\text{NO}_3\text{Cl}$ , MW 464). Although approaching, in some cases, the molecular weights of the more volatile plasticisers (DBP, MW 278), it is doubtful if these species approach their volatility. Extensively conjugated molecules, such as those which display colour, have less rotational freedom and are usually significantly less volatile than more flexible molecules of a similar size. A rationale may require consideration of the respective entropy gains for vaporisation, but the magnitude of the effect can clearly be seen for simple hydrocarbons. For example, dodecane (MW 170, bp  $216^\circ\text{C}$ ) and tetradecane (MW 198, bp  $254^\circ\text{C}$ ) are significantly more volatile than the polycyclic aromatics phenanthrene (MW 178, bp  $340^\circ\text{C}$ ) or pyrene (MW 202, bp  $393^\circ\text{C}$ ). The inference that may be drawn is that extensive conjugation can add in excess of  $100^\circ\text{C}$  to the boiling point of a material in this molecular weight range.

260. The effect on vapour pressure at processing temperatures for such a boiling point increase can be estimated from the Clausius Clapeyron equation (Appendix II). The hypothetical case of the high volatility additive (i.e. the notional plasticiser with a vapour pressure of 20 mmHg at  $200^\circ\text{C}$ ) can be represented by a liquid which has a normal boiling point of  $280^\circ\text{C}$  and latent heat = 100 kJ/mole. Increasing this boiling point to  $400^\circ\text{C}$ , with latent heat as before, reduces this  $200^\circ\text{C}$  vapour pressure to 0.4 mmHg. This is a reduction of nearly two-orders of magnitude.

261. Volatility data on dyes for plastics are not available, but in the absence of information to the contrary it will be taken that they have some, albeit small, volatility. On the basis of the above discussions and examples, it will be assumed here that dyes have the volatility and other migration

characteristics of low volatility plasticisers or antioxidants as discussed earlier. With respect to the technology of compounding or conversion, this can be taken as the same as that for antioxidants (Section 9).

262. Thus with respect to the possible volatilisation or migration of dyes, the environmental considerations will be the same as the least volatile antioxidants; with respect to dust or particulate emissions, the environmental considerations of both pigments and dyes can be assumed to be analogous to those for fillers.

## 11.2 Estimating percentage (%) losses

263. The loss factors for colourants can be estimated as follows.

### 11.2.1 Raw materials' handling

264. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or will settle and losses will be to solid waste or to waste water as a result of wash down. It is possible that emissions to waste water could also occur in the event of paper sacks being recycled, but at a different location.

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water

$F_{\text{handling, air}} = 0\%$

$F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags

For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water

$F_{\text{handling, air}} = 0\%$

$F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

265. These emission factors apply to both dyes and pigments.

### 11.2.2 Compounding

266. Initially some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water. It will be assumed here that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

For powders of Dyes  $F_{\text{compounding, water}} = 0.051\%$

particle size  $<40 \mu\text{m}$   $F_{\text{compounding, air}} = 0.001\%$

Pigments  $F_{\text{compounding, water}} = 0.05\%$

$F_{\text{compounding, air}} = 0\%$

For powders of dyes  $F_{\text{compounding, water}} = 0.011\%$

particle size  $>40 \mu\text{m}$   $F_{\text{compounding, air}} = 0.001\%$

pigments  $F_{\text{compounding, water}} = 0.01\%$

$F_{\text{compounding, air}} = 0\%$

### 11.2.3 Conversion

#### 11.2.3.1 Pigments

267. Ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of attrition of compound the loss factors are as follows.

For grinding/machining  $F_{\text{conversion, water}} = 2.5\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

For all other operations  $F_{\text{conversion, water}} = 0.01\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

#### 11.2.3.2 Dyes

268. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

Open processes solid articles  $F_{\text{conversion, water}} = 0.005\%$   
 $F_{\text{conversion, air}} = 0.005\%$

Open processes foamed articles  $F_{\text{conversion, water}} = 0.01\%$   
 $F_{\text{conversion, air}} = 0.01\%$

Partially open processes  $F_{\text{conversion, water}} = 0.003\%$   
 $F_{\text{conversion, air}} = 0.003\%$

Closed processes  $F_{\text{conversion, water}} = 0.001\%$   
 $F_{\text{conversion, air}} = 0.001\%$

269. For processing significantly in excess of 200°C (see Section 9.1.3), the above emission factors should be increased by 10x.

### 11.2.4 Small sites

270. For smaller sites (<750 tonnes plastic per year) emission factors related to volatile emissions should be increased by 10x. (If higher temperature processing is involved, the need for this further increase of 10x in addition to that in the section above should be considered on a case-by-case basis.) Similar increases in emission factors related to dust emissions should also be considered on a case-by-case basis.

### 11.2.5 Service life

#### 11.2.5.1 Pigments

271. Ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of degradation and abrasion the loss factors are as follows.

$$F_{\text{service life, water}} = 0.01\% \text{ over the service life of the plastic}$$

$$F_{\text{service life, air}} = 0\%$$

#### 11.2.5.2 Dyes

Indoor service, leaching to liquid waste	$F_{\text{service life, water}} = 0.05\% \text{ over lifetime}$
Indoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\% \text{ over lifetime}$
Outdoor service, leaching to environment	$F_{\text{service life, water}} = 0.16\% \times T_{\text{service}}$ (where $T_{\text{service}}$ = service life of product in years; see <b>Table 4.3</b> )
Outdoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\% \text{ over lifetime}$

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

#### 11.2.6 Disposal

272. The factors apply to both pigments and dyes.

273. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

274. For incineration, organic materials will be completely destroyed ( $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0\%$ ). There may be residues of inorganic materials in the ash, which will be disposed of as solid waste. Similar considerations to those above for landfill may apply.

## 12 UV AND OTHER WEATHERING STABILISERS

### 12.1 General description

275. Whilst ultraviolet and weathering stabilisers share some of the molecular characteristics of colourants, in that they are characteristically aromatic, they are generally of lower molecular weight. All are solids, the lowest molecular weight examples including phenyl salicylate (MW 214) and hydroxy-methoxy-benzophenone (MW 228). These molecular weights are lower than for many plasticisers and antioxidants and so some volatility might be expected, as is indeed indicated by comparisons of some reduced pressure boiling points. Phenyl salicylate (bp 173°C/12 mmHg) may be a little less volatile than di-isobutyl phthalate (bp 183°C/12 mmHg) and certainly substantially more volatile than tri-m-cresyl phosphate (bp 260°C/15 mmHg). In the absence of other numerical data, it is assumed that volatility considerations are similar to those for antioxidants, and the same model is used as for Section 9.

276. These additives work within the polymer phase and thus would be expected to dissolve at least partially in the plastic. A fine particle size is not therefore a pre-requisite and so a susceptibility to dustiness is not necessarily expected. However, the likelihood of such fine particles forming cannot be discounted and hence the 40 µm threshold should not be ignored.

### 12.2 Estimating percentage (%) losses

#### 12.2.1 Raw materials' handling

277. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The emission factors, for a worst case scenario, are as follows:

For powders of particle size <40 µm,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water

$F_{\text{handling, air}} = 0\%$

$F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags

For powders of particle size >40 µm,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water

$F_{\text{handling, air}} = 0\%$

$F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

#### 12.2.2 Compounding

278. Initial losses will be to atmosphere, but ultimately particulates will settle, and vapours will condense to some extent, resulting in losses to both solid waste and aqueous washings. It will be assumed here that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

For powders of particle size <40 µm	low volatility group	$F_{\text{compounding, water}} = 0.051\%$ $F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.055\%$ $F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.075\%$ $F_{\text{compounding, air}} = 0.025\%$
For powders of particle size >40 µm	low volatility group	$F_{\text{compounding, water}} = 0.011\%$ $F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.015\%$ $F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.035\%$ $F_{\text{compounding, air}} = 0.025\%$

### 12.2.3 Conversion

279. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

Open processes solid articles	$F_{\text{conversion, water}} = 0.005\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.025\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.125\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.005\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.025\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.125\%$ (high volatility group)

Open processes foamed articles	$F_{\text{conversion, water}} = 0.01\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.05\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.25\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.01\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.05\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.25\%$ (high volatility group)

Partially open processes	$F_{\text{conversion, water}} = 0.003\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.015\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.075\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.003\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.015\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.075\%$ (high volatility group)

Closed processes	$F_{\text{conversion, water}} = 0.001\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.005\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.025\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.001\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.005\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.025\%$ (high volatility group)

280. For processing significantly in excess of 200°C (see Section 9.1.3), the above emission factors should be increased by 10x.

#### 12.2.4 *Small sites*

281. For smaller sites (<750 tonnes plastic per year) emission factors related to volatile emissions should be increased by 10x. (If higher temperature processing is involved, the need for this further increase of 10x in addition to that in the section above should be considered on a case-by-case basis.) Similar increases in emission factors related to dust emissions should also be considered on a case-by-case basis.

#### 12.2.5 *Service life*

Indoor service, leaching to liquid waste	$F_{\text{service life, water}} = 0.05\%$ over lifetime
Indoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\%$ over lifetime
Outdoor service, leaching to environment	$F_{\text{service life, water}} = 0.16\% \times T_{\text{service}}$ (where $T_{\text{service}}$ = service life of product in years; see <b>Table 4.3</b> )
Outdoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\%$ over lifetime

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

#### 12.2.6 *Disposal*

282. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

283. Emissions from incineration are considered to be negligible, so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0\%$  for incineration.

## 13 POLYMERIC IMPACT MODIFIERS

### 13.1 General description

284. Polymeric impact modifiers are elastomer or elastomer/polymer blends used to increase the resistance of plastics to fracture by interrupting the spread of cracks following a sudden impact. Increased impact resistance can be imparted to brittle plastics by the dispersion of rubbery particles into these materials.

285. Polymeric impact modifiers are low modulus (i.e. rubbery) materials which are blended into plastics, usually forming a separate phase. The degree to which such phase separation occurs is governed by thermodynamic considerations and is clearly dependent on the nature of polymeric additive (i.e. the low modulus polymer) and the nature of the polymers into which it is blended. Impact modifiers may include traditional rubbers such as natural rubber, but copolymers such as from acrylonitrile with butadiene, or from ethylene with vinyl acetate, or from ethylene with propylene are common choices.

286. **Modified Copolymers.** In recent years the trend has been towards increasing complexity of molecular structure, with up to four different monomers involved. Examples include ethylene-propylene -maleic anhydride copolymer or that from ethylene-propylene-maleic anhydride and ethylidene norbornene. Such examples may not necessarily be synthesised in a single polymerisation process, but may require a chemical conversion of an existing polymer. The trend towards more complex polymeric types for use as impact additives may reflect this increasing interest in post-polymerisation chemical modification.

287. The comments here refer to the polymeric molecules themselves and not to any low molecular weight impurities they may contain. It should be recognised that both solvent and monomer residues may be present when post-polymerisation chemical modification has been employed, but their environmental fate has not been considered here.

#### 13.1.1 *Raw materials' handling*

288. The polymers are conventionally supplied in the form of bales or granules, their surface tack (spontaneous adhesion) often preventing their handling in fine powder form. Some grades, however, are available in powder form with particle sizes of 40 microns ( $\mu\text{m}$ ) or less. Moreover their low specific gravities (compared with fillers) can make them prone to flying dust. In such instances, the worst case scenario (i.e. particle size  $<40 \mu\text{m}$  with a total loss of 1.6%) considered for fillers may be prudently applied here.

#### 13.1.2 *Compounding*

289. The physical form of the polymeric impact additive will influence how it is introduced into the plastic. For example, material from bales will first be converted into strips prior to feeding into the polymer. Effectively zero loss can be expected for strip feeding. For granules, finite, albeit small,



losses may be expected and the worst case scenario would be a loss of 0.01% as in the case of fillers with a particle size of >40 µm. For powders, losses may be somewhat higher owing to their susceptibility to dust generation and a worst case scenario could give rise to losses of 0.05% as in the case of fillers with particle sizes of <40 µm.

### **13.1.3 Conversion**

290. These additives are organic polymers which become an integral part of the plastic, whether phase separated or not. It is unlikely that any mechanical operation can separate polymeric impact modifiers from the plastics into which they are mixed. Loss on conversion is effectively zero.

### **13.1.4 Service life**

291. The absence of a simple physical means for separating these components applies also to service. Polymeric impact modifiers are high molecular weight materials and similar in character to the plastic itself and thus not readily susceptible to selective extraction. In this context the work of Roe et al (15) has some relevance. They studied the influence of molecular weight on diffusion and found (for MW range 250 - 1200) the diffusion constant D varied as:

$$D \propto M^{-1.33} \quad \text{where } M = \text{Molecular Weight}$$

292. If this or a similar relationship applies over the wider molecular weight range exhibited by polymeric impact modifiers (M may be infinite if the rubber phase is cross-linked), then migration of a polymeric additive is virtually impossible.

### **13.1.5 Disposal**

293. By virtue of the argument above, loss of additive through leaching by water is not considered important. Thus disposal by landfill could not be expected to lead to separation and loss. Ultimately the loss of additive would be by degradation within the plastic itself (which would also degrade).

