



Creating markets for recycled resources

Develop a process to separate brominated flame retardants from WEEE polymers

Final Report

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Abstract

This final report summarises the practical trials and process design work conducted during a three phase project funded by WRAP to develop a process to separate brominated flame retardants (BFRs) from waste electrical and electronic equipment (WEEE) polymers.

The work shows that the modified **Creasolv¹ process** for extraction of brominated flame retardants from WEEE polymers has potential to be commercially viable in the UK context at a throughput of 10,000te/year. The Creasolv process was originally developed by Fraunhofer IVV in Germany and has been modified further in the course of this project in collaboration with Fraunhofer IVV.

The Creasolv process will remove most BFR types from styrenic WEEE polymers. Work done for this project has shown that styrenic polymers constitute over half of collectable WEEE polymers and that they contain the great majority of the BFRs found in WEEE thermoplastics. It has not been tested with the newer BFR types such as brominated epoxy oligomers because these are not yet found in significant quantities in real WEEE.

A second process called Centrevap has also been developed in the course of this project and tested at technical scale. Tests have shown that it cannot achieve significant reductions in BFR content. However it does offer good potential as a robust, flexible and relatively cost-effective process for removal of insoluble impurities down to submicron size from a wide range of polymer types.

Both processes should be able to compete with landfill disposal or incineration (£45/te gate fee) as treatment methods for segregated polymer streams. Creasolv will compete for BFR removal, Centrevap should be suitable for removal of other insoluble impurities. They will compete with export of the WEEE polymer outside the EU (current sales value of around £100/te) if the finished high grade compounded recyclate can be sold at about 80% of virgin compound price.

Environmental impact comparisons conducted during Phase 2 of the project and updated for this final report indicate that both of the recommended processes have a net environmental gain across all environmental impact categories and that the proposed treatment routes are a substantially better environmental option than landfill and also a better option than incineration with energy recovery.

The report recommends that the modified Creasolv process developed during this project is the best commercial and environmental option for treatment of styrenic WEEE polymers containing brominated flame retardants.

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¹ Creasolv[®] is a registered trade name of Fraunhofer Group. Throughout this report, where the term 'Creasolv' is used it refers to the registered trade name Creasolv[®].

Executive summary

This is the final report for a project to develop a process to separate brominated flame retardants from WEEE polymers. It summarises the practical trials and process design work which were conducted during the project.

The European WEEE Directive encourages closed loop recycling by electronics manufacturers (but does not make it mandatory in the first implementation of the directive).

The Waste Resources Action Programme (WRAP) www.wrap.org.uk is a major UK Government programme established to accelerate resource efficiency by creating stable and efficient markets for recycled materials and products and removing barriers to waste minimisation, re-use and recycling.

Resource efficiency means making better use of resources by reducing the volume of waste generated and maximising the use of recovered materials in the economy, in products and process.

WRAP is a not-for-profit company limited by guarantee, backed by funding from DEFRA, DTI and the devolved administrations of Scotland, Wales and Northern Ireland. WRAP works with the public, private and community sectors throughout the EU with the aim of promoting resource efficiency within the UK.

WRAP has identified that one of the barriers to closed loop recycling of polymers from waste electrical and electronic equipment (WEEE) is the need to remove unwanted additives from the polymers before they can be re-used.

An important group of additives which need to be removed are the brominated flame retardants (BFRs). Two of these, Penta and Octa Bromodiphenylether (BDE) are already banned from use in new products by the 'Penta Directive'. Other brominated flame retardants are not restricted by European law but several major European electronics manufacturers have still decided to restrict their use to below 0.1% in new electronic products.

WRAP initiated this project to develop a process to separate brominated flame retardants from mixed WEEE polymers. WRAP expects that if a commercially viable treatment process can be developed it will help to encourage increased recycling of WEEE polymers and thereby increase diversion of these materials from landfill.

Axion Recycling www.axionrecycling.com has been engaged by WRAP to lead the project. It worked with academic and commercial collaborators as appropriate to conduct the research.

The industry that is developing in the UK for the treatment of WEEE falls into two distinct types of operation:

- Large-scale, bulk shredding plants producing a mixed stream of polymers and other materials
- Manual dismantling systems generating a stream of individual polymer components, usually relatively clean and partially sorted by polymer type

In order to find a 'total process' solution for the removal of BFRs from these different plastic waste streams, it is also necessary to assess the costs, efficiency and yields of the polymer identification and mechanical sorting techniques that could be used to separate the valuable non-BFR polymers for direct recycling and deliver a concentrated feed of BFR-containing polymers to a BFR-treatment process.

The project has therefore researched and tested both separation and sorting techniques for WEEE polymers and the BFR treatment processes themselves.

The project was organised in three phases with a review of objectives at the end of each phase:

1. Literature search and consultations with the electrical and electronics industry
2. Lab scale testing and economic/ environmental evaluation of a range of alternative treatment solutions
3. More in-depth testing and process design for the most promising solution followed by dissemination of the results of the work

Three interim reports were published by WRAP during the course of the project and are available for download from the WRAP website www.wrap.org.uk/publications. This final report summarises the conclusions of the interim reports. It includes new results from the final large scale trials of the two most promising process options and updates of the commercial and environmental impacts of these options.

Readers wishing to review all of the detailed project work will need to read all three interim reports in conjunction with this final report.

Note that the BFR polymer treatment processes that were developed in the course of this study are still likely to require 2-4 years of further development before they can be deployed commercially at large scale. Until commercially viable treatment processes are available, the options available for disposal of BFR-containing WEEE polymers will be export for recycling outside the EU, landfill or incineration with energy recovery.

The conclusions and recommendations of the project are as follows:

- Mechanical separation followed by a solvent-based process that removes brominated flame retardant additives from the BFR-containing polymers is likely to be a better environmental and commercial option for treatment of WEEE plastics than landfill, incineration with energy recovery or feedstock recycling
- Tests of the key elements of the 'Centrevap' process have demonstrated that it can remove insoluble additives down to around 0.5 micron provided that the density of the additive particles is significantly greater than 0.95. For example, the process removed antimony trioxide additive very efficiently. However the solvent combination used for the Centrevap process trials did not allow the removal of brominated flame retardants to the standard set for this project because the BFRs were partially soluble in the chosen solvent.
- Although the Centrevap process as tested during this project is potentially attractive for producing clean particle-free polymers it is not appropriate for BFR removal – the specific objective of this project.
- High quality, almost BFR-free recycled HIPS/ABS polymer has been produced in the course of the project by the Creasolv process from real WEEE polymers in tonnage-scale process trials.
- Mechanical properties of the recyclates produced by both the Creasolv and Centrevap process routes were good. However there was a significant reduction in the impact strength of the Creasolv recyclate.
- Removal of residual solvent in the final product is important for both process options and requires further process development.
- The Creasolv process should be commercially viable for treatment of segregated BFR-containing styrenic polymers from WEEE in the UK context if it can sell the recyclate at 60% of virgin compound price (around £560/te) and charge a gate fee of £45/te to compete with landfill.
- If the Creasolv process can produce really high grade compound valued at 80% of virgin material (£750/te) then it should be commercially viable when competing with current export prices to China for the input material (around £100/te). Recent market research by Axion indicates that end-users are increasingly prepared to pay 80-90% of virgin price for high grade recycled polymers.
- A combination of the Creasolv and Centrevap processes, although more expensive in capital cost terms, has potential to provide the benefits of both process options, delivering finished polymer with very low levels of BFR content and essentially particle-free.
- The process know-how generated during this project is available to license in the UK on commercial terms from WRAP and Fraunhofer IVV.

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1. Purpose of this report

This is the final report for the WRAP project, 'Develop a process to separate Brominated Flame Retardants from WEEE Polymers'

The project was funded by WRAP as a result of a call for R&D proposals to find ways to treat polymers containing brominated flame retardants in line with the requirements of the WEEE Directive.

Flame retardants are the most important group of plastics additives having a total market value of 9 billion Euros/year. Brominated flame retardants (BFR's) have the highest market share by value and represent 11.8% of the market share by volume². Over 75 different types of BFRs are produced with the majority being used in electrical and electronic applications.

It is estimated that around 7% by weight of all WEEE plastics contain brominated flame retardants, with the majority concentrated in brown goods and small WEEE items³.

The WEEE Directive requires the separation of plastics containing brominated flame retardants prior to recycling, energy recovery or disposal.

At present no commercially viable processes are available to extract BFRs from WEEE plastics and there are few options available to separate polymers containing BFRs from polymers that do not contain BFRs. Some polymers containing BFRs are currently processed in non-ferrous metal smelters, where separation is not required and the majority are landfilled.

WRAP initiated this project in order to find commercially viable ways to remove BFRs from WEEE polymers and thereby create a better opportunities for general recycling of WEEE polymers and in particular for closed loop recycling of WEEE polymers back into new E+E equipment.

² 'Flame retardants – FAQs', CEFIC information booklet, downloadable from www.cefic-efra.com

³ 'Analysis of plastics consumption and recovery in Europe' – detail workings, Sofres Consulting, 2003

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2. Objectives

Overall objectives of the project were to:

- Set target performance criteria for the BFR separation process to be developed. This was achieved by interviewing a representative group of electrical and electronic equipment manufacturers to establish their criteria for use of WEEE polymer recyclate.
- Identify and test a number of alternative process designs for separation of brominated flame retardants from WEEE polymers.
- Evaluate the alternative process options against alternative disposal routes in terms of:
 - Technical feasibility
 - Commercial viability
 - Environmental impact
- Further develop the most commercially viable process options by practical trials at an appropriate scale.
- Disseminate the findings to a broad and relevant audience within the electrical and electronic industry and the recycling sector

3. Method

The following methodology has been adopted for the project:

- Research the literature for work done to date on BFR removal from plastics.
- Interview electronic and electrical product designers to establish target acceptance criteria for the recycled polymers. This will set the performance targets for the process design phase.
- Investigate the available techniques for the identification and sorting of plastics containing BFRs.
- Identify all potential processes for removal of BFRs from WEEE polymers
- Conduct a detailed evaluation of the above processes, in three phases:
 - Phase 1:** A desk based comparison to screen out unviable options
 - Phase 2:** Laboratory scale trials of a shortlist of technologies
 - Phase 3:** Larger-scale pilot plant trials of the leading options coupled with commercial and environmental impact assessments

Phase 1:

- Reviewed the literature to identify potential WEEE polymer treatment processes
- Reviewed the literature to estimate the likely composition of WEEE polymers that are likely to be collected in future
- Reviewed the legislation governing treatment of WEEE polymers
- Assessed the hazards associated with brominated flame retardants likely to be found in WEEE polymers
- Conducted a market survey of leading electronics manufacturers to assess likely demand and the specifications that they would be likely to apply to recycled polymers from the type of process to be developed in the course of this project

Phase 2:

- Tested and assessed a broad range of the WEEE polymer identification and bulk separation techniques that will be required to produce a separated stream of BFR-containing polymers for treatment by the processes to be developed in this project
- Conducted laboratory trials of the key process steps for each of the shortlisted BFR polymer treatment process options
- Prepared outline process description, flowsheet, mass balance and capital cost estimates for each process option at a throughput of 10,000te/yr plastic
- Identified possible markets for the products from the different process options and estimated likely revenues
- Prepared initial financial projections with similar assumptions for each option
- Conducted an environmental impact assessment for each process option
- Compared technical feasibility, economic returns and environmental impact of the process options and, as a benchmark, compared them also with the alternative disposal routes of landfill and incineration.

Phase 3:

- Conducted larger scale and more detailed process optimisation trials for the Creasolv and Centrevap process options using appropriate pilot facilities in order to develop more detailed process design data. These trials were conducted at up to 2500 litre scale.
- Prepared detailed plant flowsheets and capital plant cost estimates.
- Updated the commercial and environmental impact assessments for the Creasolv and Centrevap process options

Scope of this study

Extraction of brominated flame retardants from printed circuit boards and from very small, complex WEEE items such as mobile phones and MP3 players will not be considered in this project.

Several studies have made it clear that the most popular existing treatment route for these items – feeding to precious metal smelter furnaces - is likely to remain competitive with all other treatment methods for the foreseeable future⁴. This is because printed circuit boards and small WEEE items contain significant quantities of precious metals relative to their weight. These can be recovered efficiently by smelters.

The hydrocarbon component of these items acts as a reducing agent in the smelter and the ceramics and glass contribute as fluxes. Precious metal smelters include sophisticated gas cleaning systems which capture any halogenated compounds that are liberated in the smelter flue gas.



Mobile phones: an example where dismantling effort and cost is high and polymer recovery is low

⁴ Plastic recovery from waste electrical and electronic equipment in non-ferrous smelter processes, Frank Mark and Theo Lehner, Plastics Europe Technical report, 2002, (available from Plastics Europe website www.apme.org)

4. Reporting

The three interim reports on the project and this final report may be downloaded from WRAP's website: www.wrap.org.uk/publications.