294. With respect to incineration, the polymeric additive is combustible and so there will be no release to the environment.

## **13.2 Estimating percentage (%) losses**

### **13.2.1 Raw materials' handling**

295. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The loss factors, for a worst case scenario, are as follows.

For powders of particle size <40 µm,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water

$$F_{\text{handling, air}} = 0\%$$

$$F_{\text{handling, waste}} = 1.0\% \text{ to solid waste as residue in bags}$$

For powders of particle size >40 µm,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water

$$F_{\text{handling, air}} = 0\%$$

$$F_{\text{handling, waste}} = 0.01\% \text{ to solid waste as residue in bags}$$

For bales and strips,  $F_{\text{handling, water}} = 0\%$

$$F_{\text{handling, air}} = 0\%$$

$$F_{\text{handling, waste}} = 0\%$$

### 13.2.2 *Compounding*

296. Initially some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or waste water. On the basis of susceptibility to dust generation the loss factors are as follows (it is assumed that the dust will finally be released to waste water due to cleaning etc.).

For powders of particle size <40 μm	$F_{\text{compounding, water}} = 0.05\%$
	$F_{\text{compounding, air}} = 0\%$

For pellets and powders of particle size >40 μm	$F_{\text{compounding, water}} = 0.01\%$
	$F_{\text{compounding, air}} = 0\%$

For bales and strips	$F_{\text{compounding, water}} = 0\%$
	$F_{\text{compounding, air}} = 0\%$

### 13.2.3 *Conversion*

$$F_{\text{conversion, water}} = 0\%$$

$$F_{\text{conversion, air}} = 0\%$$

### 13.2.4 *Service life*

$$F_{\text{service life, water}} = 0\%$$

$$F_{\text{service life, air}} = 0\%$$

### 13.2.5 *Disposal*

For landfill,  $F_{\text{disposal, water}} = F_{\text{disposal, air}} = \text{zero}$  (additive does not migrate from polymer; it may degrade with the polymer).

For incineration,  $F_{\text{disposal, water}} = F_{\text{disposal, air}} = \text{zero}$  (material destroyed).

## 14 ANTI-STATIC AGENTS

### 14.1 General description

297. Anti-static agents are added to polymers to prevent the build-up of surface charge. To achieve this they may function as lubricants or to create conductive channels. In the former role they are present to reduce friction and hence the opportunity for charge generation. In the latter role they serve to dissipate any charge which is created. Organic materials containing both polar and non-polar groups in the molecule provide one generic type of anti-static agent, and these can function by both mechanisms. Carbon black and particulate metals (powders, flakes, etc.) provide a second generic type, and these function by the second mechanism.

298. Organic anti-static agents include, for example, amines, amides, ammonium salts, alkyl sulphates and alkyl phosphates. All contain long-chain alkyl or alkyloxy groups and are intended to have only partial solubility in the polymer. As a result they are expected to migrate to the surface where they can be most effective.

299. Organic anti-static agents are therefore characteristically solids with molecular weights high enough to suggest low volatility. Nevertheless such molecular weights (250+) are still no higher than those for typical plasticisers, and some anti-static agents (phosphate esters) are structurally similar to plasticisers. Thus measurable volatility cannot be ruled out. Also, their propensity to migration can create an additive-rich surface layer which provides a high susceptibility to leaching losses and an increased opportunity for additive loss through attrition.

300. Hence organic anti-static agents are unusual additives in that they are not designed to remain within the bulk of the plastics into which they are compounded. In the absence of any published model for the environmental loss of anti-static agents, and in view of the diversity of chemical types used, it is proposed that a general model be adapted from existing models in this document. In this case the model to be used will assume that:

- (i) volatility may be as high or low as the full range of plasticisers,
- (ii) leachate or attrition losses will be as high as for any of the additives considered so far.

301. The latter assumption is a reflection of the intended accumulation of anti-static agent in the surface layers. Indeed such a condition may be deliberately created by post-fabrication spraying or dipping, using solutions of the anti-static agent in water or alcohol. This is not a conventional compounding technology, and incorporation losses (which are thought to be minimal) are not considered here. Losses in service, however, are potentially high.

302. Information on the losses of plasticisers from products in use is given in Sections 8.1.4.1 and 8.1.4.2, and loss factors presented in Section 8.2.4. As some anti-static agents are found mostly in the surface layers, the estimates of release from thin films produced by Quackenboss (7) may be more appropriate for vapour losses in these cases (Section 8.1.4.1). For leaching losses, studies have been carried out on removal of plasticisers from thin films at elevated temperatures. The greatest losses

(0.5% per hour) were seen at 58°C in turbulent water (7), but with a range of plasticiser types and an absence of turbulence losses closer to 0.5% per day were observed (4). Unless specific rates or conditions of use are known, it is suggested that a rate of 0.5% per day is used for those anti-static agents which tend to occur at the surface of the plastic.

303. Metal fillers or carbon black operate within the bulk of the plastic and, having no solubility at all in the plastic, have no mechanism for migration. Environmental considerations here are analogous to those for fillers, both with respect to raw materials' handling and to disposal. As with fillers, there are some anti-static agents which will survive incineration.

304. A distinction must therefore be made between the different types of anti-static agent for the purposes of estimating releases, into "organic" and "inorganic" as described in Section 6.1.1. It must be emphasised that this distinction is on the basis of properties and not on composition. On the basis of such a distinction, elemental carbon will be taken here as inorganic. For the most part therefore, and with the inclusion of a wider range of volatilities for the organic types, a model similar to that for dyes and pigments (Section 11) can be applied. However, the release factors from plastics in service are higher for those additives which tend to migrate to the surface.

## 14.2 Estimating percentage (%) losses

305. The loss factors for anti-static agents can be estimated as follows.

### 14.2.1 Raw materials' handling

306. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The emission factors, for a worst case scenario, are as follows:

For powders of particle size <40 µm,	$F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$ to solid waste/water
	$F_{\text{handling, air}} = 0\%$
	$F_{\text{handling, waste}} = 1.0\%$ to solid waste as residue in bags
For powders of particle size >40 µm,	$F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$ to solid waste/water
	$F_{\text{handling, air}} = 0\%$
	$F_{\text{handling, waste}} = 0.01\%$ to solid waste as residue in bags

### 14.2.2 Compounding

307. Initially some emissions will be to atmosphere, but ultimately all particulates will be removed or settle, and vapours will condense to some extent, resulting in losses to both solid waste and waste water (via aqueous washing). It will be assumed here that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

For powders of particle size <40 µm - dry blending and Banbury blending	low volatility group	$F_{\text{compounding, water}} = 0.051\%$
		$F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.055\%$
		$F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.075\%$
		$F_{\text{compounding, air}} = 0.025\%$

	involatile	$F_{\text{compounding, water}} = 0.05\%$
		$F_{\text{compounding, air}} = 0\%$
- plastisol blending	all volatility groups	$F_{\text{compounding, water}} = 0.05\%$
		$F_{\text{compounding, air}} = 0\%$
For powders of particle size $>40 \mu\text{m}$ - dry blending and Banbury blending	low volatility group	$F_{\text{compounding, water}} = 0.011\%$
		$F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.015\%$
		$F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.035\%$
		$F_{\text{compounding, air}} = 0.025\%$
	involatile	$F_{\text{compounding, water}} = 0.01\%$
		$F_{\text{compounding, air}} = 0\%$
- plastisol blending	all volatility groups	$F_{\text{compounding, water}} = 0.01\%$
		$F_{\text{compounding, air}} = 0\%$

### 14.2.3 Conversion

#### 14.2.3.1 Inorganic

308. Ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of attrition of compound the loss factors are as follows.

For grinding/machining  $F_{\text{conversion, water}} = 2.5\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

For all other operations  $F_{\text{conversion, water}} = 0.01\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

#### 14.2.3.2 Organic

309. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

Open processes solid articles  $F_{\text{conversion, water}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.125\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.125\%$  (high volatility group)

Open processes foamed articles  $F_{\text{conversion, water}} = 0.01\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.05\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.25\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.01\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.05\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.25\%$  (high volatility group)

Partially open processes  $F_{\text{conversion, water}} = 0.003\%$  (low volatility group)

$$F_{\text{conversion, water}} = 0.015\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, water}} = 0.075\% \text{ (high volatility group)}$$

$$F_{\text{conversion, air}} = 0.003\% \text{ (low volatility group)}$$

$$F_{\text{conversion, air}} = 0.015\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, air}} = 0.075\% \text{ (high volatility group)}$$

Closed processes

$$F_{\text{conversion, water}} = 0.001\% \text{ (low volatility group)}$$

$$F_{\text{conversion, water}} = 0.005\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, water}} = 0.025\% \text{ (high volatility group)}$$

$$F_{\text{conversion, air}} = 0.001\% \text{ (low volatility group)}$$

$$F_{\text{conversion, air}} = 0.005\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, air}} = 0.025\% \text{ (high volatility group)}$$

310. For processing significantly in excess of 200°C (see Section 9.1.3), the above emission factors should be increased by 10x.

#### 14.2.4 *Small sites*

311. For smaller sites (<750 tonnes plastic per year) emission factors related to volatile emissions should be increased by 10x. (If higher temperature processing is involved, the need for this further increase of 10x in addition to that in the section above should be considered on a case-by-case basis.) Similar increases in emission factors related to dust emissions should also be considered on a case-by-case basis.

#### 14.2.5 *Service life*

##### 14.2.5.1 *Inorganic*

312. Ultimately all particulates will settle and losses will be to solid waste or aqueous washings. On the basis of degradation and abrasion the loss factors are as follows.

$$F_{\text{service life, water}} = 0.01\% \text{ over the service life of the plastic}$$

$$F_{\text{service life, air}} = 0\%$$

##### 14.2.5.2 *Organic*

313. Vapour losses will be to atmosphere. Leachate losses will be to liquid waste.

For losses from surface (leaching loss)

$$F_{\text{service life, water}} = 0.5\% \text{ per day (note that this means complete release in 200 days)}$$

Rate of loss to atmosphere =  $1.1 \times 10^6 \times VP$  % per year (VP = vapour pressure mmHg)

$$F_{\text{service life, air}} = 1.1 \times 10^6 \times VP \times T_{\text{service}} \% \text{ (} T_{\text{service}} \text{ = service life in years; see Table 4.3)}$$

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

#### **14.2.6 Disposal**

314. Factors apply to the annual tonnage used in the region being considered.

315. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

316. For incineration, organic substances will be destroyed so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0$  for incineration. There may be residues of inorganic materials left in the ash, which will be disposed of as solid waste - similar considerations to those above will apply.

## 15 FLAME RETARDANTS

### 15.1 General description

317. Flame retardants, like anti-static agents, are generally solids and may be organic or inorganic. Organic flame retardants function by intercepting active species, such as oxy-radicals, or by breaking down to release agents which can function in the same way. Inorganic flame retardants function in a variety of ways, some as above and some by the release of an inert gas or by undergoing highly endothermic decompositions. Any one flame retardant may function by more than one mechanism and useful co-operation effects ("synergism") are obtained with combinations of flame retardants.

The terms inorganic and organic are used in this section in a more traditional substance composition-related way than in Section 6.1.1 (and elsewhere in the document), but the comments on solubility in the polymer and volatility from Section 6.1.1 are also relevant.

318. Flame retardants are intended to work within the bulk of the plastic and therefore will be expected to be either fully dissolved in the plastic or dispersed as an (insoluble) second phase. Organic flame retardants would be expected to be in the former category and an analogy with plasticisers is evident. Some phosphate plasticisers are also known to have flame retardant action: thus there will be opportunities for volatile loss during compounding as discussed earlier in Sections 8 and 9.

319. The more commonly used organic flame retardants contain halogens, often bromine. As these are usually poly-substituted, volatility might be thought low due to the relatively high molecular weights. For example, the molecular weights of phosphate esters can be increased well beyond 500 by polybromination. However, an inference that such high molecular weights will confer a substantial lack of volatility should not be drawn since polyhalogenated organics are characteristically more volatile than non-halogenated compounds of similar molecular weight. Thus, although polybrominated flame retardants are very often solids, the absence of volatility should not be assumed.

Compound	Mol. Wt.	Weight loss at 200°C (%)
Tetrabromophthalic anhydride	464	0.3
Tetrabromobisphenol A	544	0.1
Pentabromodiphenyl ether	565	1.3
Hexabromocyclododecane	641	7.0
Octabromodiphenyl ether	785	0.5
Decabromodiphenyl ether	959	0.0

320. The data above gives comparative data for TGA analysis at 2°C/min (RT to 200°C) for a selection of bromine-containing flame retardants (**16**). Of these, hexabromocyclododecane gives almost the same order of weight loss as di-2-ethylhexyl phthalate (9.5% to 200°C) which is almost half the molecular weight. These flame retardants are designed to release hydrogen bromide at the temperatures at which plastic ignites and so this weight loss could, in part, be due to decomposition.



321. In the case of organic flame retardants, there is therefore the potential for both dust generation in handling and volatile losses in compounding. The volatility is nonetheless limited and will be taken here to be similar to that of the least volatile of plasticiser and antioxidant groups as defined in Sections 8 and 9. However, for some flame retardants the actual volatility may be more comparable with the medium or even high volatility groups defined for plasticisers, and here it may be more appropriate to use the equivalent emission factors derived for plasticisers in the same volatility grouping.