The first interim report was published in January 2005. It:

- Provides general information on flame retardants and their applications
- Reviews the legislative background
- Reviews the existing state of the art in separation and treatment of polymers containing BFRs
- Reports on the market survey of electrical and electronic equipment manufacturers
- Identifies potential separation and treatment solutions for WEEE polymers containing BFRs
- Recommends which process options should be investigated further in phase 2 of the project

The second interim report was published in August 2005. It:

- Describes the treatment solutions for WEEE polymers containing BFRs that were identified for laboratory testing in Phase 2
- Describes the technical evaluation methodology employed during Phase 2
- Summarises the results of the laboratory trials conducted during the technical evaluation
- Summarises the results of WEEE polymer separation trials conducted during Phase 2 in order to isolate BFR-containing WEEE polymers
- Presents the 6 outline BFR-treatment process designs that were selected for economic and environmental impact evaluation as a result of the technical evaluation and process design exercise
- Presents the results of the economic and environmental impact comparisons
- Recommends which process option should be taken forward for more detailed larger scale testing and evaluation in Phase 3 of the project.

The third interim report was published in March 2006. It:

- Describes the results of practical technical scale testing of the Creasolv and Centrevap process options
- Updates the process design work conducted in Phase 2
- Updates the economic evaluations conducted in Phase 2

This final report:

- Summarises the results presented in the three interim reports
- Presents the results of large scale trials of the Creasolv and Centrevap process options that were conducted during the first quarter of 2006
- Updates the process designs for the Creasolv and Centrevap process options based on the results of the large scale trials
- Presents a further process option that combines the best features of the Centrevap and Creasolv processes.
- Updates the commercial evaluations and environmental impact assessments that were conducted in Phases 2 and 3

Much of the technical detail of the Creasolv process is not described in the public reports, either because it is confidential information of Fraunhofer Institute Verpackung und Verfahrenstechnik (Fraunhofer IVV) or because it may potentially be patented jointly by WRAP and Fraunhofer IVV. The full technology package will be made available under license to commercial users of the process.

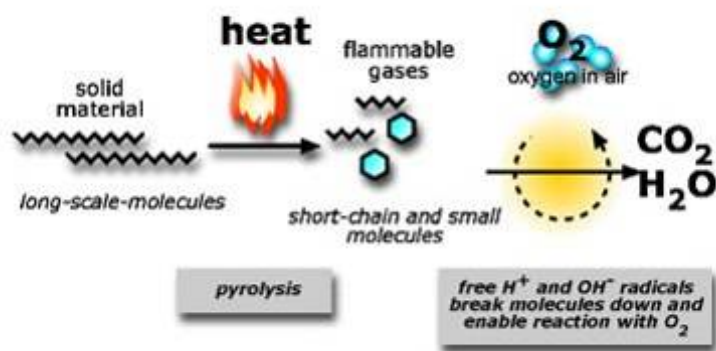
Some of the technical detail of the Centrevap process is also not described in this public report because it may be patented and/or retained as licensable knowhow by WRAP.

5. Types of BFR used now and in the past

5.1. Characteristics of common BFRs found in WEEE

There are many different flame retardants, and these work in a number of different ways. Some flame retardants are effective on their own, other products are used mainly or only as "synergists", acting to increase the effect of other types of flame retardant.

To understand how flame retardants work it is first necessary to understand how polymeric materials burn. Solid polymer materials do not burn directly, they must first be decomposed by heat (pyrolysis) to release flammable gases. The long chain polymer molecules are broken down by the heat of the fire into smaller molecules which become gases at high temperature. Visible flames appear when these flammable gases burn with the oxygen (O₂) in the air.



Chemistry of a burning polymer⁵

The gas flame is maintained by the action of high energy "radicals" (H⁺ and OH⁻ in the gas phase) which decompose molecules to produce free carbon which can react with oxygen in air to "burn" to CO₂, generating heat energy.

If solid materials do not break down into gases, then they will only smoulder slowly and often self extinguish, particularly if they "char" and form a stable carbonaceous barrier which prevents access of the fire to the underlying material.

The flame retarding mechanism of halogenated flame retardants is as follows:

When exposed to high temperatures, the halogenated flame retardant molecule releases bromine (Br) or chlorine (Cl), as free ions (Br⁻ or Cl⁻) which react with partially decomposed hydrocarbon molecules in the flame to produce HBr or HCl. These then react with the high-energy radicals to give water and the much lower energy Br⁻ or Cl⁻ ions, which are then available to begin a new cycle of free radical removal.

As development of the flame is retarded by the flame retardant 'mopping up' the free radicals in the flame the polymer starts to form a carbonaceous char at the surface which further inhibits development of the fire.

The effectiveness of halogenated flame retardants depends on the quantity of the halogen atoms they contain (eg. 10 bromine atoms in one molecule of deca-DBP) and also, very strongly, on the control of the halogen release. Because chlorine is released over a wider range of temperatures than bromine, it is then present in the flame zone at lower concentrations, and so is less effective. Bromine is released over a narrow temperature range, thus resulting in optimal concentrations in the flame zone.

⁵ Diagram and explanation courtesy of European Flame Retardants Association www.cefic-efra.com

Brominated flame retardants are generally compounded in polymers with antimony trioxide.

Antimony trioxide does not have flame retarding properties on its own, but is an effective synergist for halogenated flame retardants. It acts as a catalyst, facilitating the breakdown of halogenated flame retardants to active molecules. It also reacts with the halogens to produce volatile antimony halide compounds, which are themselves directly effective in removing the high energy radicals which feed the flame phase of the fire, thus reinforcing the flame suppressing effect of the halogenated flame retardants.

When added to PVC, antimony trioxide acts to suppress flames by activating the chlorine present in the plastic itself.

BFR's are mostly used in electronics and electrical equipment where they can be found in plastic housings, connectors and printed circuit boards. They can also be found in wire and cable insulation. Common applications are:

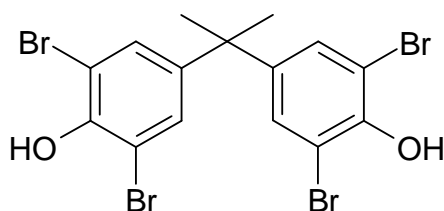
There are at least 75 different types of commercially available BFRs but only 30-40 are widely used in electrical and electronic (E&E) equipment^{6 7}. They are added to E&E plastics in powder or pellet form.

From a recycling point of view brominated flame retardants fall into two broad groups; 'Backbone' flame retardants and 'Matrix' flame retardants:

5.1.1. 'Backbone' flame retardants

These flame retardants tend to bond chemically with the polymer itself or are themselves large polymer-type molecules. Backbone brominated flame retardants include brominated polystyrene, brominated epoxy oligomer and TBBPA.

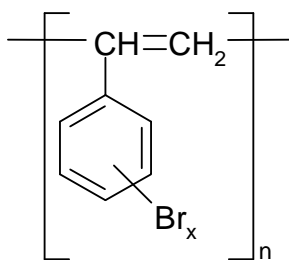
- Tetrabromobisphenol-A (TBBPA) in ABS/Polycarbonate and epoxy resin for printed circuit boards.



Tetrabromo bisphenol A

TBBPA bonds through the OH (phenol) groups at each end of the molecule. Note that TBBPA does not bond with some polymer types and therefore acts as a matrix flame retardant in these applications.

- Brominated (poly)styrene in polyester and polyamide.



Brominated polystyrene

⁶ 'Brominated Flame Retardants – A Nuisance in Thermal Waste Processing?', Tohka A. & Zevenhoven R., TMS Fall 2002 Extraction and Processing Division Meeting on Recycling and Waste Treatment in Mineral and Metal Processing: Technical and Economic Aspects, Lulea, Sweden June 16-20 2002

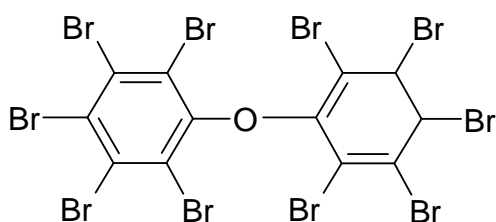
⁷ 'Recycling of Bromine from Plastics containing Brominated Flame Retardants in State-of-the-Art Combustion Facilities' Vehlow, Bergfeldt, Hussinger, Jay et al. APME, 2000

5.1.2. 'Matrix' flame retardants

'Matrix' brominated flame retardants include the polybrominated diphenyl ethers and TBPE. They reside in the polymer matrix as free molecules and do not bind chemically with the polymer itself.

Because they are not chemically bound to the polymer they can in principle diffuse out of the polymer matrix under the right conditions and are therefore likely to be easier to remove from the polymer using the types of process considered in this research than the 'backbone' flame retardants.

- Deca bromodiphenylether (Deca BDE) in styrenes (ABS, HIPS etc), polyolefins (PP, PE), polyester and polyamide (Nylon)⁸.



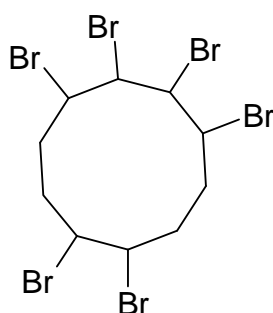
Decabromodiphenyl ether

Penta and Octa bromodiphenylethers (BDE) were used as a flame retardants in WEEE items in the past but have now been phased out in Europe due to concerns over potential toxicity of penta BDE and possible propensity to dioxin formation at elevated temperatures. Octa BDE has been phased out because it contains more than 0.1% penta BDE.

Penta BDE was used in circuit boards (phenolic paper type) and is therefore unlikely to be present in the polymers treated in this study other than in trace quantities. Octa BDE was used in a wider range of polymers, including ABS and HIPS, but it is considered to have very much lower lower toxicity potential compared to Penta BDE.

Polymers containing both penta and octa BDE are likely to be present in the WEEE stream for many years to come, although in small and reducing quantities.

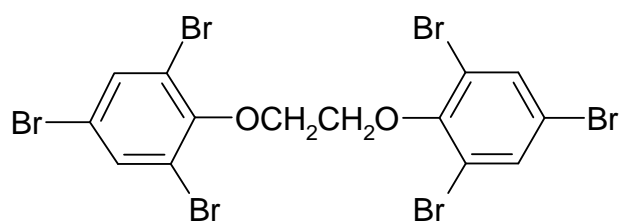
- Hexabromocyclodecane (HBCD) is used in HIPS and PS foam for construction applications. HBCD is used only rarely in E&E equipment.



1,2,5,6,9,10-Hexabromocyclodecane

⁸ Molecule diagrams courtesy of Dr Lina Mehta, Centre for Environmental Research Brunel University

- Bis (tribromophenoxy) ethane (TBPE) in ABS



Bis(tribromophenoxy)ethane

One of the primary environmental concerns regarding the polybrominated diphenyl ethers and some of the other brominated flame retardants is their potential to form brominated dioxins and benzofurans when they are subjected to heat during recycling processes such as compounding, extrusion or moulding. These compounds are of concern because there is evidence of human toxicity⁹. Dioxin formation is more likely when penta and octa BDE are subjected to heat than for deca BDE.

Recent research has indicated that end of life polymers containing certain polybrominated diphenylethers may exceed the limits for brominated dioxins and benzofurans that are set out in the German Dioxin Ordinance¹⁰.

Backbone flame retardants are more stable than matrix flame retardants when reprocessed using heat processes such as extrusion because they effectively become part of the polymer molecule itself.

Recent research by Technopolymer in Japan demonstrated that TBBPA and brominated epoxy oligomer performed better than certain non-halogenated flame retardants in terms of dioxin formation when the polymers in which they were compounded were recycled. Certain other mechanical properties of the polymers were also maintained better in the polymers that contained TBBPA or brominated epoxy oligomer¹¹.

There are many other types of brominated flame retardants developed by different companies for specialist applications, However those listed above are the ones most commonly found in waste electronic and electrical equipment.

⁹ 'Brominated Flame Retardants: A Novel Class of Developmental Neurotoxicants in our Environment?', Eriksson P, Jakobsson E, Environ Health Perspect, 109, pp903-908, 2001

¹⁰ 'Polymers in WEEE contain PBDD/F in the ppb-Range', Schlummer M, Brandl, F, Maeurer A, Gruber L, Wolz, G, Organohalogen Compounds V66, 2004

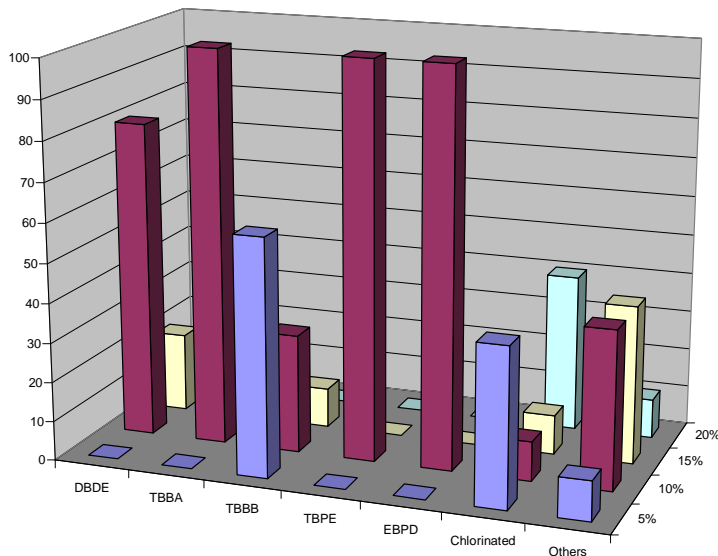
¹¹ 'Comparison of the Recyclability of Flame-Retarded Plastics', Imai T, Hamm S, Rothenbacher K, Journal of Environmental Science and Technology, 2004

5.2. Assessment of likely concentrations by polymer type and typical synergist additives found alongside them

The European COMBIDENT project¹² analysed a range of WEEE polymer samples to establish whether or not they contained brominated flame retardants. The final report only publishes this data for some of the fractions collected. For example it reported that 22% of the samples collected by MIREC (a recycler) and Philips (a producer) contained halogenated flame retardants.

The COMBIDENT project did not necessarily collect samples which were truly representative of the full spectrum of WEEE polymers. This was because the aim of the project was to develop detection and identification techniques, not bulk sorting technology.

The COMBIDENT project also analysed the polymer samples that contained flame retardants to measure the quantity of flame retardant present in each sample:



Quantity of flame retardant present in samples from COMBIDENT project that were flame retarded¹³

These results show that the most common flame retardants found in WEEE polymers, DBDE and TBBA, are likely to be present in concentrations in the range 5-10% in polymers that are flame retarded.

Discussions with representatives of the flame retardant industry indicate that antimony trioxide synergist will almost always be present with brominated flame retardants in thermoplastics and is likely to be added at concentrations in the range 3-5%. Antimony trioxide is not generally used in thermosets such as those used in printed circuit boards.

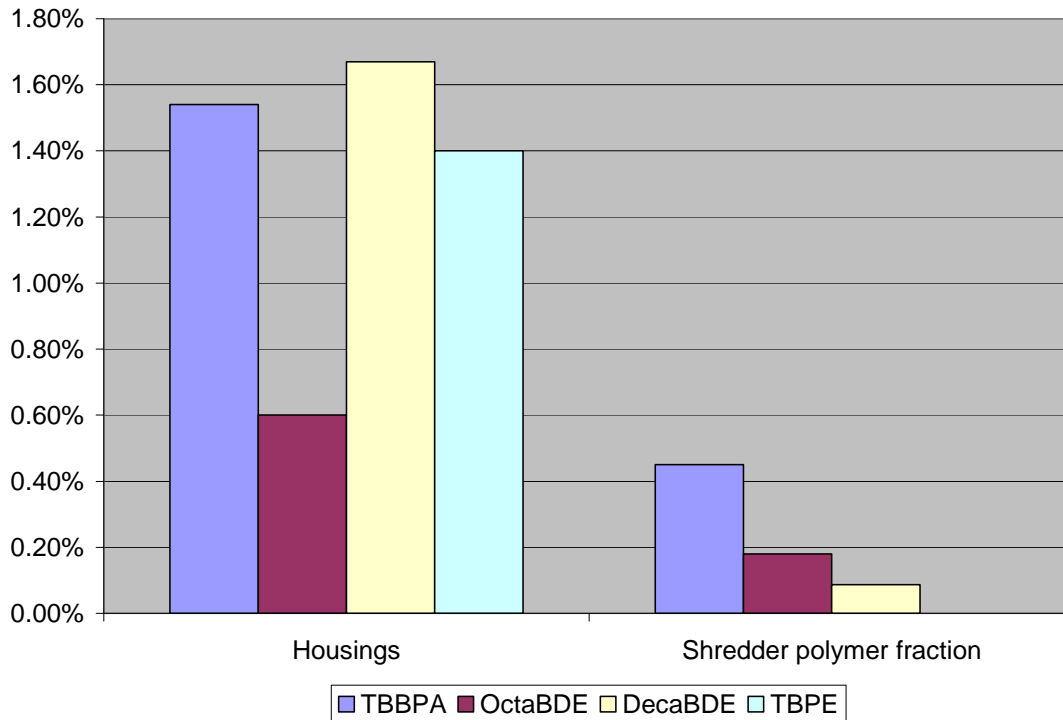
¹² Fraunhofer-Institut für Chemische Technologie (Fh-ICT) 'High Quality Plastic Materials From Electronic Wastes by use of Combined Identification Methods and New Handling Technologies (COMBIDENT). Exploitation Report Contract No. BRPR – CT98-0778. Dec 2001. Project funded by the European Commission under the Industrial & Materials Technologies Programme

¹³ Diagram courtesy of Fraunhofer ICT, Pfinztal, Germany

As a comparison, recent work at the Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany¹⁴ measured the concentrations of brominated flame retardants in:

- Manually dismantled computer monitor, TV-set and telecommunication equipment housings (5 samples)
- Polymer residue from mixed WEEE shredding after metal removal (4 samples)

Average concentrations measured in these samples were:



Average BFR concentrations in WEEE polymer samples collected by Fraunhofer IVV

Concentrations measured in the shredder polymer fraction were probably lower due to the dilution effect of other products like large household goods that are less likely to contain BFRs than computer monitors, TV sets and similar equipment.

¹⁴ 'Polymers in WEEE contain PBDD/F in the ppb-Range', Schlummer M, Brandl, F, Maeurer A, Gruber L, Wolz, G, Organohalogen Compounds V66, 2004

6. Likely mix of polymers in WEEE

WEEE items contain a complex mix of materials including a range of different, often incompatible, polymer types. This complicates the task of recycling WEEE.



Child's electronic toy before and after dismantling into components and polymer types

There is limited reliable data available in the public literature on the amounts of different polymer types present in typical WEEE collected in the UK.

Three studies are reviewed here:

6.1. European COMBIDENT project

The European Combident project led by Fraunhofer ICT in Germany tested a wide range of sorting and identification techniques for WEEE polymers. The study reported in December 2001¹⁵.

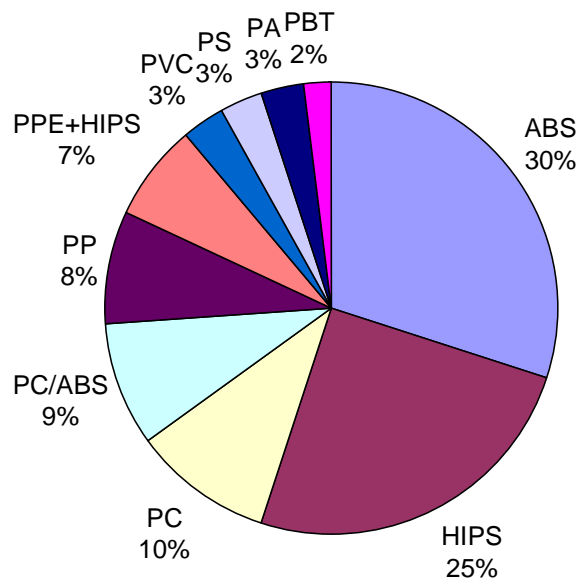
The project identified that WEEE is generally collected in three major groups, each with different composition and processing requirements:

Products	Brown goods, IT equipment	Office equipment, small household appliances, toys, telecommunications equipment	Large white goods
Typical polymers	HIPS, ABS, PC, PC/ABS, PP, PVC	PET, PA, PE, PBT, PMMA	HIPS, PP, PVC
Flame retardants	Deca BDE, OctaBDE, TBBA, HBCD, Sb2O3	Halogenated polyolefins, Ammonium polyphosphates, Melamine compound, Al and Mg hydroxides	Rarely present
Notes	Often hand dismantled to gain access to valuable circuit boards and other components	The WEEE stream with the lowest recycling rate at present.	Generally processed in the UK by vehicle shredders or by specialist fridge processors, both of whom are primarily interested in the ferrous and non-ferrous metals content

¹⁵ COMBIDENT Final Technical Report, EU Contract No BRPR-CT98-0778, December 2001

Note that large white goods are believed to contain only small amounts of flame retarded polymers. Discussions with shredder companies who have investigated these products indicate that in these applications polymers containing flame retardants are generally only used for printed circuit boards, electrical connectors, some cables and in areas with a specific risk of heating.

The COMBIDENT trial obtained 634 polymer samples from 5 collaborating companies, both WEEE recyclers and electronic equipment manufacturers. The precise origin of these samples is not clear from the report but is believed to be primarily waste electronic equipment. The composition of each sample was analysed during the project as follows:



Mix of WEEE polymer samples tested by the COMBIDENT Project¹⁶

As these samples were contributed by a range of companies over an extended period the mix may not be representative of typical WEEE collected in the UK.

¹⁶ Diagram courtesy of Fraunhofer ICT, Pfinztal, Germany

6.2. UK small household WEEE recycling project for Hampshire Natural Resources Trust

To help address the shortage of data on the composition of real WEEE polymers in the UK a project funded by the Hampshire Natural Resources Trust and Onyx Environmental Trust and co-ordinated by Axion Recycling Ltd^{17 18} collected a representative sample of 90 items of small WEEE over ten weeks at a civic amenity site operated by Lewisham Council in North London.

The sample excluded large white goods and metal-rich items as these were collected in a separate skip for processing by a metal recycler.

IT equipment was also included in the trial although all TV sets and CRT monitors were segregated for specialist processing by a CRT dismantler.



Sample of small WEEE collected for HNRT dismantling trial

These items were manually dismantled by experienced operatives at Bruce Metals Ltd, an IT recycler in Sheffield and the resulting fractions were analysed by staff of the Wolfson Electrostatics Centre at Southampton University.

Each item was weighed prior to dismantling and then broken down into component parts. The resulting parts were then weighed and catalogued. The plastic components from each WEEE item were placed into labelled bags and transported to Southampton for analysis. The 90 items of WEEE produced a total of approximately 100 kilograms of mixed plastic and were obtained from the following appliances:

- 16 Audio (stereo, radio/cassette, CD, portables, home)
- 14 Vacuum Cleaners
- 8 IT peripherals (printers etc)
- 6 Fans/heaters
- 5 Visual (TV, video recorders, satellite)
- 5 Lighting/lamps

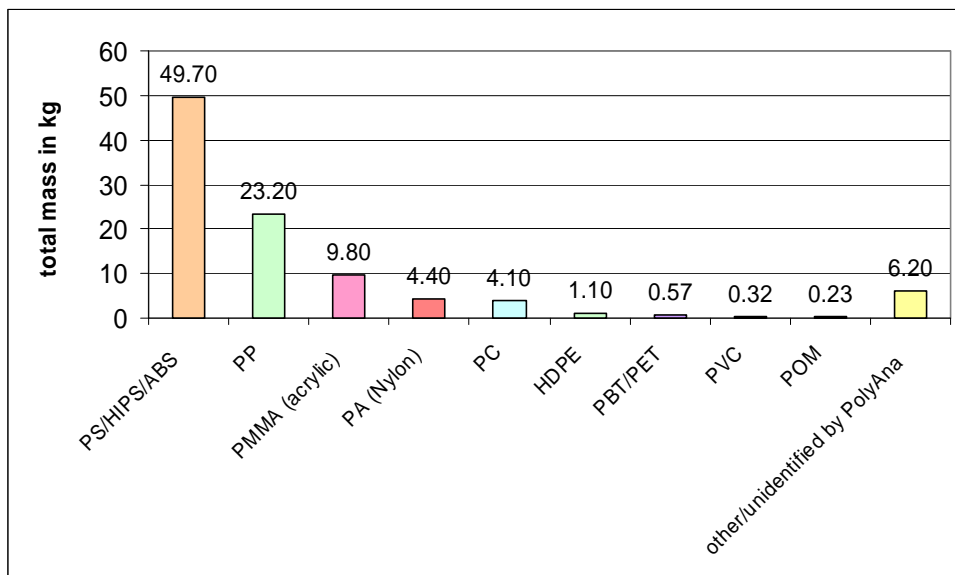
¹⁷ Wolfson Electrostatics report 357/GLH for HNRT, 'Plastics Identification for use in Recycling Waste Electrical and Electronic Equipment (WEEE) - STUDY PHASE REPORT'. June 2004.

¹⁸ Axion Recycling, K Freegard, presentation at UK Plastics Recycling conference, Telford, June 2004.