322. Inorganic flame retardants will form a separate dispersed phase within the plastic, similar to that formed by fillers. Indeed, chemical similarities with fillers may be noted; inorganic flame retardants include metal oxides, hydroxides and carbonates, and fine particle forms are necessary for optimum activity. For these materials the environmental loss considerations will be essentially as those for fillers. Taken together therefore the combined model is not dissimilar to that for colourants.

## 15.2 Estimating Percentage (%) Losses

323. The loss factors for flame retardants can be estimated as follows.

### 15.2.1 Raw materials' handling

324. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or waste water as a result of wash down. Emissions to waste water may also occur in the event of paper sacks being recycled at a different location.

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags  
 For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

### 15.2.2 Compounding

325. Initially some emissions will be to atmosphere, but ultimately all particulates will be removed or settle, and vapours will condense to some extent, resulting in losses to both solid waste and waste water (via aqueous washing). It will be assumed here that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

For powders of low volatility group	$F_{\text{compounding, water}} = 0.051\%$
particle size $<40 \mu\text{m}$ (default)	$F_{\text{compounding, air}} = 0.001\%$
medium volatility group	$F_{\text{compounding, water}} = 0.055\%$
	$F_{\text{compounding, air}} = 0.005\%$
high volatility group	$F_{\text{compounding, water}} = 0.075\%$
	$F_{\text{compounding, air}} = 0.025\%$
inorganic	$F_{\text{compounding, water}} = 0.05\%$
	$F_{\text{compounding, air}} = 0\%$
For powders of low volatility group	$F_{\text{compounding, water}} = 0.011\%$

particle size >40 µm (default)	$F_{\text{compounding, air}} = 0.001\%$
medium volatility group	$F_{\text{compounding, water}} = 0.015\%$
	$F_{\text{compounding, air}} = 0.005\%$
high volatility group	$F_{\text{compounding, water}} = 0.035\%$
	$F_{\text{compounding, air}} = 0.025\%$
inorganic	$F_{\text{compounding, water}} = 0.01\%$
	$F_{\text{compounding, air}} = 0\%$

326. As explained in above, it is expected that most organic flame retardants will fall into the low volatility grouping. However, some flame retardants may be more volatile than this and so the emission factors for the appropriate medium or high volatility groupings could be considered in these cases.

### 15.2.3 Conversion

#### 15.2.3.1 Inorganic

327. Ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of attrition of compound the loss factors are as follows.

For grinding/machining  $F_{\text{conversion, water}} = 2.5\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

For all other operations  $F_{\text{conversion, water}} = 0.01\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

#### 15.2.3.2 Organic

328. Initial losses will be to atmosphere. Subsequent condensation could result in losses to liquid waste. On the basis of volatile losses the loss factors for worst case conditions are as follows. Factors apply to the quantities used on the plastics processing site.

329. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

Open processes solid articles  $F_{\text{conversion, water}} = 0.005\%$  (low volatility group - default)  
 $F_{\text{conversion, water}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.125\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (low volatility group - default)  
 $F_{\text{conversion, air}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.125\%$  (high volatility group)

Open processes foamed articles  $F_{\text{conversion, water}} = 0.01\%$  (low volatility group - default)  
 $F_{\text{conversion, water}} = 0.05\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.25\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.01\%$  (low volatility group - default)  
 $F_{\text{conversion, air}} = 0.05\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.25\%$  (high volatility group)

Partially open processes

	$F_{\text{conversion, water}} = 0.003\%$ (low volatility group - default)
	$F_{\text{conversion, water}} = 0.015\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.075\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.003\%$ (low volatility group - default)
	$F_{\text{conversion, air}} = 0.015\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.075\%$ (high volatility group)

Closed processes

	$F_{\text{conversion, water}} = 0.001\%$ (low volatility group - default)
	$F_{\text{conversion, water}} = 0.005\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.025\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.001\%$ (low volatility group - default)
	$F_{\text{conversion, air}} = 0.005\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.025\%$ (high volatility group)

330. As explained in above, it is expected that most organic flame retardants will fall into the low volatility grouping. However, some flame retardants may be more volatile than this and so the emission factors for the appropriate medium or high volatility groupings could be considered in these cases.

331. For processing significantly in excess of 200°C (see Section 9.1.3), the above loss factors should be increased by 10x.

#### 15.2.4 *Small sites*

332. For smaller sites (<750 tonnes plastic per year) loss factors related to volatile emissions should be increased by 10x. (If higher temperature processing is involved, the need for this further increase of 10x in addition to that in the section above should be considered on a case-by-case basis.) Similar increases in emission factors related to dust emissions should also be considered on a case-by-case basis.

#### 15.2.5 *Service life*

##### 15.2.5.1 *Inorganic*

333. Ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of degradation and abrasion the loss factors are as follows.

$F_{\text{service life, water}} = 0.01\%$ over the service life of the plastic
$F_{\text{service life, air}} = 0\%$

##### 15.2.5.2 *Organic*

Indoor service, leaching to liquid waste	$F_{\text{service life, water}} = 0.05\%$ over lifetime
Indoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\%$ over lifetime
Outdoor service, leaching to environment	$F_{\text{service life, water}} = 0.16\% \times T_{\text{service}}$ (where $T_{\text{service}}$ = service life of product in years; see <b>Table 4.3</b> )
Outdoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\%$ over lifetime

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

### **15.2.6 Disposal**

334. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

335. For incineration, organic substances will be destroyed so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0\%$  for incineration. There may be residues of inorganic materials left in the ash, which will be disposed of as solid waste - similar considerations to those above will apply.

## 16 PRESERVATIVES (BIOCIDES)

### 16.1 General description

336. Protection against fungicidal or bacteriological attack is achieved by the use of established biocides such as organotin or organomercury compounds, or by phenolics or their derivatives. Examples of the latter are the alkyl hydroxybenzoates ( $\text{HOC}_6\text{H}_4\text{CO}_2\text{R}$ ) or the chlorophenols such as 2,2'-thiobis(4,6-dichlorophenol). 8-Hydroxyquinoline or copper bis(8-hydroxyquinoline) are also used, as are other metal salts, notably of antimony, arsenic or borates. These may be expected to embrace a range of solubilities in the polymer and a tendency to surface migration cannot be ruled out, yet as preservatives for plastic, a primary requirement is that these additives at least remain within it.

337. The above reference to permanence is intended to clarify the function of these materials, as similar materials may also be used in anti-fouling applications where the requirement is to keep the surface clean rather than protect the plastic. In the latter role the additive is sacrificial as it is intended to be released into the environment (i.e. marine) where it may be considered that its biocidal action lies. Thus such additives may be perceived as operating in a slow-release manner.

338. That similar types of chemicals may be made to function in both media (i.e. within the plastic or the environment outside it) is made possible by the use of chemically labile species. Thus it is chemical breakdown products (from hydrolysis) of these additives which are most likely to function in this slow-release role. As it is not usually the additive itself which migrates out of the plastic, anti-fouling action will not be considered in this discussion, but the existence of this form of biocidal action should be noted when considering the wider environmental implication of preservatives.

339. Within the established preservatives for plastics, even the most volatile are solids. Thus 8-hydroxyquinoline has a normal boiling point of only  $267^\circ\text{C}$ , but melts at  $73\text{-}75^\circ\text{C}$ . Methyl-p-hydroxybenzoate melts at  $125\text{-}128^\circ\text{C}$  but boils with decomposition at around  $275^\circ\text{C}$ . Whilst such examples are comparable in volatility with the most volatile of phthalates (dimethyl phthalate, bp  $284^\circ\text{C}$ ) the handling characteristics are those of solids.

340. Recognisable, albeit lower, volatility exists for organometallics such as bis(tributyltin) oxide (bp  $210\text{-}214^\circ\text{C}/10\text{ mmHg}$ ), and may be assumed to occur with other organic preservatives such as chlorinated phenol derivatives which have molecular weights no higher than commodity antioxidants. Yet not all preservatives may be considered volatile in this sense; zinc borate for example is a solid of melting point  $980^\circ\text{C}$ . To estimate environmental release, a distinction should be made between organic (including organometallic) and inorganic types. Organic types may be taken as similar to antioxidants (in their full volatility range) once mixing has been accomplished. Inorganic types must be considered analogous to fillers from initial handling through to ultimate disposal. These various considerations suggest an environmental loss model similar to that in Section 14 for anti-static agents, but with losses from plastics in use as for plasticisers (as preservatives have less tendency to migrate to the surface as anti-static agents).

## 16.2 Estimating percentage (%) losses

341. The loss factors for preservatives can be estimated as follows.

### 16.2.1 Raw materials' handling

342. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The loss factors, for a worst case scenario, are as follows.

For powders of particle size  $<40\ \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags

For powders of particle size  $>40\ \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

### 16.2.2 Compounding

343. Initial losses will be to atmosphere, but ultimately particulates will settle, and vapours will condense to some extent, resulting in losses to both solid waste and aqueous washings. It will be assumed here that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

For powders of particle size $<40\ \mu\text{m}$	low volatility group	$F_{\text{compounding, water}} = 0.051\%$ $F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.055\%$ $F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.075\%$ $F_{\text{compounding, air}} = 0.025\%$
For powders of particle size $>40\ \mu\text{m}$	low volatility group	$F_{\text{compounding, water}} = 0.011\%$ $F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.015\%$ $F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.035\%$ $F_{\text{compounding, air}} = 0.025\%$

### 16.2.3 Conversion

344. Factors apply to the quantities used on the plastics processing site.

#### 16.2.3.1 Inorganic

345. Ultimately all particulates will settle and losses will be to solid waste or aqueous washings. On the basis of attrition of compound the loss factors are as follows.

For grinding/machining  $F_{\text{conversion, water}} = 2.5\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

For all other operations  $F_{\text{conversion, water}} = 0.01\%$  to solid waste/water  
 $F_{\text{conversion, air}} = 0\%$

### 16.2.3.2 Organic

346. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

Open processes solid articles  $F_{\text{conversion, water}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.125\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.025\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.125\%$  (high volatility group)

Open processes foamed articles  $F_{\text{conversion, water}} = 0.01\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.05\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.25\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.01\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.05\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.25\%$  (high volatility group)

Partially open processes  $F_{\text{conversion, water}} = 0.003\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.015\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.075\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.003\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.015\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.075\%$  (high volatility group)

Closed processes  $F_{\text{conversion, water}} = 0.001\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.005\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.001\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.025\%$  (high volatility group)

347. For processing significantly in excess of 200°C (see Section 9.1.3), the above emission factors should be increased by 10x.

### 16.2.4 Small sites

348. For smaller sites (<750 tonnes plastic per year) emission factors related to volatile emissions should be increased by 10x. (If higher temperature processing is involved, the need for this further increase of 10x in addition to that in the section above should be considered on a case-by-case basis.) Similar increases in emission factors related to dust emissions should also be considered on a case-by-case basis.

## 16.2.5 *Service life*

### 16.2.5.1 *Inorganic*

349. Ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of degradation and abrasion the loss factors are as follows.

$$F_{\text{service life, water}} = 0.01\% \text{ over the service life of the plastic}$$

$$F_{\text{service life, air}} = 0\%$$

### 16.2.5.2 *Organic*

Indoor service, leaching to liquid waste	$F_{\text{service life, water}} = 0.05\% \text{ over lifetime}$
Indoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\% \text{ over lifetime}$
Outdoor service, leaching to environment	$F_{\text{service life, water}} = 0.16\% \times T_{\text{service}}$ (where $T_{\text{service}}$ = service life of product in years; see <b>Table 4.3</b> )
Outdoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\% \text{ over lifetime}$

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

## 16.2.6 *Disposal*

350. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

351. For incineration, organic substances will be destroyed so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0$  for incineration. There may be residues of inorganic materials left in the ash, which will be disposed of as solid waste - similar considerations to those above will apply.



## 17 CURING AGENTS

### 17.1 General description

352. The process of "cure" involves the cross-linking of polymer chains. Once cross-linked, the product has infinite molecular weight and is no longer capable of flow without some chemical breakdown of the network (i.e. scission of the cross links). The extent of this physical change governs the processing regime and cross-linked polymers (the so-called "thermosetting" plastics) are often obtained from dedicated formulations using specialised fabrication techniques (hand lay-up, etc.). In such dedicated systems, the cross-linking agent is not necessarily an additive per se, but is more properly a co-monomer introduced early in the polymerisation process. Such cross-linking agents (styrene, formaldehyde, etc.) would indeed be described as monomers rather than additives.

353. There are some initiators and catalysts for this cross-linking process which may be introduced at the outset, in network-forming polymerisations or as additives in thermoplastic compounding. The former include hydroperoxides, dialkyl- or diaryl- peroxides and sometimes peroxide decomposition promoters (redox salts, tertiary aromatic amines). The latter include organic peroxides as above or speciality reaction catalysts such as organotin compounds for promoting silanol condensations. Commonly, it is these various peroxides which are termed "curing agents". There are both solid and liquid types.