- 5 Kettles
- 5 Lawnmowers
- 4 Telephones/answer machines
- 4 Irons
- 1 Food mixer
- 1 Toy
- 1 Hair drier
- 1 Sewing machine
- 1 Coffee machine
- 1 Air conditioner unit
- 1 Foot massager

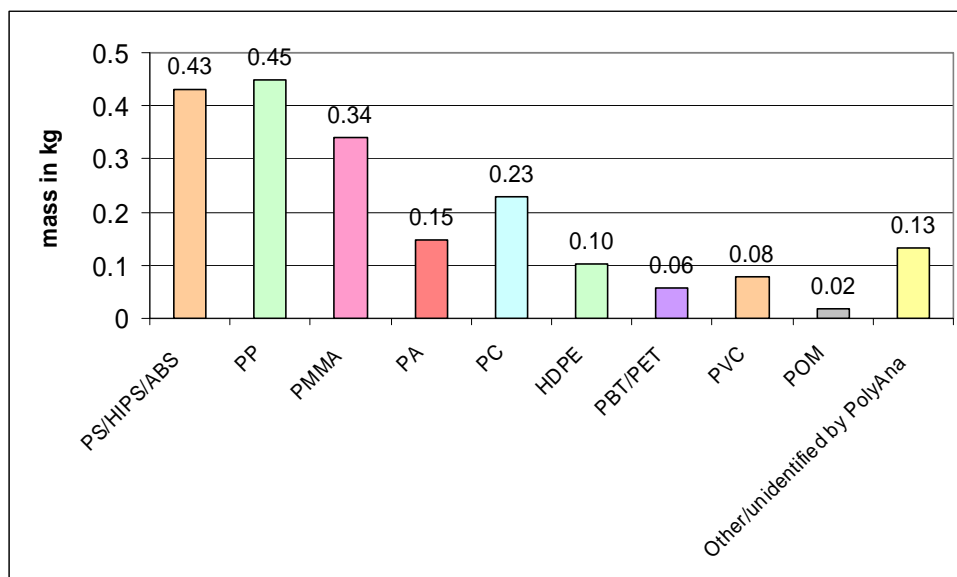
In the Wolfson Electrostatic laboratories at Southampton University, the plastic parts from the 90 items of WEEE were examined with an FT-IR spectrometer for identification. Using this equipment with its 'General' polymer database (comprising 20 common plastics spectra) most of the plastics were identified. A separate spreadsheet was drawn up for each of the items on which both the mass and type of plastic used in its manufacture were recorded. From these spreadsheets it was then possible, within the constraints of the database, to analyse the amount and type of plastics used.

Figure 4.1c below shows the total plastics content obtained from the 90 items divided into basic polymer groups. It was found that around 50% by weight of the total plastic recovered was styrene based. Polypropylene (PP) constituted the next most common material but was less than half as prolific. The styrenes (ABS/HIPS/PS) and PP were the most common plastics used in moulded equipment housings and casings. PMMA (acrylic) was the next most prolific polymer.



Mass of polymer types in 100kg of plastic from mixed small WEEE

Simple analysis of the data obtained from the 90 WEEE items indicated that styrene based plastics were used for the casings of most of the appliances encountered in this investigation. Exceptions to this were lawnmowers (mainly PP) which needed to be robust and not prone to cracking or shattering and small items with heaters such as irons, kettles and hair dryers. Figure 4.1d gives an indication of the average mass of the plastic part according to its polymer group.



Average mass of plastic parts in ~100kg of plastic from 90 WEEE items

As expected the styrene and polypropylene components, which are the plastics mainly used in equipment housing, had the largest average component mass ~0.4-0.5kg. Acrylic (PMMA) and polycarbonate (PC) are often used in transparent form and are found in casings, fascia panels and covers.

Although the average mass of styrene is high there is an enormous variation in the size of the component parts recovered. During dismantling it is easy and indeed often necessary to break some of the components in order to remove them, adding to the variation in the mass distribution. This also has significant implications for determining polymer type and BFR content since:

- many pieces will not be marked or labelled and
- the ID method used should be able to work on small pieces if such pieces are to be recycled.

The study at Southampton did not attempt to identify which polymers contained BFRs.

6.3. EBFRIIP separation study at PHB Netherlands

As a further comparison, a practical study for EBFRIIP in 2004 at the PHB recycling company in the Netherlands treated 30 tonnes of mixed small WEEE (IT equipment, brown goods and other household electrical equipment)¹⁹. This material was shredded and passed through an advanced bulk separation facility operated by PHB.

This facility is claimed to be capable of separating BFR-containing polymers from polymers without BFRs.

The approximate split of the polymer output streams from this trial was as follows:

Material	Weight %
Low BFR PS/ABS	58%
Low BFR PP/HDPE	8%
BFR polymer fractions (mainly PS/ABS)	29%
PVC and Rubber	5%
Total	100%

This does not imply that the BFR polymer fraction contained only polymers with BFRs. The nature of PHB's process is that it does not perform a perfect separation so the BFR-containing polymer fraction will contain some polymers without BFR content. This data is therefore not fully accurate however it indicates that less than 30% of the polymer materials in small WEEE collected by PHB using a state of the art industrial scale process contained BFRs.

¹⁹ 'Recycling of WEEE Plastic Waste at PHB', Study for EBFRIIP, PPAJ van Schijndel and JMN van Kasteren, TU Eindhoven, Netherlands, April 2004

Improvements to the separation efficiency of processes like PHB's will be required if concentrated BFR-containing fractions are to be generated as feed streams for processes of the type investigated in this project.

6.4. Conclusions

WEEE polymers are a complex mixture of polymer types. Hard data on composition of typical WEEE streams is difficult to obtain however it is clear that styrenic polymers predominate with the major fractions comprising:

- HIPS
- ABS
- ABS/Polycarbonate

Polypropylene is also present in significant quantities along with PVC and polyamide. There is then a 'tail' of small quantities of many different types of engineering polymers.

Brominated flame retardants are most likely to be present in HIPS, ABS and ABS/polycarbonate components. They are less likely to be present in polypropylene components, however there is a growing market for BFRs for use in polypropylene in E&E equipment. In due course new processes may need to be developed to remove these flame retardants from polypropylene in WEEE.

Brominated flame retardants are more likely to be present in small brown goods, IT equipment and small domestic appliances than in large white goods. Many of these smaller items are made in Asia where the use of brominated flame retardants is growing.

Brominated flame retardants have not been used in TV housings manufactured in Europe since 1993²⁰ although they are still used in circuit boards and connectors. However they are still likely to be used in TV housings made outside Europe, particularly in China and other Far Eastern countries, where consumption of brominated flame retardants is growing. They may also be used in TVs for the Japanese and American markets where the view of manufacturers and legislators is that the risk to life and health of fire from TVs is greater than the potential environmental impact of including brominated additives in the polymers. **Televisions containing BFRs will therefore still enter the waste stream in Europe for many years to come.**

²⁰ European Brominated Flame Retardants Industry Panel www.ebfrip.org

7. Environmental effects of BFRs and related additives in WEEE polymers

7.1. Environmental effects of BFRs

The main concerns of environmental campaigners about brominated flame retardants are:

- Evidence of neurotoxic effects, possible reproductive interference and uptake of certain brominated flame retardants by mammals in laboratory studies²¹
- Possible formation of more toxic and accumulative products such as lower brominated biphenyl ether congeners and brominated dibenzofurans as a result of decomposition of certain types of brominated flame retardant in the environment^{22 23}
- Widespread occurrence of certain brominated flame retardants across the World including the Arctic in top predators (birds and mammals, including terrestrial species)²⁴

A recent study by the campaigning organisation Clean Production Action in the United States analysed wipe samples from 19 working computer monitors in offices to measure the levels of different brominated flame retardant types present on the screens²⁵. The study found an average of 65 picograms/ sq cm of DecaBDE on each monitor plus smaller quantities of octa and nona BDE and TBBPA. However the study does not record any ill effect associated with these levels of exposure

It has been shown that some PBDEs may form toxic polybrominated dibenzo furans (PBDFs) and polybrominated dibenzo dioxins (PBDDs) during the elevated temperature processes used to mould or extrude polymers during recycling processes²⁶. In this work numerous tests were undertaken to isolate and quantify these substances. When they were detected it was usually in negligible amounts.

Studies in Sweden found that workers at WEEE dismantling plants, where dust containing flame retardants is spread in the air, had 70 times the level of one form of flame retardant compared with a control group of hospital cleaners²⁷. However when conventional occupation hygiene techniques were introduced at the dismantling plants exposure levels dropped substantially.

EU risk assessments for Penta and Octa BDE have concluded that they may present a risk to human health²⁸. Octa BDE is included because it contains more than 0.1% Penta BDE, not because it is thought to present a significant human health risk in its own right.

A recent risk assessment for the European Union has concluded that Deca BDE is safe from the point of view of both environmental impact and human health²⁹ and indicates that no further risk reduction measures are necessary for Deca-BDE, based on supporting evidence collated since the early 1990s.

²¹ 'Brominated Flame Retardants: A Novel Class of Developmental Neurotoxicants in our Environment?', Eriksson P, Jakobsson E, Environ Health Perspect, 109, pp903-908, 2001

²² 'Reductive debromination of commercial polybrominated biphenyl mixture Firemaster BP6 by anaerobic microorganisms from sediments', Morris PJ et al, Appl Environ Microbiol, 58, pp3249-3256, 1992

²³ 'A quantitative structure-activity relationship for the direct photohydrolysis of meta-substituted halobenzene derivatives in water', Stegeman MHL et al, Chemosphere, 26, pp837-849, 1992

²⁴ 'Report from the National Arctic Monitoring and Assessment Programme in Greenland and Faroe Islands 1997-2001', Danish EPA

²⁵ 'Brominated Flame Retardants in Dust on Computers' McPherson A, Thorpe B, Blake A, June 2004, www.computertakeback.org

²⁶ 'Diphenylether, Octabromo derivative - European Union risk assessment report', Final Report, France and United Kingdom, 2003

²⁷ 'Flame retardant exposure: polybrominated diphenyl ethers in blood from Swedish workers', Sjodin et al, Environmental Health Perspectives, 107, 1999

²⁸ 'Diphenylether; pentabromo derivative, European Risk Assessment Report', Final Report, France and United Kingdom, 2002 and 'Diphenylether; octabromo derivative, European Risk Assessment Report', Final Report, France and United Kingdom, Aug 2003

There is a trend towards the use of 'backbone' flame-retardants that are chemically bound to the polymer matrix in preference to the 'matrix' flame-retardants, some of which may leach and/or form dioxin analogues at elevated temperatures more readily.

In most applications Tetrabromobisphenol A (TBBPA) acts as a 'reactive' flame retardant.

TBBPA is currently undergoing an EU risk assessment and definitive answers with respect to its toxicity to man and the environment are expected in the near future. To date the human health part of the TBBPA risk assessment has identified no risks of concern.

7.2. Environmental effects of antimony trioxide synergist used with BFRs

The antimony trioxide synergist which is almost always present with brominated flame retardants has been classified as harmful with limited evidence of carcinogenic effect when handled in powder form and is not toxic to the environment. Antimony trioxide is supplied to polymer compounders in granule form, which substantially reduces the chance of exposure.

Once antimony trioxide is embedded in the polymer there is no risk at all according to the assessments that have been carried out to date.

The HSE listed that the main adverse effect from antimony compounds was that of carcinogenicity, which is the effect, which was used to promulgate the maximum exposure limit (MEL) for occupational exposures to antimony compounds. The data was based on animal studies and on a human lung cancer study. However it could not be concluded whether the observed lung cancers were attributable to antimony or other metals that were likely to have been present, most notably arsenic, which is a proven carcinogen.

7.3. Environmental effects of other additives in WEEE

Brominated flame retardants are only one group among many different additive types used in WEEE polymers. The health and environmental impacts of many of these other additives classes are still unknown.

Occupational hygiene assessments of the use of recycled polymers from WEEE in new products should bear this in mind.

The processes developed during this project do not attempt to remove any of these other additives.

²⁹ http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/ADDENDUM/decabromodiphenylether_add_013.pdf

7.4. Occupational Hygiene issues when reprocessing polymers from WEEE that contain BFRs

This section assesses the likely occupational hygiene issues for three alternative types of recycling plants for WEEE polymers

7.4.1. Recycling of WEEE plastic using mechanical separation methods

This assessment is based on a description of an advanced mechanical recycling process for WEEE polymers that operates in Europe³⁰.

Process description

The mechanical recycling plant operator has developed a method to separate and recycle mixed plastic from WEEE that contains bromine-based flame-retardants. It is reported that the process can separate plastics containing BFRs from those that do not. The recovery rate for the non-BFR plastics is 65 %, or 94 % including the flame retardant fraction.

In other words, 65% of the original plastic content is available for recycling and the remaining 29 % would also be available providing that the technology is available to reduce the halogen (chlorine and bromine) content below that which is specified in the RoHS and Penta directives, (ie levels of less than 0.1 % for both the Penta and Octa brominated diphenyl ethers).

Before being sent to the recycling plant, the waste plastics are pre-treated at another factory, which processes the 'brown' goods stream by hand picking items containing batteries or asbestos. The whole of the stream is then shredded, followed by the handpicking of metals. The remaining material is fed through a hammer mill and magnet to remove the metals. Following this, the sized material undergoes sieving, air classification and granulation leaving several fractions including; copper, aluminium, iron, mixed plastic and a dust fraction.

³⁰ 'Recycling of WEEE plastic waste at PHB', van Schijndel P, van Kasteren J, TU Eindhoven, Study for European Brominated Flame Retardant Industry Panel, April 2004

Safety aspects of the preliminary treatment process

Collection and Transport

It is assumed that a similar process would be used for the collection and transport of the waste from the consumers to the landfill, incinerator or the place of recycling. If WEEE is collected in a responsible manner there should be no more risk to health or of emissions to the environment than during normal use of the equipment.

Storage

Commercial WEEE processing operations in the UK, Scandinavia and other parts of Europe demonstrate that WEEE can be stored safely with minimal damage if the material is caged and covered.



Waab Sweden - Example of good quality storage of collected WEEE

There is a possibility of potentially toxic substances leaching into the ground during the prolonged storage of bulk WEEE material at an incinerator, waste-recycling station or at a landfill site. The evidence available suggests that, owing to their physio-chemical properties (such as low water solubility and high octanol-water partition coefficients) none of the three commercially available brominated diphenyl ethers (Penta, Octa and Deca BDPE) would leach appreciably into landfills. Therefore, providing that suitable storage facilities are in place, and these are managed effectively, at the recycling site in question, there should be negligible risk of the release of brominated DPE into the ground or the air.

Pre-treatment

There will clearly be a risk to health associated with hand dismantling of WEEE items and the hand separation of components containing asbestos and other items that are prescribed by the WEEE Directive such as beryllium, mercury and polychlorinated biphenyls (PCBs).

It is assumed that most of the components containing hazardous materials that are present in the waste will be in good condition and could be separated by hand, without generating meaningful concentrations of airborne emissions. However, there will probably be some isolated situations where damaged components are encountered. In these cases, the site operative can wear appropriate personal protective equipment including respiratory protective equipment where necessary.



Dismantling operations must be well controlled to protect the health and safety of operatives

There is also a possibility that some of these products may be damaged prior to or during the transport and subsequent storage of the waste. Damage may also occur or be existing damage made worse due to inclement weather, whilst the material are being stored.

Safety aspects of the mechanical recycling process for the mixed plastic fraction

A typical mechanical recycling process for mixed WEEE plastic fractions includes size reduction in several stages followed by a series of separation steps to separate polymer types and remove impurities. These processes may be conducted wet or dry. At the end of the process the polymer may be compounded to produce granules in an extruder or the product may be sold as chip for direct re-use.

The separation process will generate a wide variety of dust fractions, which will include dust containing metals, plastics and general dust containing both 'total inhalable' (the fraction which is inhalable) and 'respirable' (the fraction that is fine enough to reaches the insides of the lungs) fractions of particulate. The main metals in the dust are reported to be copper, aluminium and iron, although it should be noted none of these are particularly toxic in metallic form. It is possible that some heavy metals will be present, presumably as alloys or amalgams and provided that these are not heated (to produce the elemental metal or rather metal oxide) they will remain in metallic form and thereby relatively innocuous.

The plastics will contain the original base polymers, along with whatever other substances were used in their manufacture, including brominated and other flame-retardants and additives such as antimony oxides. The risk

assessments to date have shown that, whilst there is a theoretical possibility of the leaching of certain substances, for example brominated flame-retardants from plastics, the actual risks presented by these are very low. Furthermore, the risks presented by the constituents of the brominated flame-retardants in their manufacture (and assumed to be similar during recycling) have been shown by the EU risk assessments to be low, providing that good occupational hygiene principles are adopted. It follows that the risks of exposure to hazardous substances, in particular to the constituents of the plastics, in the preliminary processing of the brown goods should remain low providing sound occupational hygiene principles are observed.

The main treatment will have similar risks associated with it, although the particulate that will be handled will be finer than that at the pre-treatment stage. Many of the processes involve treatment with water, which will suppress the generation of dust.

As for the pre-treatment process, the risks of exposure to hazardous substances during the processing of the waste stream should remain low, providing sound occupational hygiene principles are observed.

Emissions to the environment

Providing that all of the dusty processes are fitted with suitable local exhaust ventilation (LEV) and that the exhaust from such processes are controlled through adequate filtering mediums, before being exhausted to the atmosphere or being returned to the workplace, the emissions to the environment should remain negligible.

Since it has been suggested that the exposures to the personnel should be low, then providing that the control measures are maintained in good working order, it follows that fugitive emissions should also remain negligible.

Breakdown and transformation products

There is a theoretical possibility of dibenzofurans and dibenzo-p-dioxins being formed from brominated diphenyl ethers, mainly at elevated temperatures (but also by other routes and as a result of impurities in the polymer) during the handling of brominated diphenyl ethers. However the available information for recycling of plastics indicates that there is little or no increase in the amounts of gases or vapours that are formed.

7.4.2. Recovery in non-ferrous metal smelting processes

This assessment is based on a description of a trial by the Swedish company Boliden and the Association of Plastics Manufacturers in Europe (APME) to process WEEE polymers in a non-ferrous metal smelting furnace³¹.

The objective of the study was to consider the viability of adding waste PCs into the feed stream of the Zinc Fuming Furnace that is currently in routine operation at the Ronnskar plant of Boliden Minerals AB in Sweden. The plant recovers waste printed circuit boards in a Kaldo furnace.

The project description concludes that the process yields high rates of metal recovery and that the plastic serves a dual purpose both as a reducing agent for the process itself and as a source of energy for the smelting.

WEEE Pre-treatment

The Waste electrical and electronic equipment (WEEE) used in the study was transported by train from various sources in Scandinavia and was pre-screened to remove components that were known to contain mercury.

A hammer mill shredder with a magnetic iron separator was used to prepare the bulky material. After sampling, the weee material was transferred to the Ronnskar smelter.

During the mechanical treatment of the waste, there was no increase in temperature above that which is normally encountered during the routine treatment of the scrap. The mix containing the PC scrap was transferred by truck to a conveyor. The conveyor loaded the scrap into the silos, which were located above the zinc-fuming furnace. The PC scrap/slag mixture and pelletised steel making dust were drawn from the silos and fed to the fuming furnace.

It was reported that the operatives charged the furnace using the procedures that they normally adopted for the charging of printed circuit boards and the fuming process did not deviate from its usual performance.

Safety aspects of the process

Collection, transport and storage

The issues will be identical to those for mechanical recycling described above, with negligible risk of emissions to environment during these stages of the process

Pre-treatment

There should be negligible risk to health from brominated compounds as a result of the pre-treatment process since this involved the removal of only mercury and cadmium-containing components. However there would be risk of exposure to mercury and cadmium compounds if the pre-treatment process is poorly controlled

Treatment at the Ronnskar smelter

The furnace will contain varying amounts of metals, notably heavy metals. Although the furnace is provided with extraction, there may be a possibility of the operatives being exposed to various metal vapours or metal oxides that will form as a result of condensation in the air and as dross on the surface of the molten metal.

It was reported that air sampling was undertaken for heavy metals and dioxins during the study and that all of the results were below the actual or recommended Swedish occupational exposure limits (OELs).

Analysis was also carried out for halogen-containing organic compounds: chlorinated PCDD/Fs, brominated PBDD/Fs and mixed brominated and chlorinated PBCDD/Fs. The results obtained varied significantly, and there was no correlation between the amount of PXDD/Fs and their source or age.

The average PXDD/Fs content of all the samples of waste E+E plastics met the German emission regulations.

³¹ 'Plastics Recovery from Waste Electrical and Electronic Equipment in Non-Ferrous Metal Processes' Mark F, Lehner T, APME Technical Paper, 2002.

Emissions to the environment

It is reported that the charging area to the Kaldo furnace is encapsulated and provided with extraction to a dust control unit (bag house) and that the process gas stack is connected to a venturi scrubber. Post combustion takes place at around 1200 °C with a residence time of more than 2 seconds, in which case there is negligible risk of the formation of brominated dibenzofurans and dibenzo-p-dioxins or the chlorinated equivalents. Therefore, it is unlikely that there will be meaningful emissions from the furnace.

7.4.3. Recovery in a state of the art incinerator

The final treatment option considered in this section is incineration. A comprehensive study was undertaken for EBRIP and APME at the TAMARA pilot scale municipal solid waste combustion plant in the Karlsruhe Research Centre ³².

The results of the study indicate that it is technically feasible to recycle bromine in WEEE plastic containing brominated fire retardants by using modern municipal solid waste combustion plants providing they are equipped with suitable wet scrubbing systems. The TAMARA study showed that it was possible to recover commercial bromine based products such as bromine, hydrogen bromide or sodium bromide.

The standard fuel used at the TAMARA plant is a mixture of 70% organic green waste and 30% refuse derived fuel (RDF). For this study the RDF was replaced by an equivalent quantity of WEEE from shredded mixed polymers, television housings and printed circuit boards.

The conclusions of the study indicate that under optimum conditions, modern municipal solid waste combustion facilities that are equipped with wet scrubbing systems can be used to recover energy from polymers containing BFRs.

³² 'Recycling of bromine from plastics containing brominated flame retardants in state-of the-art combustion facilities' Vehlow et al, Forschungszentrum Karlsruhe, Waste Management Research, 18, pp131-140, 2000

7.5. Conclusions

Concerns have been raised over the environmental and human health impacts of only certain classes of brominated flame retardants. These are the polybrominated biphenyls, polybrominated diphenyl ethers (in particular, penta and octa BDE).

Principal concerns are:

- Some of them have been shown to bioaccumulate in a wide range of organisms
- It is believed that they may have neurotoxic effects and/or effects on human reproductive processes
- Some of them may decompose to produce toxic polybrominated dioxins and furans (PBDD/F) when subjected to elevated temperature processing

It should be emphasised that many other types of additives are used today and have been used in WEEE in the past. These include a wide range of pigments and surface treatments, plasticizers, impact modifiers, fillers. The environmental and health impacts of reprocessing most of these compounds are unknown.

Brominated additives have been studied in much greater detail but nobody knows the balance of risk between these materials and other additives which may be present in the polymers to be recycled.

The occupational health and safety issues for the substances that will be handled by most existing WEEE recycling processes after dismantling should be well established and known.

For example, there will be numerous 'classical' occupational exposure scenarios associated with the recovery of metal in a smelting process. From the relatively low exposures due to handling the metal to the higher exposures as a result of 'drossing off' the metal oxides that form on the upper surface of molten metal pots right through to the high exposures associated with maintenance work on the melting pots.

It is unlikely that the introduction of WEEE to the input streams of most of these processes will cause a significant increased risk to health, for the operatives who actually carry out the work, over and above any of the existing risks that are inherent in the process in question. In many instances, the metal oxides or various gases that are produced will be more toxic than the flame-retardants that are being recovered.

However, low temperature recovery or recycling processes will always have a much lower risk of emissions and of dioxin formation than high temperature solutions but they may have increased risk of other emissions such as solvents.

8. EU and UK legislation applying to polymers containing BFRs

8.1. General EU legislation, standards and codes of practice

Most waste management activities and strategies in the UK are now driven by EU Directives. This legislative framework can be considered in terms of:

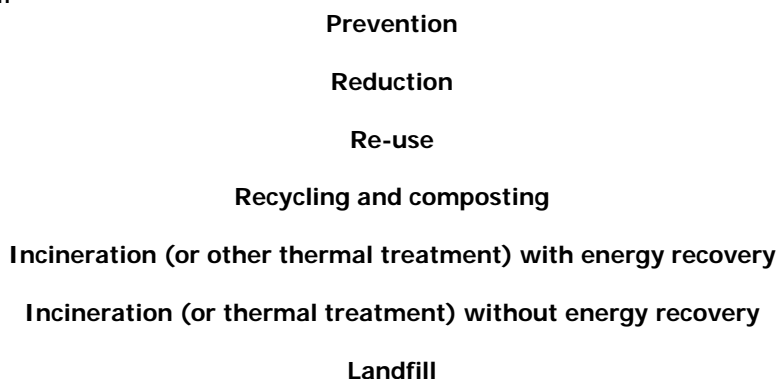
- **Horizontal legislation** : Waste Framework Directive, hazardous waste, waste shipments, Environmental Information Regulations
- **Waste treatment standards** : Landfill Directive, Waste Incineration Directive, Environmental Impact Directive, Strategic Environmental Assessment Directive
- **End-of-Life product waste stream Directives** : packaging, end-of-life vehicles, WEEE, batteries, biowaste

8.1.1. The Waste Framework Directive

The key Directive is the **Waste Framework Directive of 1975 (75/442/EEC) as amended in 1991 (91/156/EEC)**. This stresses the fundamental importance of waste prevention and makes a distinction between :-

- **Qualitative** waste prevention and reduction – using less toxic or less hazardous resources and/or producing less toxic or less hazardous wastes (and using less in quantitative terms)
- and
- **Quantitative** waste prevention and reduction – using less resources and/or producing less wastes in tonnage terms or in terms of resources/waste per unit of product/service

The Waste Framework Directive also placed waste prevention in the context of the waste hierarchy, emphasising the move away from landfill:



Possible re-use applications for WEEE – near the top of the waste hierarchy

A key element in the Directive involves the 'disposer' in defining waste:

'waste' means any substance or object which the holder disposes of or is required to dispose of

'disposal' means:

- the collection, sorting, transport and treatment of waste as well as its storage and tipping above or below ground
- the transformation operations necessary for its re-use, recovery or recycling

Inherent in these definitions is the 'certainty' of waste being disposed, although inclusion of 'transformation operations' under the heading of disposal creates complications for re-use, recovery and recycling. This interpretation has led to problems as to when (if) waste ceases to be waste if it is recycled or recovered. It is possible that amendments will be made to the Waste Framework Directive definitions as part of the Thematic Strategies published in 2005 (see below).