354. The chemical instability of organic peroxides places restrictions on their handling. There are basic safety considerations, and it may be anticipated that such reactive materials will be handled with greater care than used for other plastics additives. Thus to some extent, the care necessary in handling will help to limit environmental loss, although agglomeration effects may still present problems in bag emptying. If accidentally spilled, their lifetimes may be too short to present a hazard to either atmospheric or aqueous environments. Once in the plastic, they would begin to decompose as fabrication commences and would be expected to be fully destroyed once fabrication is complete.

### 17.2 Estimating percentage (%) losses

#### 17.2.1 Raw materials' handling

##### 17.2.1.1 Solid curing agents

355. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The loss factors, for a worst case scenario, are as follows:

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water

$$F_{\text{handling, air}} = 0\%$$

$$F_{\text{handling, waste}} = 1.0\% \text{ to solid waste as residue in bags}$$

For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water

$$F_{\text{handling, air}} = 0\%$$

$$F_{\text{handling, waste}} = 0.01\% \text{ to solid waste as residue in bags}$$

*17.2.1.2 Liquid curing agents*

356. Losses will be to liquid waste. On the basis of incidental losses,

$$F_{\text{handling, water}} = 0.01\% \text{ (i.e. minimal)}$$

$$F_{\text{handling, air}} = 0\%$$

**17.2.2 Compounding**

*17.2.2.1 Solid curing agents*

357. Initially some losses will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or waste water. On the basis of susceptibility to dust generation the loss factors are as follows.

For powders of particle size <40 µm

$$F_{\text{compounding, water}} = 0.05\%$$

$$F_{\text{compounding, air}} = 0\%$$

For pellets and powders of particle size >40 µm

$$F_{\text{compounding, water}} = 0.01\%$$

$$F_{\text{compounding, air}} = 0\%$$

*17.2.2.2 Liquid curing agents*

358. Initial losses will be to atmosphere. Vapours will condense to some extent, resulting in losses to both solid waste and aqueous washings. It will be assumed here that the volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

$$F_{\text{compounding, water}} = 0.005\%$$

$$F_{\text{compounding, air}} = 0.005\%$$

**17.2.3 Conversion, service life and disposal**

Assume  $F_{\text{conversion}} = F_{\text{service life}} = F_{\text{disposal}} = \text{zero}$  (material destroyed) for both air and water.

## 18 BLOWING AGENTS

### 18.1 General description

359. Blowing agents are required to produce "cellular" or "foamed" plastics and may operate by either physical or chemical means. Physical blowing agents are volatile liquids, compressed liquefied gases or gases themselves. Examples include low molecular weight hydrocarbons, chlorocarbons or chlorofluorocarbons, or vapours and gases such as carbon dioxide and nitrogen. Chemical blowing agents include materials which can break down on heating to yield either carbon dioxide (sodium bicarbonate) or nitrogen (organic nitrogen compounds - azo derivatives, hydrazides, etc.). Thus the range of blowing agents used in plastics is diverse, embracing gases, liquids and solids, both organic and inorganic.

360. Any assessment of environmental release should clearly acknowledge this wide difference in character and, more specifically, the difference in blowing agent action. In making such an assessment it must be known whether the additive is a physical or chemical type.

361. By their nature, physical blowing agents will need special containment in handling and present limited opportunities for loss unless accident or malfunction occurs. Such special containment could include pressurised pipework, and leakage from taps and valves is not unusual. This must be accommodated in the loss factor and a nominal value of 1% is used here.

362. Once in the plastic the physical blowing agents will change to vapour or gaseous form as they first fill the cells of the foamed structure they create. An exchange with atmospheric gases will then follow at a rate dependent on permeation through the cell walls. Complete release to the atmosphere will eventually ensue, perhaps in only a matter of hours.

363. Chemical blowing agents are powders which may be handled in conventional fashion if their chemical stability allows this. Once in the plastic and taken to their decomposition temperatures, they may be expected to be completely destroyed. Indeed, when the plastic is of the thermoplastic type, this exchange must be completed before dimensional stability can be assured and thus a brief period of 'in-situ' storage may be an essential part of the conversion process.

364. For thermosetting (i.e. cross-linked) plastics, dimensional stability may be obtained before this exchange is complete and residues of the blowing agent may be carried through into the product foam. This is most likely to occur with higher molecular blowing agents where diffusion will be retarded somewhat as a consequence of the molecular sizes involved. A worst case scenario is that no exchange takes place in the cross-linked product before it leaves the factory. Such a scenario must recognise that losses will still occur during the process of conversion whilst the cross-linked structure is forming. For a rigid polyurethane or polyisocyanurate insulating foams, which may be blown to forty-fold or even fifty-fold volume expansions, a materials balance on representative formulations suggest perhaps a 50% loss of blowing agent on conversion. On this basis only the remaining 50% will be lost on service.

365. Only the physical blowing agents include molecules large enough to allow diffusion losses to extend into service and this situation is only of technical importance for thermosetting plastics. Thus the respective loss factors must be dependent on the generic type of plastic; i.e. whether thermoplastic or thermosetting.

366. Another type of chemical which may be required for blowing is a nucleating agent. Nucleating agents are introduced to prevent the formation of super-saturated solutions within the plastic by offering sites for cell formation. Such nucleating agents are commonly fine suspended particles (i.e. like fillers). Nucleating agents are often not required when chemical blowing agents are used (the solid residue from decomposition providing a suitable site), but may be expected to be used when physical blowing agents are employed.

## 18.2 Estimating percentage (%) losses

### 18.2.1 Raw materials' handling

#### 18.2.1.1 Chemical blowing agents (solids)

367. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The loss factors, for a worst case scenario, are as follows.

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags  
 For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

#### 18.2.1.2 Physical blowing agents (liquids and gases)

368. Losses will be to atmosphere. On the basis of incidental losses (leakages in pipes, etc),

$F_{\text{handling, water}} = 0\%$   
 $F_{\text{handling, air}} = 1\%$

### 18.2.2 Compounding

#### 18.2.2.1 Chemical blowing agents

369. Initially some losses will be to atmosphere, but ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of susceptibility to dust generation the loss factors are as follows.

For powders of particle size  $<40 \mu\text{m}$   $F_{\text{compounding, water}} = 0.05\%$   
 $F_{\text{compounding, air}} = 0\%$   
 For pellets and powders of particle size  $>40 \mu\text{m}$   $F_{\text{compounding, water}} = 0.01\%$   
 $F_{\text{compounding, air}} = 0\%$

*18.2.2.2 Physical blowing agents*

370. Practical constraints with physical blowing agents usually result in compounding and conversion being carried out as rapid sequential processes in essentially the same equipment. A combined loss factor will be discussed below.

**18.2.3 Conversion***18.2.3.1 Chemical blowing agents*

Assume  $F_{\text{compounding/conversion}} = \text{zero}$  (additive destroyed) for both water and air.

*18.2.3.2 Physical blowing agents*

Thermoplastic materials

$$\begin{aligned} F_{\text{compounding, water}} + F_{\text{conversion, water}} &= 0\% \\ F_{\text{compounding, air}} + F_{\text{conversion, air}} &= 100 - F_{\text{handling, air}} \% \end{aligned}$$

Thermosetting materials

$$\begin{aligned} F_{\text{compounding, water}} + F_{\text{conversion, water}} &= 0\% \\ F_{\text{compounding, air}} + F_{\text{conversion, air}} &= 50 - F_{\text{handling, air}} \% \end{aligned}$$

**18.2.4 Service life***18.2.4.1 Chemical blowing agents*

$F_{\text{service life}} = \text{zero}$  (additive destroyed or already lost) for both air and water.

*18.2.4.2 Physical blowing agents*

Thermosetting materials

$$\begin{aligned} F_{\text{service life, water}} &= 0\% \\ F_{\text{service life, air}} &= 100\% \text{ of compound which reaches this stage} \end{aligned}$$

*All other types*

$F_{\text{service life}} = \text{zero}$  (additive destroyed or already lost) for both air and water.

**18.2.5 Disposal**

$F_{\text{disposal}} = \text{zero}$  (additive destroyed or already lost) for both air and water.

## 19 HEAT STABILISERS

### 19.1 General description

371. There are some types of plastic that have insufficient thermal stability to survive even the short-term temperature excursions in conventional thermoplastics' processing. PVC is one such example which can start to undergo thermal decomposition (dehydrochlorination) at temperatures around 70°C. Other halogen-containing polymers may undergo similar decomposition, whilst polyvinyl acetate can decompose with the loss of acetic acid. For these polymers which have limited thermal stability, appropriate heat stabilisers are required to provide appropriate protection during processing.

372. Such thermal elimination reactions are themselves subject to catalysis by acids, producing an element of autocatalytic character and making the polymers especially vulnerable to additives which are themselves acidic. Thus successful heat stabilisers are acid acceptors but they do not generate potentially destabilising species by reaction with that acid. For example, basic lead salts are widely used in PVC stabilisation because the lead chloride formed does not itself promote PVC dehydrochlorination. Specific examples used include basic lead carbonate (white lead), dibasic lead phosphite or tribasic lead sulphate.

373. Other heavy metal compounds may be used, including salts of organic species such as barium phenate or cadmium laurate. Carboxylates or mercaptides are used in organometallic stabilisers such as dioctyltin dilaurate or dibutyltin di-iso-octylthioglycollate. Such is the range of possibilities, and the concern over producing an abundance of a single potentially destabilising by-product, that multi-component combinations of metal salts or soaps, etc. are often used. Thus a variety of individual species may be encountered, singly or in combination, as heat stabilisers for plastics.

374. Not all heat stabilisers are involatile inorganic salts or organic derivatives of such high molecular weight to preclude concerns over volatility. Metal soaps can sublime and an organometallic heat stabiliser, such as dibutyltin diacetate (bp 145°C at 10 mmHg) is more volatile than many plasticisers. The list of possibilities is not only limited to metal compounds, as other acid acceptors, such as amines or epoxides are also used. Of these, the former includes materials as volatile as 2-phenylindole (bp 250°C at 10 mmHg). Thus it must be recognised that heat stabilisers encompass a diversity of molecular types, organic or inorganic and singly or in combination. They may be as volatile as plasticisers or as involatile as fillers: the majority are solids, but some (e.g. commercial dibutyltin dilaurate) are liquids.

The use of the terms "volatile solids and "non-volatile solids" in this section should be taken as analogous to the "organic" and "inorganic" terms in Section 6.1.1.

375. Against this varied background, there is the restriction that compounding temperatures will not be as high as for many plastics owing to ultimate limitation on thermal stability. Compounding conditions and process temperatures may be taken as similar to those for PVC, as indeed PVC is the largest tonnage plastic requiring heat stabilisation. Thus the environmental model similar to that for plasticiser emission (Section 8.2) is used here for the liquid and volatile solid heat stabilisers. Such a model cannot cover the inorganic salts, although the latter must be in fine particulate form (for good dispersion in the plastic when there is negligible solubility) and therefore similar in environmental character to fillers. For inorganic salts the model for fillers using the particle size criteria of <40 µm and >40 µm is appropriate.

## 19.2 Estimating percentage (%) losses

### 19.2.1 Raw materials' handling

#### 19.2.1.1 Solids

376. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The loss factors, for a worst case scenario, are as follows.

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags

For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

#### 19.2.1.2 Liquids

377. Losses will be to liquid waste.

$F_{\text{handling, water}} = 0.01\%$  (for all volatility groups)  
 $F_{\text{handling, air}} = 0\%$  (for all volatility groups)

### 19.2.2 Compounding

#### 19.2.2.1 Non-volatile solids

378. Initially some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water. On the basis of susceptibility to dust generation the loss factors are as follows.

For powders of particle size  $<40 \mu\text{m}$   $F_{\text{compounding, water}} = 0.05\%$   
 $F_{\text{compounding, air}} = 0\%$

For powders of particle size  $>40 \mu\text{m}$   $F_{\text{compounding, water}} = 0.01\%$   
 $F_{\text{compounding, air}} = 0\%$

#### 19.2.2.2 Volatile solids

379. Initially some emissions will be to atmosphere, but ultimately all particulates will be removed or settle, and vapours will condense to some extent, resulting in losses to both solid waste and waste water (via aqueous washing). It will be assumed here that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

For powders of low volatility group  $F_{\text{compounding, water}} = 0.051\%$   
 particle size  $<40 \mu\text{m}$  - dry  $F_{\text{compounding, air}} = 0.001\%$   
 blending and Banbury medium volatility group  $F_{\text{compounding, water}} = 0.055\%$

blending	high volatility group	$F_{\text{compounding, air}} = 0.005\%$ $F_{\text{compounding, water}} = 0.075\%$
-plastisol blending	all volatility groups	$F_{\text{compounding, air}} = 0.025\%$ $F_{\text{compounding, water}} = 0.05\%$ $F_{\text{compounding, air}} = 0\%$
For powders of particle size $>40 \mu\text{m}$ - dry blending and Banbury blending	low volatility group	$F_{\text{compounding, water}} = 0.011\%$ $F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.015\%$ $F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.035\%$ $F_{\text{compounding, air}} = 0.025\%$
- plastisol blending	all volatility groups	$F_{\text{compounding, water}} = 0.01\%$ $F_{\text{compounding, air}} = 0\%$

### 19.2.2.3 Liquids

For dryblending and Banbury blending	$F_{\text{compounding, water}} = 0.001\%$ (low volatility group)
	$F_{\text{compounding, water}} = 0.005\%$ (medium volatility group)
	$F_{\text{compounding, water}} = 0.025\%$ (high volatility group)
For plastisol compounding	$F_{\text{compounding, air}} = 0.001\%$ (low volatility group)
	$F_{\text{compounding, air}} = 0.005\%$ (medium volatility group)
	$F_{\text{compounding, air}} = 0.025\%$ (high volatility group)
	$F_{\text{compounding, water}} = 0\%$ (all volatility groups)
	$F_{\text{compounding, air}} = 0\%$ (all volatility groups)

## 19.2.3 Conversion

### 19.2.3.1 All solids

380. Ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water. On the basis of wear of plastic material the loss factors are as follows.

For grinding/machining	$F_{\text{conversion, water}} = 2.5\%$ to solid waste/water
	$F_{\text{conversion, air}} = 0\%$
For all other operations	$F_{\text{conversion, water}} = 0.01\%$ to solid waste/water
	$F_{\text{conversion, air}} = 0\%$

### 19.2.3.2 Volatiles

381. Factors apply to the quantities used on the plastics processing site, and represent to total loss. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

For calendering	$F_{\text{conversion, water}} = 0.005\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.025\%$ (medium volatility group)



$$F_{\text{conversion, water}} = 0.125\% \text{ (high volatility group)}$$

$$F_{\text{conversion, air}} = 0.005\% \text{ (low volatility group)}$$

$$F_{\text{conversion, air}} = 0.025\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, air}} = 0.125\% \text{ (high volatility group)}$$

For extrusion

$$F_{\text{conversion, water}} = 0.001\% \text{ (low volatility group)}$$

$$F_{\text{conversion, water}} = 0.005\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, water}} = 0.025\% \text{ (high volatility group)}$$

$$F_{\text{conversion, air}} = 0.001\% \text{ (low volatility group)}$$

$$F_{\text{conversion, air}} = 0.005\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, air}} = 0.025\% \text{ (high volatility group)}$$

For blown film

$$F_{\text{conversion, water}} = 0.005\% \text{ (low volatility group)}$$

$$F_{\text{conversion, water}} = 0.025\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, water}} = 0.125\% \text{ (high volatility group)}$$

$$F_{\text{conversion, air}} = 0.005\% \text{ (low volatility group)}$$

$$F_{\text{conversion, air}} = 0.025\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, air}} = 0.125\% \text{ (high volatility group)}$$

For injection moulding

$$F_{\text{conversion, water}} = 0.001\% \text{ (low volatility group)}$$

$$F_{\text{conversion, water}} = 0.005\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, water}} = 0.025\% \text{ (high volatility group)}$$

$$F_{\text{conversion, air}} = 0.001\% \text{ (low volatility group)}$$

$$F_{\text{conversion, air}} = 0.005\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, air}} = 0.025\% \text{ (high volatility group)}$$

For spread coating

$$F_{\text{conversion, water}} = 0.005\% \text{ (low volatility group)}$$

$$F_{\text{conversion, water}} = 0.025\% \text{ (medium volatility group)}$$

$$F_{\text{conversion, water}} = 0.125\% \text{ (high volatility group)}$$

382. If information on the specific process being used is not available, then the following factors are suggested for a medium volatility substance.

Default (for a medium volatility Substance)

$$F_{\text{conversion, water}} = 0.005\% \text{ (closed processes)}$$

$$F_{\text{conversion, water}} = 0.015\% \text{ (partially open processes)}$$

$$F_{\text{conversion, water}} = 0.025\% \text{ (open processes)}$$

$$F_{\text{conversion, air}} = 0.005\% \text{ (closed processes)}$$

$$F_{\text{conversion, air}} = 0.015\% \text{ (partially open processes)}$$

$$F_{\text{conversion, air}} = 0.025\% \text{ (open processes)}$$

383. These factors apply to the production of solid articles. For foamed articles, losses are estimated to be double those for open processes.

#### 19.2.4 *Small sites*

384. All the above values relate to situations where fume elimination equipment is in operation, i.e. larger sites. For smaller sites (<250 tonnes plasticiser per year, which corresponds to ~750 tonnes of plastic) the emission factors related to volatile emissions should be increased by 10x. (If higher temperature processing is involved, the need for this further increase of 10x in addition to that in the section above should be considered on a case-by-case basis.) Similar increases in emission factors related to dust emissions should also be considered on a case-by-case basis.

## 19.2.5 *Service life*

### 19.2.5.1 *Solids*

385. Ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of degradation and abrasion the loss factors are as follows.

$$F_{\text{service life, water}} = 0.01\% \text{ over lifetime}$$

$$F_{\text{service life, air}} = 0\%$$

### 19.2.5.2 *Volatiles*

386. Factors apply to the annual tonnage used in the region being considered.

Indoor service, leaching to liquid waste	$F_{\text{service life, water}} = 0.05\% \text{ over lifetime}$
Indoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\% \text{ over lifetime}$
Outdoor service, leaching to environment	$F_{\text{service life, water}} = 0.16\% \times T_{\text{service}}$ (where $T_{\text{service}}$ = service life of product in years; see <b>Table 4.3</b> )
Outdoor service, volatility to atmosphere	$F_{\text{service life, air}} = 0.05\% \text{ over lifetime}$

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

## 19.2.6 *Disposal*

387. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

388. For incineration, organic substances will be destroyed so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0$  for incineration. There may be residues of inorganic materials left in the ash, which will be disposed of as solid waste - similar considerations to those above will apply.

## 20 SLIP PROMOTERS

### 20.1 General description

389. Slip promoters are additives which are capable of migrating to the surface of the plastic to ease processing (i.e. increase extrusion rates, etc.). They achieve this by an appropriate combination of molecular size (for rapid diffusion) and partial solubility. Examples of such materials include Ca and Zn stearates, waxes and fatty acid amides or esters.

390. Such materials are generally waxy, but often available as soft powders. Handling losses may be similar to fillers and the model based on size criteria is appropriate for raw materials handling and dust generation during compounding. They are expected to migrate to the surface rapidly on heating and therefore can be lost by attrition or, in some cases, volatilisation, as some metal soaps (zinc stearate) are capable of sublimation. Indeed the absence of a volatile risk cannot be assumed for any such metal soap. Thus there could be both particulate and volatile losses throughout compounding and conversion cycle. In this respect the environmental losses are similar to the organic anti-static agents (Section 14.2) and a similar model will be used here. As for anti-static agents, a distinction between “inorganic” and “organic” on the basis of properties is made (see Section 6.1.1).

### 20.2 Estimating percentage (%) losses

391. The loss factors for slip promoters can be estimated as follows.

#### 20.2.1 Raw materials' handling

392. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The emission factors, for a worst case scenario, are as follows.

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water

$F_{\text{handling, air}} = 0\%$

$F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags

For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water

$F_{\text{handling, air}} = 0\%$

$F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

#### 20.2.2 Compounding

393. Initial losses will be to atmosphere, but ultimately particulates will be removed or will settle, and vapours will condense, resulting in losses to both solid waste and aqueous washings. It will be assumed here that all particulate losses will eventually be to waste water and that volatilisation loss will condense to some extent and eventually be released 50% to air and 50% to waste water. These assumptions are included in the emission factors given below.

For powders of particle size <40 µm	low volatility group	$F_{\text{compounding, water}} = 0.051\%$ $F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.055\%$ $F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.075\%$ $F_{\text{compounding, air}} = 0.025\%$
For powders of particle size >40 µm	low volatility group	$F_{\text{compounding, water}} = 0.011\%$ $F_{\text{compounding, air}} = 0.001\%$
	medium volatility group	$F_{\text{compounding, water}} = 0.015\%$ $F_{\text{compounding, air}} = 0.005\%$
	high volatility group	$F_{\text{compounding, water}} = 0.035\%$ $F_{\text{compounding, air}} = 0.025\%$

### 20.2.3 Conversion

#### 20.2.3.1 Inorganic

394. Ultimately all particulates will settle and losses will be to solid waste or waste water. On the basis of attrition of compound the loss factors are as follows (as worst case, to waste water).

For grinding/machining	$F_{\text{conversion}} = 2.5\%$
For all other processes	$F_{\text{conversion}} = 0.01\%$

#### 20.2.3.2 Organic

395. These losses will initially be to air at elevated temperature. However subsequent condensation could result in losses to liquid waste. As a worst case it could be assumed that 50% of this is lost to waste water and 50% is lost to the atmosphere. This assumption has been used in the emission factors reported below.

Open processes solid articles	$F_{\text{conversion, water}} = 0.005\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.025\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.125\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.005\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.025\%$ (medium volatility group)
Open processes foamed articles	$F_{\text{conversion, water}} = 0.125\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.125\%$ (high volatility group)
	$F_{\text{conversion, water}} = 0.01\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.05\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.25\%$ (high volatility group)
Partially open processes	$F_{\text{conversion, air}} = 0.01\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.05\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.25\%$ (high volatility group)
	$F_{\text{conversion, water}} = 0.003\%$ (low volatility group)
	$F_{\text{conversion, water}} = 0.015\%$ (medium volatility group)
	$F_{\text{conversion, water}} = 0.075\%$ (high volatility group)
	$F_{\text{conversion, air}} = 0.003\%$ (low volatility group)
	$F_{\text{conversion, air}} = 0.015\%$ (medium volatility group)
	$F_{\text{conversion, air}} = 0.075\%$ (high volatility group)

Closed processes  $F_{\text{conversion, water}} = 0.001\%$  (low volatility group)  
 $F_{\text{conversion, water}} = 0.005\%$  (medium volatility group)  
 $F_{\text{conversion, water}} = 0.025\%$  (high volatility group)  
 $F_{\text{conversion, air}} = 0.001\%$  (low volatility group)  
 $F_{\text{conversion, air}} = 0.005\%$  (medium volatility group)  
 $F_{\text{conversion, air}} = 0.025\%$  (high volatility group)

396. For processing significantly in excess of 200°C (see Section 9.1.3), the above emission factors should be increased by 10x.

#### 20.2.4 *Small sites*

397. For smaller sites (<750 tonnes plastic per year) emission factors related to volatile emissions should be increased by 10x. (If higher temperature processing is involved, the need for this further increase of 10x in addition to that in the section above should be considered on a case-by-case basis.) Similar increases in emission factors related to dust emissions should also be considered on a case-by-case basis.

#### 20.2.5 *Service life*

##### 20.2.5.1 *Inorganic*

398. Ultimately all particulates will settle and losses will be to solid waste or aqueous washings. On the basis of degradation and abrasion the loss factors are as follows.

$$F_{\text{service life, water}} = 0.01\% \text{ over service life}$$

$$F_{\text{service life, air}} = 0\%$$

##### 20.2.5.2 *Organic*

399. Vapour losses will be to atmosphere. Leachate losses will be to liquid waste.

For losses from surface (leaching loss)

$$F_{\text{service life, water}} = 0.5\% \text{ per day (note that this means complete release in 200 days)}$$

Rate of loss to atmosphere =  $1.1 \times 10^6 \times \text{VP}$  % per year (VP = vapour pressure mmHg)

$$F_{\text{service life, air}} = 1.1 \times 10^6 \times \text{VP} \times T_{\text{service}} \% \text{ (} T_{\text{service}} = \text{service life in years; see Table 4.3)}$$

An alternative method for estimating the emission factor for vapour losses over the service life of additives from polymers in general is included in Appendix IV.

#### 20.2.6 *Disposal*

400. Landfill, leaching losses to water ( $F_{\text{disposal, water}}$ ). These will depend on many factors, relating to the type of landfill as well as to the properties of the additive and the nature of the polymer in which it has been used. The maximum potential loss could be calculated from the amount of additive remaining in the plastic at disposal, but it is very unlikely that this amount would be released. The volatilisation loss from landfill is likely to be limited ( $F_{\text{disposal, air}} = 0\%$ ).

401. For incineration, organic substances will be destroyed so  $F_{\text{disposal, air}} = F_{\text{disposal, water}} = 0$  for incineration. There may be residues of inorganic materials left in the ash, which will be disposed of as solid waste - similar considerations to those above will apply.

## 21 VISCOSITY AIDS

### 21.1 General description

402. Viscosity aids are additives which are used to regulate the viscosity of PVC-plasticiser- solvent mixtures during processing. They are suspended particles where the particles themselves are polymers which have a low affinity for plasticiser.

403. To avoid reinforcement effects, these particles must be of suitably low modulus, a requirement which excludes the use of mineral or other fillers. Thus these additives are polymers - different from PVC - present in fine particulate form. These materials therefore possess something of the character of fillers with respect to handling and the model based on size criteria (Section 7) is applicable here. For subsequent stages the model described for polymeric impact modifiers (Section 13) is applicable. Viscosity aids have exceptionally high molecular weights and therefore volatile losses are negligible.

### 21.2 Estimating percentage (%) losses

#### 21.2.1 Raw materials' handling

404. Factors apply to the quantities used on the plastics processing site.

405. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water as a result of wash down. Material remaining in packaging (bags) will be assumed to go to solid waste from the plastics processing site. The loss factors, for a worst case scenario, are as follows.