A number of important draft EU Communications³³ were circulated for consultation in October 2005, and published in December 2005. Alongside the publication of these documents it became apparent that the EU Commission was planning to simplify existing waste legislation, by re-writing and combining 18 EU Directives and six regulations covering the sector.³⁴

In January 2006, a 'composite' report was published titled 'EU Waste Policy : The Story Behind the Strategy'.³⁵

This 'overview' stresses the link between the Sixth Environment Action Programme (6th EAP, 2002-2012) and the development of the Thematic Strategy on Waste Prevention and Recycling, given the priorities of climate change, health and quality of life, natural resources and waste. The review comments on the generally negative view of waste and the need to move towards a more flexible regulatory framework promoting a recycling society – "... a society that avoids wastage and uses the resources that are found in waste".

Early EU Directives did not specify the environmental emission parameters for various waste management options. However, more recent Directives address some of these issues, e.g. the Landfill Directive which specifies methane emissions and the Waste Incineration Directive which specifies dioxins. Four outstanding issues were identified:

- past legislation addressed visible, and often acute, environmental problems. New policies need to be based on wider information that is currently not available, but still focussing on environmental protection
- the link between waste generation and economic growth
- the potential to increase use of the resources embedded in waste, either for recycling or for energy recovery – thus reducing demand for primary resources
- the need to re-consider the role of trans-frontier movements for recycling

An emphasis is placed on the 'triangular' links, first put forward in 2003, between the Thematic Strategy on Sustainable Use of Resources, Integrated Product Policy and the Thematic Strategy on the Prevention and Recycling of Waste, with the latter being the key driver. These have been extensively discussed by stakeholder/focus groups, workshops and meetings of experts.

A key issue raised is whether weight or volume indicators are the most appropriate indicators of the environmental burdens of waste, in the context of waste prevention.

The waste hierarchy is supported, but for specific waste streams energy recovery may be environmentally preferable to recycling. For example the document argues that incineration may be the best option for mixed contaminated plastics. Given the existing end-of-life product Directives, improving recycling markets is potentially more important than promoting material-based recycling, but this will be reviewed in five years time.

³³ This is a personal summary of key points. Readers are advised to refer to the actual draft Documents.

³⁴ <http://europa.eu.int/comm/environment/waste/strategy.htm>

³⁵ http://europa.eu.int/comm/environment/waste/pdf/story_book.pdf

Reference is made to the need for:

- streamlining waste legislation
- clarifying the continued role of the waste hierarchy, including waste prevention and definitions of recovery and disposal, and the definition of waste
- common EU standards and an EU recycling market
- an overall eco-efficient recycling and recovery policies covering all waste materials (existing Directives based on waste-streams cover only 7% of total waste volumes)
- a good knowledge base informs waste policy

A timetable of 'next steps' is provided leading to 2008 and the entry into force of the revised Waste Framework Directive, together with other related measures and activities, with the Waste Strategy to be reviewed in 2010.

The position of the European Commission was clarified further during 2005 by the following proposal:

Communication from the Commission (2005). Proposal for a Directive of the European Parliament and of the Council on waste. Brussels, 21.12.2005, COM(2005) 667 Final

This is intended to revise and optimise the provisions of the Waste Framework Directive 75/442/EC (as amended by 91/156/EEC), and is expected to come into force in 2008:

- "This Directive lays down measures with a view to reducing the overall environmental impacts, related to the use of resources, of the generation and management of waste.
- For the same purposes, it also makes provision whereby the Member States are to take measures, as a matter of priority, for the prevention or reduction of waste production and its harmfulness and, secondly, for the recovery of waste by means of re-use, recycling and other recovery operations".

With the main amendments being:

- the introduction of an environmental objective
- clarification of the notions of recovery and disposal
- clarification of the conditions for the mixing of hazardous waste
- introduction of a procedure to clarify when a waste ceases to be a waste for selected waste streams, with compost and aggregates being the first to clarified (by 2008)

Article 3 keeps the same definition of waste:

- 'waste' means any substance or object which the holder discards or intends or is required to discard

But adds a new definition of recycling:

- 'recycling' means the recovery of waste into products, materials or substances whether for the original or other purposes. It does not include energy recovery.

Article 5 in Chapter II is titled 'recovery':

- Member States shall take the necessary measures to ensure that all waste undergoes operations that result in it serving a useful purpose in replacing, whether in the plant or in the wider economy, other resources which would have been used to fulfil that function, or in it being prepared for such a use.

Article 11 on Secondary products, materials and substances:

- With a view to determining whether it is appropriate to deem certain wastes to have ceased being waste, to have completed a re-use, recycling or recovery operation, and to reclassify that waste as secondary products, materials or substances, the Commission shall assess whether the following conditions are met :-
 - reclassification would not lead to overall negative environmental impacts
 - a market exists for such a secondary product, material or substance

In this context, a significant amendment to the definition of Recovery in Annex II (replacing Annex IIB) is provided:

R1 Use principally as a fuel or other means to generate energy.

This includes incineration facilities dedicated to the processing of municipal solid waste only where their energy efficiency is equal to or above :-

- o 0.60 for installations in operation and permitted in accordance with applicable Community legislation before 1 January 2009
- o 0.65 for installations in operation and permitted in accordance with applicable Community legislation after 31 December 2008

$$\text{Energy efficiency} = ((E_p - (E_f + E_i)) \cdot 0.97) / (E_w + E_f)$$

E_p means annual energy exported calculated with energy in the form of electricity multiplied by 2.6 (GJ/y)

E_f means annual energy input to the system from fuels contributing to the production of steam (GJ/y)

E_w means annual energy contained in the treated waste (GJ/y)

E_i means annual energy imported excluding E_w and E_f (GJ/y)

0.97 is a factor accounting for energy losses due to bottom ash and radiation

8.1.2. The Landfill Directive

The Council Directive (99/31/EC) on the landfill of waste is seen as possibly the most important Directive likely to affect the UK, with bans on tyres and other materials to landfill, an end to co-disposal (landfilling of hazardous and non-hazardous wastes in the same landfill) and targets for the diversion of biodegradable municipal wastes from landfill. The Directive also sets down a classification of landfill sites:

- landfill for hazardous waste (including relevant hazardous components of WEEE)
- landfill for non-hazardous waste
- landfill for inert waste

In February 2004, the European Parliament called for a ban on landfilling of all waste by 2025 as part of the forthcoming EU Thematic Strategy on the Prevention and recycling of Waste (see below):

- ban on landfilling of untreated biodegradable waste by 2010
- ban on landfilling of recyclables by 2015
- ban on landfilling of recoverable waste by 2020
- ban on landfilling all residual waste by 2025 – except where 'unavoidable' or hazardous

At the same time, the resolution points to the 'importance of energy recovery for sustainable waste management' in meeting the landfill ban.

8.1.3. The Waste Incineration Directive

The Council Directive (00/76/EC) on the incineration of waste (known as the Waste Incineration Directive or 'WID') repeals the 1989 Municipal Waste Incineration Directive (89/429/EEC and 89/369/EEC) and the Hazardous Waste Incineration Directive (94/67/EC) with effect from 28th December 2005. The Waste Incineration (England and Wales) Regulations 2002 (SI 2002 No. 2980) came into force on 28th December 2002 and Edition 2 of Guidance on Directive 00/76/EC on the incineration of waste was published in August 2004. This Directive applies immediately to all new incinerators and will apply to existing installations with effect from 28th December 2005, implementation in the UK being carried out mainly under the existing Pollution Prevention and Control (PPC) regime:

- regulation of larger incinerators and co-incinerator as Part A(1) activities by the Environment Agency
- regulation of smaller Part A(2) or Part B incinerators by Local Authorities

8.1.4. The RoHS Directive

Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS) (02/95/EC) (The 'RoHS Directive') is a daughter directive of the Waste Framework directive. It aims to improve qualitative waste prevention in waste electrical and electronic equipment (WEEE).

The RoHS directive requires that from 1st July 2006 new E+E equipment put on the market does not contain:

- Lead
- Mercury
- Cadmium
- hexavalent chromium
- polybrominated biphenyls (PBBs)
- polybrominated diphenylethers (PBDEs)

Penta and Octa diphenylether are already phased out (in concentrations above 0.1% by mass) by the Marketing and Use Directive of 15 August 2004 (2003/11/EC). However Deca BDE is still widely used in electronic equipment and the bromine industry has resisted its inclusion in the RoHS list due to the positive outcome of the EU environmental impact risk assessment for Deca BDE.

The RoHS Directive gives producers a clear guarantee that no individual EU Member States will be able to introduce separate bans or restrictions on any other substance than those specified in the RoHS Directive. A review of the RoHS Directive to potentially integrate new substances to be phased out will only take place from 2005.

This Directive has major implications for manufacturers (and component suppliers), importers, brand owners and potentially even retailers who must be able to demonstrate that their products are RoHS compliant and do not exceed threshold limits for toxic substances. Sellers of refurbished products will also be affected.

In Europe in April 2005, the Technical Adaptation Committee (TAC) took a vote on the draft Commission Decision amending the RoHS Annex to include two further exemptions - deca BDE in polymeric applications and lead in lead-bronze bearing shells and bushes.

On 15th and 21st October 2005, exemptions to the RoHS Directive were published as Commission Decisions in the Official Journal and became law. Applications that will be exempt include the use of lead in optical and filter glass and electronic ceramic parts, and cadmium in electrical contacts.³⁶

The RoHS Directive came into force on 1st July 2006.

In a note circulated in June 2006, the European Commission advised that the exemption for deca-BDE in polymeric applications does not apply, as commercial formulations of deca contain nona-BDE which was/is covered by the RoHS ban.

³⁶ http://www.dti.gov.uk/sustainability/weee/RoHS_Exemptions_October2005.pdf

8.1.5. The WEEE Directive

The **Waste Electrical and Electronic Equipment (WEEE) Directive (2002/96/EC)** is European environmental legislation. It is one of a small number of European Directives which implement the principle of "extended producer responsibility". Under this principle producers are required to take responsibility for the environmental impact of their products, especially when they become waste. The WEEE Directive applies this in relation to electrical and electronic equipment (EEE).

The broad aim of the WEEE Directive is to address the environmental impacts of WEEE and to encourage its separate collection and subsequent treatment, reuse, recovery, recycling and environmentally sound disposal.

The Directive seeks to improve the environmental performance of all operators involved in the lifecycle of EEE especially those dealing with WEEE. Accordingly it sets certain requirements relating to the separate collection of WEEE, standards of its treatment at permitted facilities, and sets targets for its recycling and recovery.

The following table shows the collection recovery and recycling targets to be reached by 31st December 2006. The Directive was published in the Official Journal in February 2003, and Member States had until August 2004 to introduce relevant national legislation (the UK has still to do so).

WEEE Directive Targets (by 31st December 2006)

Category of WEEE	Recovery %	Recycling %
1. Large household appliances	80	75
2. Small household appliances	70	50
3. IT + telecom equipment	75	65
4. Consumer equipment	75	65
5. Lighting equipment	70	50
6. Electrical + electronic tools	70	50
7. Toys, leisure and sport	70	50
8. Medical devices	n/a	n/a
9. Monitoring /Control instruments	70	50
10. Automatic dispensers	80	75
Gas discharge lamps	80	80

It appears likely that Local Authorities will have a role to play in 'collecting/receiving' WEEE items from households, but most household waste composition data does not contain information broken down into the above ten categories of WEEE. Civic amenity sites are seen as having a key role, but there are implications for site licence conditions and the need for impervious surfaces and weatherproof storage facilities.