For powders of particle size  $<40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.5) = 0.6\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 1.0\%$  to solid waste as residue in bags  
 For powders of particle size  $>40 \mu\text{m}$ ,  $F_{\text{handling, water}} = (0.1 + 0.1) = 0.2\%$  to solid waste/water  
 $F_{\text{handling, air}} = 0\%$   
 $F_{\text{handling, waste}} = 0.01\%$  to solid waste as residue in bags

#### 21.2.2 Compounding

406. Factors apply to the quantities used on the plastics processing site.

407. Initially, some emissions will be to atmosphere, but ultimately all particulates will be removed or settle and losses will be to solid waste or to waste water. On the basis of susceptibility to dust generation the loss factors are as follows:

For powders of particle size  $<40 \mu\text{m}$   $F_{\text{compounding, water}} = 0.05\%$   
 $F_{\text{compounding, air}} = 0\%$





**22 REFERENCES**

1. N.G. Stanley-Wood, "Size Enlargement", Ch. 9 in "Principles of Powder Technology", ed. M.J. Rhodes, Wiley, Chichester, 1990.
2. M.J. Rhodes, School of Powder Technology, Department of Chemical Engineering, Bradford University, personal communication.
3. R.G. Dorman, "Dust Control and Air Cleaning", Pergamon Press, Oxford, 1974.
4. J.K. Sears and J.R. Darby, "The Technology of Plasticisers", Wiley, New York, 1982.
5. Cadogan et al, Progress in Rubber and Plastics Technology, 1994, **10** (1), 1 (see also CEFIC report D/1996/3158/9)
6. A.C. Poppe, Kunststoffe German Plastics, 1991, **81**, 310-313.
7. H.M. Quackenboss Jr., Plasticisers in Vinyl Chloride Resins, Ind. Eng. Chem., 1954, 46, 1335-1344.
8. Environ Corporation, see CEFIC Report D/1996/3158/9).
9. Menzel, Kunststoffe, 1996, **86**, 992-996.
10. C.J. Hawick and S. McCardy, J. Vinyl and Additive Technology, 1996, **2**(2), 134-142.
11. Forbo Forshaga report by B. Johnart, 30/4/96.
12. Patuska, Kautch Gummi Kunststoffe, 1988, **41**, 451.
13. Yu.I. Temchin, E.F. Burmistrov and V.V. Zalevskii, Soviet Plastics, 1967(3), 74.
14. P.D. Calvert and N.C. Billingham, J. Appl. Polym. Sci., 1979, 24, 357.
15. R.J. Roe, H.E. Bair and C. Gieniewski, J. Appl. Polym. Sci., 1974, 18, 843.
16. R. Gächter and H. Müller, "Plastics Additives Handbook", Henser, Munich, 1985.
17. F.T. Miles, Ind. Eng. Chem., 1943, 35, 1052.

**APPENDIX I - ACRONYMS FOR POLYMERS**

PE	Polyethylene
PET	Polyethene Terephthalate
HDPE	High Density PE
PEEK	Polyether Ketones
LDPE	Low Density PE
ABS	Acrylonitrile Butadiene Styrene
MDPE	Medium Density PE
SAN	Styrene Acrylonitrile Copolymer
LLDPE	Linear LDPE
PS	Polystyrene
PP	Polypropylene
EPS	Expanded PS
PVC	Polyvinylchloride
PU	Polyurethane
PA	Polyamides (Nylons)
PMMA	Polymethyl Methacrylates
PPS	Polyphenylene Sulphides
PVdC	Polyvinylidenechloride

## APPENDIX II - VAPOUR PRESSURE AND VOLATILE LOSS

### Vapour Pressure and Temperature

A commonly used approach to the estimation of vapour pressure is by means of the Clausius Clapeyron equation. Provided that the latent heat of vaporisation is known, then the vapour pressure ( $P_T$ ) at a given temperature T can be estimated from the known vapour pressure at a different temperature (200°C) according to the expression:

$$\ln P_T = \ln P_{200} + \frac{L}{R} \left( \frac{1}{473} - \frac{1}{T} \right)$$

If R (the universal gas constant) is 8.31 J/(mol K) and L (latent heat) is taken as a nominal 100 kJ/mol, then the expression for vapour pressure P (measured in atmospheres) at 423 K (150°C) becomes simply:

$$\ln P_{150} = \ln P_{200} - 3.0$$

Miles (5) attempted to produce empirical expressions for deriving vapour pressure from the normal boiling point but in this case only for solvents. The Miles approach does have merit in its simplicity, and appears to be amenable to application to the sorts of liquids employed in PVC plasticisation with appropriate modification. Thus for an approximate estimate of vapour pressure at 150°C (423K), we would suggest the Miles' expression be amended to:

$$\log P = 0.4 M^{0.5} (1 - T_b/423),$$

where P = vapour pressure in atmospheres

M = molecular weight

T<sub>b</sub> = normal boiling point (K)

The sort of correlation achieved can be seen by the data below.

Plasticiser	M	T <sub>b</sub> (K)	calculated P mmHg	measured P mmHg
Dimethyl phthalate	194	557	13	13
Diethyl phthalate	222	569	6.7	6.3
Dibutyl phthalate	278	613	0.76	0.8
Diisobutyl adipate	258	555	7.5	6.0
Tributyl phosphate	266	562	5.4	7.3

### Vapour Losses at Equilibrium

When volatile losses are concerned, the simplest case is that of vapour-liquid partition in an enclosed system at equilibrium. Such a case could be regarded as representative of a high speed mixer. The worst case scenario might be conceived to be that for an especially volatile plasticiser such as dibutyl phthalate, when a vapour pressure of 0.8 mmHg ( $1 \times 10^{-3}$  atm) provides an airborne concentration of 1,000 ppm (v/v). Whilst this might appear to represent a significant vapour concentration (and a potential hazard in the workplace) the actual quantity which is airborne can be shown to be small. The calculation for this is given below.

The total quantity lost to vapour will be dependent on the air volume of the mixer. Thus for dibutyl phthalate in a 9 litre mixer at 423K (150°C), the amount (in moles) can be estimated from:

$$n = PV/(RT)$$

where P is in atm, V in litres, and  $R = 8.21 \times 10^{-2} \text{ atm K}^{-1} \text{ mol}^{-1}$

From which,

$$n = 0.27 \text{ mmole (76 mg)}$$

When the plasticiser is present in such a mixer in kg quantities or higher, a loss of only 76 mg to the vapour phase is clearly very small. For such a case the minimal loss factor of 0.01% is more than adequate.

To increase the proportion in the vapour phase would require an increase in the volume of the available air space; in effect a scale-up in equipment size. Such a scale-up would not usually be undertaken without a corresponding increase in ingredient (i.e. liquid) quantities and thus the distribution between liquid and vapour would not be affected. This minimal loss factor would be regarded as representative of high speed mixing in general.

A worst case scenario for volatile loss would require an increase in the air space to be effected without a proportional increase in ingredient quantities. Such a situation could occur if the mixer's contents were opened to the atmosphere whilst still hot (i.e. the lid of the mixer opened prematurely). Such a situation merits consideration, but is no longer an equilibrium case: this is considered in more detail at the end of the next section.

### Rates of Evaporation from Liquid Surfaces

Experimental data reveal that rates of evaporative loss are not necessarily directly proportional to vapour pressure. The range of rates of volatile loss are not as great as the respective range of vapour pressures. If this behaviour is amenable to description by a simple numerical relationship, then it is suggested that, for esters of organic acids, weight loss W can be related to vapour pressure P by an expression of the form:

$$W = PM^2/7500$$

where

W is the weight loss in mg/cm<sup>2</sup>/hr

P is the vapour pressure in mmHg

M is the molecular weight.

This expression can be seen to give a tolerably good fit for the adipate, sebacate, phthalates, etc. Thus for dibutyl phthalate (M=278, P=14), the estimated value of W is 140 mg/cm<sup>2</sup>/hr (experimental value 148 mg/cm<sup>2</sup>/hr), whereas for di-2-ethylhexyl adipate (M=371, P=2.3), the value of W obtained is 42.12 mg/cm<sup>2</sup>/hr (experimental value 48 mg/cm<sup>2</sup>/hr). A further order of magnitude lower in P would correspond to a plasticiser such as diisodecyl phthalate (M=447, P=0.35), and the calculated value of W for this would be 9.3 mg/cm<sup>2</sup>/hr. Whilst no experimental value of W is available in this case, the value derived is close to that which was measured for a tricresyl phosphate (7 mg/cm<sup>2</sup>/hr) which has a similar vapour pressure.

The examples chosen cover a volatility range no wider than for the three representative high, medium and low volatility plasticiser types (i.e. 20, 2.0 and 0.2 mmHg vapour pressure at 200°C). For calculation here, the same expression is applied to 150°C volatilisation for the same generic types (i.e. esters of organic acids) but represented by the following specific examples:

- (i) a high volatility plasticiser of Mol. Wt. 250, having a 1.0 mmHg vapour pressure at 150°C
- (ii) a medium volatility plasticiser of Mol. Wt. 350, having a 0.1 mmHg vapour pressure at 150°C
- (iii) a low volatility plasticiser of Mol. Wt. 450, having a 0.01 mmHg vapour pressure at 150°C

By substituting the above values of M and P into the expression

$$W = PM^2/7500$$

the following values of W can be obtained

high volatility plasticiser - 8.3 mg/cm<sup>2</sup>/hr

medium volatility plasticiser - 1.6 mg/cm<sup>2</sup>/hr

low volatility plasticiser - 0.27 mg/cm<sup>2</sup>/hr

These examples suggest that evaporation rates are reduced approximately five-fold each time when moving from "high" to "medium" to "low" volatility in the above examples.

The above calculations used molecular weight data appropriate to esters of organic acids such as adipates or phthalates, but the respective values of W and P obtained are not necessarily so limited. The data above show that the calculated value of W for a low volatility phthalate (e.g. diisodecyl phthalate) is not far removed from the experimental value for a phosphate (tricresyl) of similar volatility. Thus it appears that, provided the distinction between the different representative plasticiser types is made only in terms of vapour pressure (and not in terms of molecular weight), the above rankings in weight loss may have general applicability.

### APPENDIX III - PROCESSES AND ADDITIVES FOR SPECIFIC POLYMERS

The Figures in this Appendix map the 4 parameters for each polymer, U, U<sub>f</sub>, A<sub>f</sub> and F, giving values for each to use in calculations. The maximum fractional content of generic additives likely to be encountered in specific applications, F, were selected to permit the calculation of the greatest losses of a given additive which could arise from a given application and process.

The majority of such additives are expensive and most processors and end users seek to keep the loadings to a minimum, commensurate with obtaining the required benefits. Whilst it is not possible to estimate an average fractional content, it is reasonable to present a lower limit below which the use of an additive is significantly unlikely. **Table AIII.1** presents these lower limits in generic terms, expressed as a proportion of the maxima given in the tables.

**Table AIII.1 ..Lower Limits of Fractions of Use of Additives - expressed as a percentage of maxima quoted in Tables III.2-19**

Fillers < 40 µm	35
Fillers > 40 µm	33
Plasticisers	80
Antioxidants	30
UV Stabilisers	26
Coupling agents	21
Colourants (Pigments)	53
Anti-static agents	50
Flame retardants	48
Curing agents	65
Blowing agents	50
Heat stabilisers	29
Lubricants/slip promoters	48
Viscosity aids	15

As an example, the maximum loading for an antistatic agent used in LDPE for packaging is 0.1% (see **Table A111.2**). From the above table, the lower limit is seen to be 50% of this maximum, i.e. 0.05%. This means that for this application there is an 90% probability that the loading will lie within the limits of 0.05% and 0.1%.

No information was available on the fractional content of additives used as preservatives. Polymeric impact modifiers are added to the polymer at the compounding stage; no information is available as to the fractional content of these additives.

It should be noted that although this Appendix gives details of reasonable worst case amounts of additives that may be used in polymers, it does not necessarily follow that all of the possible additive types indicated for a given polymer will be present in all polymers of that type. The actual amounts

and combination of additive types that will be used in a given type of plastic will depend to a large extent on the final application or required properties of the final polymer.