In addition, the separate categories and potential for disassembly and reuse means that all items must be treated with care with some arguing for wrapping items to prevent damage in storage and/or transport. An 'indicative' list of EEE was published as Annex 1B to the Directive, and the targets apply to the whole product and not just the electrical/electronic component(s).

The WEEE Directive requires that Member States shall aim at achieving a minimum separate collection of 4 kilograms (at one stage the proposal was for 6 kg) on average per inhabitant per year of waste electrical and electronic equipment from private households.

Other requirements of the WEEE Directive are: -

- Member States must set up accessible collection systems, free for householders by 13th August 2005
- By 13th August 2005 individual producers must provide for the financing of WEEE collection, treatment, recovery and environmentally sound disposal - from users other than private households
- Historical 'orphan' WEEE products will be funded collectively based on market share by type of equipment
- Distributors of EEE products are responsible to accept equivalent WEEE products, free for households, on a one-to-one basis and provided they are uncontaminated
- Member States shall adopt appropriate measures so that consumers participate in the collection of WEEE and to encourage them to facilitate the process of reuse, treatment and recovery
- Member States must ensure WEEE products are taken to permitted treatment facilities

Clause 18 of the WEEE Directive encourages, but does not mandate at this stage, the incorporation of recycled content in new E+E equipment.

Finally Annex 2 of the WEEE Directive requires separate treatment for the following components of recovered WEEE:

- Capacitors containing PCBs,
- Liquid crystal displays over 150sq cm
- Mercury switches
- Asbestos (found for example in some older domestic irons)
- Polymers containing brominated flame retardants

The requirements of Annex 2 effectively mean that shredding of unsorted WEEE is a process that cannot comply with the WEEE Directive.

Some segregation or sorting and dismantling of the feed stream will always be required to ensure that the items listed above are separately treated.

The driving force for this project is the requirement in Annex 2 of the WEEE directive that polymers containing brominated flame retardants are treated separately.

The UK is late in implementing the timetable requirements of the WEEE Directive. Implementation in the UK is currently expected by mid 2007.³⁷

8.1.6. Likely future developments

The general trend of EU environmental legislation is towards tougher targets and tighter regulations.

In the short term the most immediate impact for the E&E sector will come from the review/revision of the WEEE Directive that is due in 2006. It is likely that reuse targets may be introduced to complement increased recycling and recovery targets.

As foreseen in the EU 6th Environmental Action Programme, the longer term development of EU policies will be in the context of seven Thematic Strategies, aiming for a more integrated and holistic approach to policy development.

The two Thematic Strategies of direct relevance for WEEE and BFRs are:

- COM 301: 'Prevention and Recycling of Waste'
- COM 572 'Sustainable Use of Natural Resources'.

Latest thinking on these strategies is summarised below:

8.1.6.1. Prevention and Recycling of Waste Strategy (COM(2003) 301 final)

Communication from the Commission (2005). Taking sustainable use of resources forward: A Thematic Strategy on the prevention and recycling of waste.

This communication aims to reduce the overall negative environmental impact of resource use through:

- a renewed emphasis on full implementation of existing legislation
- simplification and modernisation of existing legislation
- introduction of life-cycle thinking into waste policy (cradle to grave)
- promotion of more ambitious waste prevention policies
- more and better knowledge and information
- development of common reference minimum standards for recycling, and prevent the threat of 'eco-dumping'
- further elaboration of the EU's recycling policy, to allow the adoption of environmental criteria for specific waste flows in order to specify when they no longer fall under the scope of waste legislation, but rather are to be considered as products
- less waste to landfill
- more compost and energy recovered from waste
- more and better recycling

The document states: "As waste moves away from landfill it will move into a variety of options higher up the waste hierarchy, all of which will be better for the environment. An important part of this picture is the conversion of waste into energy and into compost, a process which is currently under-used in a number of Member States

³⁷ http://www.dti.gov.uk/sustainability/weee/Deca_BDE_Decision_October2005.pdf

The development of clean and efficient incinerators and co-incinerators, meeting the high standards set out in the Waste Incineration Directive will mean that for a number of waste flows, incineration with energy recovery will be the best option. This will help the EU meet its targets under the Directive on the promotion of electricity from renewable energy sources."

With further reference to energy from waste the document states:

"the definitions contained in present legislation as interpreted by the European Court of Justice do not promote best environmental practice, for example as regards recovering energy from waste in municipal incinerators."

"...an amendment to the Waste Framework Directive which will base the definition of recovery on the notion of substitution of resources in the economy as opposed to the specific plant."

"A first example of this approach is the use of efficiency thresholds to classify waste treatment in municipal incinerators either as recovery or as disposal. Current jurisprudence of the European Court of Justice classifies the overwhelming majority of municipal incinerators as disposal facilities. This classification may have negative implications, leading to a degradation of the environment. For example, incineration with energy recovery is usually considered as a means of diverting biodegradable municipal waste from landfills. However, there are concerns that if incineration is defined in the same category as landfilling, some local authorities may be tempted to choose the cheapest option (landfilling), which will in turn degrade the environment. Additionally, municipal incinerators with high energy efficiency are negatively discriminated in comparison with some co-incineration operations that have similar energy efficiencies but less stringent emission controls."

"A recovery definition that takes into account that energy produced by a given municipal incinerator substitutes the use of resources in other energy producing plants will better reflect the environmental benefits of incineration. However, the energy efficiency of municipal incinerators can vary dramatically. At low energy efficiencies incinerators may not be more favourable than landfill. At high energy efficiency incineration may be as favourable as mechanical recycling or bio-treatment of certain waste flows." Reference is then made to the proposed change to the definition of R1 in Annex IIB (see separately).

"Overlaps between the permit procedures set-up in the Waste Framework Directive and the Integrated Pollution Prevention and Control Directive will be removed by indicating that where an IPPC permit is held, an additional waste permit is not necessary."

Proposed guidelines on the issue of when by-products should or should not be considered as waste, based on the jurisprudence of the European Court of Justice, are expected to be published in 2006.

8.1.6.2. Sustainable Use of Natural Resources Strategy

A further influential EU document is the strategy for use of natural resources:

Communication from the Commission (2005). Thematic Strategy on the sustainable use of natural resources.

- the overall objective is to reduce the negative environmental impacts generated by the use of natural resources in a growing economy, a concept referred as de-coupling and involving life cycle assessment of impacts from cradle to grave on an EU and global scale as necessary
- to include improved knowledge (including an 'information hub')
- tools to monitor and report progress : efficiency and productivity in use of natural resources and energy, resource-specific environmental impacts, eco-efficiency, and overall indicator of ecological stress of resource use
- foster the application of strategic approaches in Member States, with sector action plans for specific economic sectors
- raise awareness
- a long term horizon of 25 years is proposed

8.2. Specific UK legislation, standards and industry codes of practice

With publication of the **The National Waste Strategy for Wales** in 2002, **Waste Strategy 2000** now applies only to England and was due to be revised in 2005. These are complemented by the **National Waste Plan for Scotland** published in 2003

These strategies focus on household and municipal waste with an emphasis on promoting waste prevention, recycling/composting and energy recovery where appropriate, but also refer to other waste streams. Local Authorities have been given statutory Best Value Performance Indicators (BVPIs) for 2003/04 and 2005/06 with reference to municipal waste.

Waste Collection Authorities also now have a statutory duty under the Household Waste Recycling Act 2003 to provide kerbside collection for two materials in place by December 2010, unless uneconomic to do so. Such provision is now being called the 'Ruddock test', after the MP who introduced the Bill to the House of Commons.

Data from Defra Municipal Waste Management Survey 2002/03 indicated that 66% of households in England received a kerbside collection of least one dry recyclable and/or green waste separate from residual waste, up from 58% in 2001/02. This statutory duty is not strictly linked with BVPI targets, which are weight-based.

Exemptions will be based on :-

- meeting/exceeding BVPI targets for recycling/composting
- obtaining an 'excellent' grading in Audit Commission CPA
- meeting/exceeding LATS targets for 2005/06

In the Consultation Paper on Guidance on the Act the only WEEE items mentioned are mobile phones, although it is likely that civic amenity sites will receive larger WEEE items.

Proposed Office of the Deputy Prime Minister (ODPM) amendments to the relevant BVPIs for 2005/06 mean that Local Authorities will have to return data on the breakdown of recyclable materials contributing to the overall recycling tonnage and percentage target, and also the kerbside collection of recyclables broken down by percentage.

A proposed new BVPI for 2005/06 covers re-use, covering Local Authorities and third parties (including the community sector) having a formal relationship with Local Authorities. Such re-use of WEEE items means that they could remain in the system for a longer period of time before being disposed of.

The Waste and Emission Trading Act of 2003 transposes key aspects of the Landfill Directive, including the definition of municipal waste and targets for diversion of biodegradable waste (including tradable allowances).

The following table shows the very small number of landfill sites now available for landfilling of hazardous wastes, including relevant WEEE items as a result of implementation of the Landfill Directive:-³⁸

Environment Agency Region	Permitted hazardous waste landfill sites	Separate cells for stable non-reactive hazardous waste
Anglian	2	2
Midlands	2	6
North East	3	4
North West	3	3
South West	1	3
Southern	1	1
Thames	1	1
Total	13	20

Of the three high-temperature incinerators in the UK one is currently mothballed, and costs are much higher than traditional co-disposal landfill methods. In October 2005 Shanks sold its hazardous waste business to Onyx, including the Fawley incinerator and eight other chemical treatment works.

³⁸ Source : Hansard 17th March 2006.

In July 2005 Defra issued new guidance indicating that, despite the above comments, mixed municipal waste is not hazardous and "... items of WEEE separated out at the civic amenity/household wastes sites or during bulky household collection" should not be treated as hazardous waste. However, "Local Authorities should ensure that they are complying with Duty of Care and know where their municipal waste, including any separately collected WEEE, is going for recovery or disposal". In addition, not all WEEE is necessarily waste and items which are separated out and are reusable or need minor repair are probably not waste.

As of 16th July 2005 civic amenity sites and waste transfer stations accepting separate collections of household hazardous waste, such as TVs and batteries, need to register as waste producers under hazardous waste regulations. Originally, the WEEE Directive was to be transposed by 13th August 2005, and changes to the above may occur when the WEEE Directive is implemented in 2006. This 'mis-match' of implementation has caused a variety of problems for producers and Local Authorities.

In April 2006 concerns were expressed by the Environment Agency about using shredding equipment to treat WEEE, which may release hazardous heavy metals and compounds. Annex II of the Directive covers the removal of such hazardous materials before shredding.

Draft Guidance for Waste Collection Authorities on the Household Waste Recycling Act 2003 issued in July 2004 has a table of 'commonly collected materials', in the context of the Government setting a statutory target for Local Authorities in England to collect at least two recyclables from the kerbside by 2010 :-

- **plastics** counts as one type of recyclable waste, however many types of polymers are collected
- **mobile phones** count as one type of recyclable waste even though different components can be treated differently
- **one off collections of bulky items** (could include WEEE ?) will not count as a type of recyclable waste

England – Waste Strategy 2006 Consultation

New targets to recycle up to half of all household waste is just one of a number of proposals in a major consultation on the Government's strategy for waste in England.

Launching the consultation, Minister for Local Environment Quality, Ben Bradshaw said "We've made some really positive progress since 2000: recycling and composting of household waste has doubled, nearly 50 per cent of packaging waste is being recycled and less waste is being sent to landfill. We need to put more effort into producing less waste in the first place, before considering how to make more use of the waste which is left by reusing, recycling, composting or using it as a fuel".

In a YouGov survey for Defra, only 3% of people always think about how they are going to get rid of the everyday items they buy when they no longer need or want it, half of people admitted that it never crosses their minds. Indeed, many people thought they were paying more for waste collection, treatment and disposal than they actually were. Most people (38%) think that it currently costs local authorities £10 per week to collect and deal with their household waste, in fact it is on average just £2 per household.

Among the measures being proposed are:

- greater focus on producing less waste in the first place by developing a greater emphasis on eco-design
- increased engagement with businesses and householders on waste prevention
- more agreements with businesses to take greater responsibility for their products at the end of their life
- new recycling and composting targets for household waste are proposed: 40% in 2010, 45% by 2015, 50% by 2020
- recovering more resources from businesses waste with new targets for a reduction in the proportion of commercial and industrial waste landfilled, more help for small businesses and a more joined up approach in managing waste from different sources facilitated by local authorities and regional bodies
- making proper use of new investment to recover energy from waste as an alternative to landfill, but not at the expense of practical waste prevention and recycling by seeing a more modest growth than original estimates. It is proposed to set a target for 67% recovery of waste by 2015 by recycling, composting, energy from waste (incineration, pyrolysis and gasification) and digestion with at least 45% composting and recycling.