**Table AIII.2 Processes and additives used with LDPE**

			<b>Blowing agents</b>	<b>Anti-oxidants</b>	<b>Slip promoters</b>	<b>Flame retardants</b>	<b>Colourants</b>	<b>Curing agents</b>	<b>Antistatic agents</b>
LDPE 710 kT	CLOSED 12%	Transport 4%				20%	3%		
		Packaging 13%			0.05%		3%		0.1%
		Housewares 43%					3%		
		Miscellaneous 40%		0.1%	0.05%	20%	3%		0.1%
	PARTIALLY OPEN 88%	Packaging 55%			0.05%		3%		0.1%
		Building 2%	4%	0.1%		20%	3%	3%	
		Electrical 2%	4%			20%	3%	3%	
	Agriculture 40%			0.05%		3%		0.1%	

**Table AIII.3 Processes and additives used with HDPE**

			<b>Anti-oxidants</b>	<b>Flame retardants</b>	<b>Anti-static agents</b>	<b>Colourants</b>	
HDPE 395 kT	CLOSED 82%	Housewares 14%				3%	
		Packaging 26%			0.3%	3%	
		Transport 14%	0.25%	20%		3%	
		Miscellaneous 46%	0.25%		0.3%	3%	
	PARTIALLY OPEN 18%	Electrical 12%			20%		3%
		Building 65%			20%		3%
		Miscellaneous 23%	0.25%			0.3%	3%

**Table AIII.4 Processes and additives used with Polypropylene**

			<b>Coupling agents</b>	<b>Anti-oxidants</b>	<b>UV stabilisers</b>	<b>Flame retardants</b>	<b>Colourants</b>	<b>Fillers &lt;40 µm</b>	
POLYPROPYLENE 500 kT	CLOSED 52%	Transport 49%	0.5%	0.5%	5%		3%	40%	
		Electronic 23%	0.5%	0.5%	5%		3%	40%	
		Miscellaneous 28%	0.5%	0.5%	5%		3%	40%	
	PARTIALLY OPEN 48%	Packaging 54%		0.5%				3%	
		Transport 8%		0.5%				3%	
		Agriculture 8%		0.5%				3%	
		Miscellaneous 30%	0.5%	0.5%	5%	5-40%	3%	40%	



**Table AIII.5 Processes and additives used with Rigid PVC**

			Blowing agents	Anti-oxidants	UV stabilisers	Lubricants	Colourants	Fillers <40 µm	Heat stabiliser
RIGID PVC 365 kT	CLOSED 81%	Packaging 19%				1%	0.5%		1%
		Electronics 2%				1%	3%	10%	3%
		Building 74%	4%	0.2%	0.5%	1%	3%	10%	5%
		Miscellaneous 5%		0.2%	0.5%	1%	3%	10%	3%
	OPEN 19%	Packaging 100%				1%	1%	10%	1%

**Table AIII.6 Processes and additives used with Flexible PVC**

			Fillers <40 µm	Plasticisers	Heat stabiliser	Flame retardants	Colourants	Lubricants
FLEXIBLE PVC 220 kT	CLOSED 25%	Miscellaneous 56%	30%	30%	5%	5%	2%	0.3%
		Building 44%	20%	30%	3%	5%	2%	0.2%
	PARTIALLY OPEN 49%	Packaging 20%	20%	30%	3%	5%	2%	0.2%
		Electrical 51%	20%	30%	3%	5%	2%	0.2%
		Miscellaneous 29%	50%	50%	2%	5%	2%	0.1%
	OPEN 26%	Clothing 46%	10%	30%	2%		2%	0.1%
		Packaging 27%		40%	2%			0.1%
		Transport 10%	10%	45%	2%		2%	0.1%
		Miscellaneous 17%	50%	50%	2%	5%	2%	0.1%

**Table AIII.7 Processes and additives used with Polystyrene**

			UV stabilisers	Flame retardants	Lubricants	Colourants
POLYSTYRENE 190 kT	CLOSED 62%	Housewares 29%	0.5%	20%		1%
		Transport 3%	0.5%	20%		1%
		Brown goods 22%		20%		1%
		White goods 22%	0.5%			1%
		Building 7%	0.5%			1%
		Miscellaneous 17%	0.5%	20%	1.2%	1%
	PARTIALLY OPEN 7%	Packaging 100%			1.2%	1%
	OPEN 31%	Packaging 79%			1.2%	1%
		White goods 9%	0.5%			1%
		Building 3%	0.5%			1%
Miscellaneous 9%		0.5%			1%	

**Table AIII.8 Processes and additives used with Expanded Polystyrene**

			Blowing agents	Flame retardants
EXPANDED POLYSTYRENE 40 kT	CLOSED 100%	Packaging 65%	6%	
		Building 31%	6%	15%
		Agriculture 4%	6%	

**Table AIII.9 Processes and additives used with ABS**

			Flame retardants	Heat stabilisers	UV stabilisers	Colourants
ABS 75 kT	CLOSED 95%	Packaging 20%		0.75%		5%
		Brown goods 40%	20%	0.75%		5%
		White goods 40%		0.75%	0.5%	5%
	OPEN 5%	White goods 75%		1.0%	0.5%	5%
		Miscellaneous 25%		1.0%	0.5%	5%

**Table AIII.10 Processes and additives used with PET**

			<b>Fillers</b>	<b>Plasticisers</b>	<b>UV stabilisers</b>	<b>Flame retardants</b>	<b>Colourants</b>
PET 72 kT	CLOSED 90%	Housewares 3%	55%	5%			3%
		Packaging 95%	55%	5%			3%
		Transport 2%	55%	5%		15%	3%
	PARTIALLY OPEN 10%	Packaging 12%					3%
		Electrical 6%					3%
		Building 50%			0.5%		3%
		Miscellaneous 32%			0.5%		3%

**Table AIII.11 Processes and additives used with Polyamides**

			<b>Coupling agents</b>	<b>Plasticisers</b>	<b>UV stabilisers</b>	<b>Flame retardants</b>	<b>Colourants</b>	<b>Fillers &lt;40 µm</b>	<b>Heat stabilisers</b>
POLYAMIDES 38 kT	CLOSED 89%	Housewares 7%	0.5%		3%		2%	40%	0.5%
		Packaging 10%					2%		0.5%
		Transport 36%	0.5%		3%	25%	2%	40%	0.5%
		Brown goods 14%	0.5%				2%	40%	0.5%
		White goods 12%			3%		2%	40%	0.5%
		Electronics 14%	0.5%			15%	2%	40%	0.5%
		Miscellaneous 7%	0.5%	1%	3%		2%	40%	0.5%
	OPEN 11%	Miscellaneous 100%			3%		2%		0.5%

**Table AIII.12 Processes and additives used with Acrylics**

			<b>Coupling agents</b>	<b>UV stabilisers</b>	<b>Fillers &lt;40 µm</b>	<b>Colourants</b>
ACRYLICS 30 kT	CLOSED 57%	Transport 45%				1%
		Building 25%				1%
		Electronics 20%				1%
		Housewares 10%	0.5%		35%	1%
	OPEN 43%	Displays* 50%			0.2%	1%
		Building 25%			0.2%	1%
		White goods 25%				1%

\*Displays - transparent/translucent panels used in illuminated signs

**Table AIII.13 Processes and additives used with Acetals**

			<b>Coupling agents</b>	<b>Anti-static agents</b>	<b>Slip promoters</b>	<b>Fillers &lt;40 µm</b>	<b>Colourants</b>	<b>Heat stabilisers</b>	<b>UV stabilisers</b>
ACETALS 14 kT	CLOSED 100%	Electronics 45%	0.5%	1.0%		30%	2%	0.2%	3%
		Transport 45%	0.5%	1.0%		30%	2%	0.2%	3%
		White goods 10%	0.5%	1.0%	25%	30%	2%	0.2%	3%

**Table AIII.14 Processes and additives used with Polycarbonate**

			<b>Coupling agents</b>	<b>Blowing agents</b>	<b>Lubricants</b>	<b>Fillers &lt;40 µm</b>	<b>Colourants</b>	<b>Heat stabilisers</b>	<b>UV stabilisers</b>
POLYCARBONATE 12 kT	CLOSED 83%	Automotive 11%					3%	0.15%	
		Electronic 60%	0.5%	4%	1.2%	40%	3%	0.15%	
		Housewares 3%		4%			3%	0.15%	0.3%
		Building 16%						0.25%	0.3%
		Packaging 4%					3%	0.15%	
		Miscellaneous 10%					3%	0.25%	0.3%
	PARTIALLY OPEN 17%	Building 88%						0.25%	0.3%
		Sports 12%						0.15%	

Although flame retardant grades are available, they tend to incorporate halogens in the main chain of the polymer and these are therefore not considered to be additives.

**Table AIII.15 Processes and additives used with Polyurethanes**

			<b>Coupling agents</b>	<b>Blowing agents</b>	<b>Fillers &lt;40 µm</b>	<b>Fillers &gt;40 µm</b>	<b>Colourants</b>	<b>Flame retardants</b>	<b>Curing agents</b>
POLYURETHANES 120 kT	CLOSED 100%	Furniture 30%	0.5%			20%		10%	
		Automotive 18%	0.5%		20%	10%	1%	10%	0.2%
		Building 17%	0.5%	10%	20%	10%	1%	10%	0.2%
		White goods 5%	0.5%			20%	1%		0.2%
		Miscellaneous 30%	0.5%	10%	20%	10%	1%		0.2%

**Table AIII.16 Processes and additives used with Unsaturated Polyester Resins**

			<b>Coupling agents</b>	<b>Curing agents</b>	<b>Colourants</b>	<b>Fillers &gt;40 µm</b>	<b>Fillers &lt;40 µm</b>
UNSATURATED POLYESTER RESINS 75 kT	CLOSED 41%	Building 25%	0.5%	0.5-3%		40%	50%
		Short-term building 25%	1%	0.5-3%		50%	50%
		Transport 15%	0.5%	0.5-3%	0.5%	40%	50%
		Electrical 15%	0.5%	0.5-3%	0.5%	40%	
		Miscellaneous 20%	1%	0.5-3%	0.5%	50%	50%
	OPEN 59%	Transport 11%	1%	0.5-3%	0.5%	50%	50%
		Marine 26%	1%	0.5-3%		50%	50%
		Building 27%	1%	0.5-3%		50%	50%
		Miscellaneous 36%	2%	0.5-3%	0.5%	70%	50%

**Table AIII.17 Processes and additives used with Phenolic Resins**

			<b>Curing agents</b>	<b>Plasticisers</b>	<b>Heat stabilisers</b>	<b>Lubricants</b>	<b>Colourants</b>	<b>Fillers &lt;40 µm</b>
PHENOLIC RESINS 28 kT	CLOSED 100%	Transport 24%	2%	1%	0.5%	2%	2%	40%
		Building 50%	2%	1%	0.5%	2%	2%	40%
		Brown and white appliances 10%	2%	1%	0.5%	2%	2%	40%
		Electrical 10%	2%	1%	0.5%	2%	2%	40%

**Table AIII.18 Processes and additives used with Amino Resins**

			<b>Curing agents</b>	<b>Plasticisers</b>	<b>Heat stabilisers</b>	<b>Lubricants</b>	<b>Colourants</b>	<b>Fillers &lt;40 µm</b>
AMINO RESINS 70 kT	CLOSED 100%	Electrical 70%	2%	1%	0.5%	2%	2%	40%
		Building 20%	2%	1%	0.5%	2%	2%	40%
		Brown and white appliances 3%	2%	1%	0.5%	2%	2%	40%
		Miscellaneous 7%	2%	1%	0.5%	2%	2%	40%

**Table AIII.19 Processes and additives used with Epoxy Resins**

			<b>Coupling agents</b>	<b>Fillers &gt;40 µm</b>	<b>Fillers &lt;40 µm</b>	<b>Colourants</b>	<b>Curing agents</b>
EPOXY RESINS 12 kT	CLOSED 100%	Electronic 44%	2%	50%	50%	5%	10%
		Construction 50%	2%	50%		5%	10%
		Aerospace and engineering 6%	3%	50%		5%	10%

## APPENDIX IV – DIFFUSION MODEL FOR PREDICTING SERVICE LIFE EMISSIONS TO AIR FROM POLYMERS

### Introduction

The following model is based on the following report: Fisk P., McLaughlin L. and Wildey R. (2006). A New Assessment of the Release of Flame Retardants from Polyurethane Foam. Report v3. Peter Fisk Associates, under contract to the Environment Agency (1). The methodology was developed to be used in environmental risk assessment of additives in polymers in general, and the above report considered how this method could also be used specifically in the case of additives in polyurethane foams.

### Theoretical background to the model

The basic assumptions used in the development of the model are outlined below.

- (i) A polymer is seen as a continuous matrix, not subject to physical or biological degradation. As foams are not continuous matrices (they contain air cells), a correction is needed to determine the “effective” thickness (see later).
- (ii) Additives are initially uniformly distributed through the polymer, without there being ‘domains’ of additive at high concentrations, and redistribution of the polymer within the matrix occurs as a result of loss from the surface.
- (iii) Additives are not chemically bound to the polymer, the only interactions being weak non-specific physical interactions or weak hydrogen bonds.
- (iv) In the quantitative modelling, the concentration of an additive in the receiving compartment (usually air) is assumed to be not influential; however this is an important factor, which is considered qualitatively.

Under such conditions, an additive molecule at the surface of a polymer may evaporate from it or be washed from it. This process can continue, and if the rate of escape from the surface is faster than the rate of diffusion to the surface (which is assumed to be the case), then in time a concentration gradient near the surface of the polymer can arise.

Diffusion of solutes in liquid solution is known to depend primarily on molecular size, temperature and viscosity of the solvent. The diffusion coefficient  $D$  is the primary descriptor of rate, as expressed in Fick's laws of diffusion. Fisk and Jonathan (2) have provided a review of the prediction of diffusion coefficients in solution. In practice, diffusion in homogeneous solution can only be measured easily where a concentration gradient exists. At a boundary between phases (e.g. aqueous and non-aqueous immiscible solutions), molecules generally cross the interface freely, particularly where this partitioning process is favoured by the position of equilibrium and the relative concentrations in the two phases.



Considering polymers, the situation is more complicated because they are not very mobile, and therefore molecules can move less easily within the polymer than they can in solution. Nevertheless, many of the same principles apply. At the polymer-air interface, it could be envisaged that the additive could accumulate on the surface, but it may be assumed that where air is circulating freely, the concentration of the additive in air will be effectively zero, and that molecules of additive reaching the surface will evaporate rapidly. The consequence is that a diffusion gradient will be established within the polymer. A further uncertainty is that in cellular foams a different mechanism may exist due to the cellular structure and the establishing of a cellular-volume/external-atmosphere exchange mechanism (Note: this is akin to the cell wall acting as a gas/vapour transport membrane rather than a semi-infinite slab (as assumed herein, applying Fickian and Case I and Case II diffusion)).

### Development of the model

The following sections develop some simple equations that can readily be applied to the migration of additives in polymers. The influence of varying different parameters on the outputs of the model are also considered.

The mathematics of diffusion in solution and polymers is complex and so some major simplifications have to be made just to generate some practical numbers.

Migration in polymers is sufficiently slow that it can be readily assumed that molecules that reach the polymer surface can volatilise or dissolve in any solvent there much faster than the diffusional rate (3). This assumption represents a reasonable worst case.

The equations used are taken from standard sources such as Crank (4).

#### *Initial rates*

Fick's second law of diffusion deals with diffusion which is time-dependent, i.e. during the period between time zero and the establishment, if it occurs, of a steady state.

Consider a newly formed polymer containing evenly-distributed additive at concentration  $C_0$  ( $\text{kg.m}^{-3}$ ). If the area of surface exposed to a sink for the substance is  $A_{\text{polymer}}$  ( $\text{m}^2$ ), then Fick's second Law can be solved such that, for small amounts of loss (up to approx. 20%), the number of kg lost  $N_{\text{add}}$  over time  $t$  (s) is given by:

$$N_{\text{add}} = 2 \times A_{\text{polymer}} \times C_0 \times \left( \frac{D_{\text{add}} \times t}{\pi} \right)^{0.5} \quad -1.$$

where  $D_{\text{add}}$  is the self-diffusion coefficient ( $\text{m}^2.\text{s}^{-1}$ ). This equation predicts that the rate of diffusion will slow with time, which is a consequence of the physical fact that the molecules near the surface will escape first, and then it takes more time for the deeper ones to reach the surface and escape. It also shows that the rate of loss is proportional to area and concentration.

The value for  $C_0$  can be estimated using the following method.

$$C_0 = \frac{F_{\text{add,polymer}} \times M_{\text{polymer}}}{100 \times V_{\text{polymer}}} = \frac{F_{\text{add,polymer}} \times A_{\text{polymer}} \times L_{\text{polymer}} \times \text{Rho}_{\text{polymer}}}{100 \times A_{\text{polymer}} \times L_{\text{polymer}}} = \frac{F_{\text{add,polymer}} \times \text{Rho}_{\text{polymer}}}{100}$$

-2

Combining equations 1, 2 gives the following equation.

$$N_{\text{add}} = 0.02 \times A_{\text{polymer}} \times F_{\text{add,polymer}} \times \text{Rho}_{\text{polymer}} \times \left( \frac{D_{\text{add}} \times t}{\pi} \right)^{0.5}$$

3

The percentage of additive lost from the polymer can then be estimated as follows. This is in a form that can be used as in Section 6.2 of the main report.

$$F_{\text{servicelife,air}} = \frac{N_{\text{add}} \times 100}{A_{\text{polymer}} \times L_{\text{polymer}} \times \text{Rho}_{\text{polymer}} \times \frac{F_{\text{add}}}{100}} = \frac{N_{\text{add}} \times 10,000}{A_{\text{polymer}} \times L_{\text{polymer}} \times \text{Rho}_{\text{polymer}} \times F_{\text{add}}}$$

-4

The diffusion coefficient represents the rate at which a molecule can diffuse through a medium. Diffusion coefficients depend on temperature, molecular size, and the viscosity of the solvent, and they can be predicted relatively easily (2). The values can either be taken from the literature or estimated using the following equation developed by Reynier *et al.* (5).

$$D_{\text{add}} = \frac{10^{(-7.83 - 0.0062 \times MW_{\text{add}})}}{10,000}$$

-5

#### Explanation of symbols:

$N_{\text{add}}$	= amount of additive lost over time t	[kg]	Suggested default value 1 m <sup>2</sup>
$A_{\text{polymer}}$	= surface area of polymer	[m <sup>2</sup> ]	
$C_0$	= initial concentration of additive in polymer on a mass/volume basis	[kg m <sup>3</sup> ]	
$D_{\text{add}}$	= diffusion coefficient for additive	[m <sup>2</sup> s <sup>-1</sup> ]	literature or equation 5 Table 4.3 and Table 6.2 of the main report
t	= time period for calculation	[s]	
$F_{\text{add, polymer}}$	= percentage of additive in polymer on a mass/mass basis	[%]	
$M_{\text{polymer}}$	= mass of polymer sample	[kg]	
$V_{\text{polymer}}$	= volume of polymer sample	[m <sup>3</sup> ]	
$L_{\text{polymer}}$	= thickness of polymer sample	[m]	Suggested default value 0.01 m. For foams the effective thickness ( $L_{\text{polymer, effect}}$ ) from equation 6 should be used
$\text{Rho}_{\text{polymer}}$	= density of polymer sample	[kg m <sup>-3</sup> ]	Suggested value 1,100 kg m <sup>-3</sup>
$MW_{\text{add}}$	= molecular weight of additive	[g mole <sup>-1</sup> ]	
$F_{\text{service life, air}}$	= percentage lost to air over a service life of time t	[%]	

It should be noted that the model is only strictly valid for up to around 20% loss of the substance from the polymer.

*Example calculations and suggested default values for using the Initial Rate Model*

For the 'demonstration' calculations, the model was set up using the following parameters, reasonably representative of polymers but not intended to be specific.

Substance molecular weight ( $MW_{add}$ ): 300 g/mol

Temperature: 25°C

Diffusion coefficient ( $D_{add}$ ):  $3 \times 10^{-15}$  m<sup>2</sup>/s

Additive content of polymer ( $F_{add, polymer}$ ): 5%

Density of polymer ( $Rho_{polymer}$ ): 1,100 kg/m<sup>3</sup>

These values were kept constant while the initial investigation was carried out. The influence of surface area and timescale on the output of the initial rate model was investigated. To simplify the calculations, it was assumed that only one surface was available for diffusion.

For a piece of plastic with thickness ( $L_{polymer}$ ) 0.1 m, the surface area available for diffusion ( $A_{polymer}$ ) was varied from 0.0001 m<sup>2</sup> to 5 m<sup>2</sup> over timescales (t) of 5, 10 and 20 years. The model outputs in grams are presented in Table AIV.1.

**Table AIV.1 Amount of additive lost (grams) as a function of surface area and timescale**

Timescale (y)	Surface area ( $A_{polymer}$ ) (m <sup>2</sup> )									
	0.0001	0.0005	0.001	0.005	0.01	0.1	1	2	3	5
5	0.0043	0.021	0.043	0.21	0.43	4.3	43	85	128	213
10	0.0060	0.030	0.060	0.30	0.60	6.0	60	121	181	302
20	0.0085	0.043	0.085	0.43	0.85	8.5	85	171	256	427

This demonstrates that the amount of substance released varies linearly with surface area and is dependent on the timescale considered. The same results, expressed as a percentage of the initial amount of additive present in the polymer (i.e. the emission factor  $F_{service\ life, air}$ ) are shown in Table AIV.2. These show that the emission factor is independent of the surface area and is only dependent on the service life.

**Table AIV.2 Percentage of additive lost ( $F_{service\ life, air}$ ) as a function of surface area and timescale**

Timescale (y)	Surface area ( $A_{polymer}$ ) (m <sup>2</sup> )									
	0.0001	0.0005	0.001	0.005	0.01	0.1	1	2	3	5
5	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%	0.78%
10	1.1%	1.1%	1.1%	1.1%	1.1%	1.1%	1.1%	1.1%	1.1%	1.1%
20	1.6%	1.6%	1.6%	1.6%	1.6%	1.6%	1.6%	1.6%	1.6%	1.6%

The effect of varying the thickness on both the amount of additive lost and the percentage of additive lost is shown in Table AIV.3 and Table AIV.4. The calculations were done using a surface area of 1 m<sup>2</sup>. As can be seen from these results, the amount of additive lost is independent of the thickness of the polymer, but the emission factor decreases with increasing thickness of the polymer.

**Table AIV.3 Amount of additive lost (grams) as a function of thickness and timescale**

Timescale (y)	Thickness (L <sub>polymer</sub> ) (m)						
	0.0001	0.0005	0.001	0.005	0.01	0.1	0.5
5	43	43	43	43	43	43	43
10	60	60	60	60	60	60	60
20	85	85	85	85	85	85	85

**Table AIV.4 Percentage of additive lost (F<sub>service life, air</sub>) as a function of thickness and timescale**

Timescale (y)	Thickness (L <sub>polymer</sub> ) (m)						
	0.0001	0.0005	0.001	0.005	0.01	0.1	0.5
5	>100%	>100%	78%	16%	7.8%	0.78%	0.16%
10	>100%	>100%	>100%	22%	11%	1.0%	0.22%
20	>100%	>100%	>100%	32%	16%	1.6%	0.31%

In terms of use in the ESD, the emission factor (F<sub>service life, air</sub>) is probably most useful to the methods presented in the main report. Based on the above analysis, this factor is dependent on both the assumed thickness of the polymer and the timescale assumed for the service life. Where these data are not available for the specific polymer/additive under consideration, realistic default values will need to be used.

For the service life, Table 4.3 and Table 6.2 of the main report give suggested values for the service life of various plastic articles, and it is suggested that these values are also used in this model in the absence of further information.

For the properties of the polymer, it is suggested that the F<sub>service life, air</sub> is calculated for a polymer with the following default properties in the absence of any further information.

$$A_{\text{polymer}} = 1 \text{ m}^2$$

$$L_{\text{polymer}} = 0.01 \text{ m}$$

$$\text{Rho}_{\text{polymer}} = 1,100 \text{ kg m}^{-3}$$

It should be noted that, although the emission factor here has been assumed to be an emission to air, the model actually estimates the amount of additive that may diffuse to the surface of the polymer. Once at the surface of the polymer it is likely that the additive will be lost by volatilisation but it is possible that other removal mechanisms may be involved. For example, if the polymer is in contact

with water (or is frequently washed) then the emission could be to water. However, for most applications, it is envisaged that the losses will be mainly to air in the first instance.

### Special considerations for foams

Owing to the nature of foams, the bulk density of a foam block is considerably lower than the density of the polymer itself before blowing. For the purposes of modelling, it can be assumed that there is no limitation to the diffusion of an additive through ‘air cells’ in the foam. If it is assumed that diffusion is occurring from one surface only, the “effective” thickness of the polymer can be determined in both the bulk density of the foam and the density of the polymer are known as follows.

$$L_{\text{polymer, effective}} = L_{\text{foam}} \times \frac{\text{Rho}_{\text{bulk, foam}}}{\text{Rho}_{\text{polymer}}} \quad -6$$

Explanation of symbols:

$L_{\text{polymer, effective}}$	= effective thickness of polymer sample	[m]	
$L_{\text{foam}}$	= thickness of foam sample	[m]	
$\text{Rho}_{\text{bulk, foam}}$	= bulk density of foam	[kg m <sup>-3</sup> ]	Typical value 30 kg m <sup>3</sup> for polyurethane foam
$\text{Rho}_{\text{polymer}}$	= density of polymer	[kg m <sup>-3</sup> ]	Typical value 1,100 kg m <sup>-3</sup>

For a “typical” large block of polyurethane foam (dimensions 60×2.2×1.25 m) the  $L_{\text{polymer, effective}}$  would be around 0.034 m rather compared with the  $L_{\text{foam}}$  of 1.25 m).

### References

1. P. Fisk, L. McLaughlin and R. Wildey, “A new assessment of the release of flame retardants from polyurethane foam”, Report v3, Peter Fisk Associates, under contract to the Environment Agency, 2006.
2. P.R. Fisk and P. Jonathan, “A new approach to the prediction of diffusion coefficients”, pages 543 to 571 in “Comprehensive Chemical Kinetics”, Volume 37, Eds. R.G. Compton and G. Hancock, Elsevier, 1999.
3. P.R. Fisk, Ford M. G. and Watson P., “The kinetics of the partitioning of compounds between octanol and water”, pages 161 to 194 in “Comprehensive Chemical Kinetics”, Volume 37, Eds. R.G. Compton and G. Hancock, Elsevier, 1999.
4. J. Crank, “The mathematics of diffusion”, Clarendon Press, 1975.
5. A. Reynier, Dole P., Humbel S. and Feigenbaum A., “Diffusion coefficients of additives in polymers. I. Correlation with geometric parameters”, J. Appl. Polymer Sci., **82**, 2422-2433.