The consultation paper Review of England's Waste Strategy A Consultation Document February 2006 and accompanying Regulatory Impact Assessment and Environment Report are available from Defra's website.^{39,40}

Deadline for comments was 9 May 2006.

Subject to the outcome of this consultation, the Government intends to publish a revised waste strategy for England later in 2006, setting out Government's vision and strategic direction on waste for the next 20 years, as well as the policies and actions which will be necessary to deliver the new strategy.

Key proposals in summary:

- increased national targets for recycling and composting of household waste (40% by 2010 and 50% by 2020)
- setting targets for landfilling commercial and industrial waste
- simplifying the regulatory system
- extending producer responsibility to cut waste and increase recycling
- keeping the pricing framework under review
- promoting behaviour changes by business and the public through information, advice and awareness raising
- greater Government leadership by example in dealing with its own waste and its procurement operations
- strategies and programmes to improve the evidence base to help us to target our policies more effectively
- prioritising products with the most significant waste impacts
- extending product stewardship by producers and retailers, and reducing waste impacts through eco-design
- promoting re-use and remanufacture
- engaging with businesses (including SMEs) to stimulate resource efficiency
- providing advice to consumers (business and the public) on environmental impacts of products
- targets for Local Authorities to reduce and recycle household waste
- piloting more recycling services for small businesses
- encouraging energy recovery but not at the expense of practicable waste prevention, recycling and composting
- placing further restrictions on use of landfill in the longer term
- an over-arching procurement strategy and increased effort on market shaping, to help local authorities make the investment needed. Continuing to develop markets for recycled materials including further standards for such materials which will allow lighter regulation
- new management plan for waste imports and exports.
- arrangements for better collection and management of household hazardous waste
- establish a Sustainable Waste Programme Board to drive delivery of the strategy and ensure coherence of waste policies. o Strengthen regional working including better partnership between local authorities at the regional level in planning for waste
- a wider strategic role for local authorities (in partnerships) to facilitate more integrated management of different waste streams
- improve the interaction of producers and compliance organisations with local authorities to deliver EU and national targets
- help the voluntary and community sector make its contribution particularly through innovation and engaging people.

³⁹ <http://www.defra.gov.uk/corporate/consult/wastestratereview/review-consult.pdf>

⁴⁰ www.defra.gov.uk/corporate/consult/wastestratereview/index.htm

8.3. UK interpretation and implementation of EU WEEE regulations

In terms of WEEE, the UK has progressed through 3 stages of consultation :-

- 31st March – 30th May 2003, Discussion Paper setting out all the implementation options
- 26th November – 1st March 2004, Consultation Paper set out preferred options
- 30th July – 29th October 2004 , Draft Regulations and Guidance

The UK consultations stalled during early 2005 when it became clear that the UK system would not be in place in time for implementation by the summer. In mid 2005 the DTI announced that implementation would be deferred until end 2006 at the earliest while the consultation process was restarted.

The new consultation process, with a combined DTI/DEFRA team commenced in the autumn of 2005

By April 2006 initial indications of the likely structure of the WEEE Directive implementation system in the UK were published by DTI.⁴¹

Another UK WEEE Consultation was published in late July 2006, seeking views of businesses, manufacturers, retailers, producers and enforcement authorities on draft regulations implementing Directives 2002/96/EC and 2003/108/EC of the European Parliament relating to waste electrical and electronic equipment. This consultation does not seek views on the provisions of the Directive itself but on the UK's proposed interpretation of it.⁴²

Malcolm Wicks, Energy Minister has given business a clear timetable for implementing the EC Directive on Waste Electrical and Electronic Equipment (WEEE).

Launching the Government's consultation on the key proposals to be introduced from 1 July 2007, Mr Wicks said: "Electrical equipment is the fastest growing category of rubbish across the European Union, with around 20kg per person produced every year, and the UK alone is now generating around 1m tonnes of the stuff every year. These proposals are good for consumers, good for responsible producers and good for our environment. By providing a way of ensuring that electronic waste no longer has to go to landfills, manufacturers and importers will have the responsibility to ensure that they plan for both their new and existing products to be recycled rather than dumped".

The consultation marks the beginning of the final phase of the Government's process for implementing the WEEE Directive. The proposals outlined in the consultation follow on from a review of our implementation proposals last December and have been developed through extensive consultation with key stakeholders to ensure that they are workable.

The key proposals are:

- a national Distributor Takeback Scheme which will establish a network of Designated Collection Facilities enabling consumers to return their used items for recycling or reuse
- obligatory registration for producers through approved compliance schemes
- Authorised Treatment Facilities, which will process WEEE and provide evidence to producers on the amount of WEEE received for treatment
- accredited reprocessing/recycling facilities who will provide evidence of reprocessing to producers
- an end-of-year settlement to ensure producers are able to meet their obligations via an "Exchange" system
- a voluntary approach for producers to show the cost of handling historical WEEE.
- implementation with effect from 1st July 2007

More detail of the latest consultation is provided in Appendix 1

⁴¹ <http://www.dti.gov.uk/innovation/sustainability/weee/page30269.html>

⁴² WEEE consultation: Part I. Draft implementation of directives 2002/96/EC and 203/108/EC on waste electrical and electronic equipment

<http://reporting.dti.gov.uk/cgi-bin/rr.cgi/http://www.dti.gov.uk/files/file32449.pdf>

8.4. Country-specific legislation which may affect design criteria across the EU

The electrical and electronics industry is largely multinational in nature, with much of the manufacturing taking place outside the EU. This means that E+E equipment is often designed and manufactured for use right across the EU or even world-wide. As a result product designers have to ensure that the equipment they are specifying will conform not only to Pan-European legislation but also to any local variations to that legislation.

Certain aspects of German and Scandinavian environmental legislation affect the use of polymers containing flame retardants as follows:

8.4.1. Germany

Germany has passed its own country-specific legislation known as the 'Dioxin chemical Banning Ordinance' of 1996⁴³ as a result of pressure from environmental campaigners. It is the only law of this type in Europe. This law restricts the amount of specified dioxins, furans and their brominated equivalents that may be present in new items placed on the market in Germany to below 1ppb TEQ for certain classes of dioxin compounds and 5ppb TEQ for a broader range of dioxin and furan compounds.

Recent research in Germany⁴⁴ has demonstrated that it is difficult to achieve these targets when Deca and octa BDE, TBPE and certain other types of 'matrix' type brominated flame retardants are used as flame retardants but they may be achieved when 'backbone' type flame retardants such as TBBPA or brominated epoxy oligomer are used⁴⁵.

8.4.2. Scandinavia

In some Scandinavian countries such as in Denmark, separate treatment of all flame retardant plastics will be required in future. This law will not directly affect the objectives of this project as we already assume that separation of polymers containing brominated flame retardants will be required

8.5. Use of recycled polymers containing brominated flame retardants in applications outside E+E equipment

The WEEE Directive and the RoHS Directive only place restrictions on use of polymers containing brominated flame retardants in E+E equipment and the WEEE Directive only requires separate treatment for recycled polymers containing BFRS that arise from WEEE.

The key directive that affects the use of polymers containing brominated flame retardants in applications outside E+E equipment is the 'Penta' Directive. **2003/11/EC (Directive of the European Parliament and of the council of 6th February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations)**

The Penta Directive states that with effect from 15th August 2004 pentabromodiphenyl ether and octabromodiphenyl ether (penta and octa BDE) may not be placed on the market or used as a substance or of preparations in concentrations higher than 0.1% by mass, and articles may not be placed on the market if they, or flame-retarded parts thereof, contain these substances in concentrations higher than 0.1% by mass.

Statutory Instrument 2004 No. 371 implemented this action in the UK as **The Controls On Pentabromodiphenyl Ether And Octabromodiphenyl Ether Regulations 2004**.

Proposals to include penta and Octa BDE in the Stockholm Convention on Persistent Organic Pollutants were proposed by the European Commission in August 2004, but opposed by the European Brominated Flame Retardant Industry Panel (EBFRIP).

⁴³ Chemikalienverbotsverordnung, Bundesgesetzblatt (1996) 818

⁴⁴ 'Polymers in WEEE contain PBDD/F in the ppb-Range', Schlummer M, Brandl F, Maurer A, Gruber L, Wolz G, Fraunhofer IVV, Organohalogen Compounds, V66, 2004

⁴⁵ 'Comparison of the recyclability of flame-retarded plastics', Imai T, Hamm S, Rothenbacher K, Technopolymer and BSEF, Environmental Science and Technology, Am Chem Soc, 2004

With regard to Deca-BDE, the final EU risk assessment for Deca-BDE is yet not officially published. The only part that is officially published is the environmental risk assessment⁴⁶. The human health part was finalised in October 2005 and is expected to be published on the European Chemicals Bureau website in early 2006.

At a meeting on 15th October 2005, the EU Member States and the European Commission discussed the Deca-BDE exemption from the RoHS Directive. At this meeting it was decided to exempt Deca BDE from the requirements of the RoHS Directive.

According to this note, "the UK said that it believed the RoHS ban on Deca-BDE was both no longer appropriate and incompatible with the other [EU Risk Assessment] legislation. A Commission official from DG Enterprise added that the risk assessment was now officially completed and that the agreed programmes were aimed at addressing any remaining concerns. Whilst some TAC members supported the UK and DG Enterprise position, two disagreed and said that the precautionary principle should be applied since there still were some unknown concerns".

In March 2006 the European Commission announced a period of consultation over possible exemptions of an annex to Directive 2002/95/EC of the European Parliament and of the Council on the restriction of the use of certain hazardous substances (ROHS) in electrical and electronic equipment.

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

According to Article 5 (2) of Directive 2002/95/EC the Commission is required to consult the relevant stakeholders before amending the annex. The results of this consultation will be forwarded to the Technical Adaptation Committee of the Directive 2002/95/EC and the Commission services will provide an account of the information received. Although the Commission will analyse the results of this stakeholder consultation carefully, please note that as with all stakeholder consultations, this action is only one part of the decision making process.

Proposal for additional exemptions:

Article 5(1)(b) of Directive 2002/95/EC provides that materials and components can be exempted from the substance restrictions contained in Article 4(1) if their elimination or substitution via design changes or materials and components which do not require any of the materials or substances referred to therein is technically or scientifically impracticable, or where the negative environmental, health and/or consumer safety impacts caused by substitution outweigh the environmental, health and/or consumer safety benefits thereof.

⁴⁶ http://ecb.jrc.it/DOCUMENTS/Existing-Chemicals/RISK_ASSESSMENT/ADDENDUM/decabromodiphenylether_add_013.pdf

9. E+E manufacturer market survey

This section describes the results of the OEM market survey conducted by Axion Recycling as part of phase 1 of the project.

9.1. Aim of the Survey

Any process development project must have a clear understanding of the market for its output products.

The target end-material from a plastics sorting and BFR extraction process will need to satisfy the technical, economic and PR-related issues laid down by the potential future users of that product.

In order to gain an understanding of these end-user acceptance criteria, it was decided to carry out a survey of some well-known manufacturers of consumer electronics. The assumption being made that the highest value use of plastics recovered from WEEE will be to incorporate them back into new E&E items. This fits with the ethos of the WEEE Directive, which states: *"producers are encouraged to integrate recycled materials in new equipment"* – clause 18.

9.2. Description of Approach

It was decided in consultation with the project steering committee and WRAP that the best quality of information would result from a series of face-to-face interviews with selected industry experts from a broad scope of manufacturing sectors across the E&E market. During such discussions it is possible to gain a much more detailed understanding of an organisation's policies and operating standards in relation to a specialist technical subject, than one could hope to achieve by a traditional mail-based survey sheet.

Over the months of October to December 2004 Keith Freegard of Axion Recycling conducted a series of 10 one-hour interviews with senior level experts employed by major electrical and electronics companies that serve the UK market. Each interview was based around a structured set of questions and covered the following subjects:-

- Recording contact's experience and operating role
- Finding out type of polymers used in new E&E goods
- Investigating current type of flame retardant systems
- Learning about organisation's response to WEEE legislation
- Current levels of recycled polymer usage
- Policy regarding future acceptance of recycled material (inc FR)
- Potential plastic parts to incorporate recycled material
- Material specifications of target components
- Contact's views about closed-loop recycling issues

Following each interview the responses were recorded and sent back to the interviewee for them to verify the accuracy of the recorded information and make any required changes. The results of these detailed discussions have been collated into the following summary. Some general themes and common policies regarding use of recycled material and flame retardants have been drawn out in the conclusions.

It was agreed that the individual company responses would be treated confidentially regarding any information that may be commercially sensitive. For this reason the names of the firms and individuals interviewed have not been included in this report. However it can be stated that each company is regarded as a brand-leader in its own market sector and that the list of names represents a broad depth of technical expertise with many years of combined industry experience.

9.3. Summary of Interview Responses

9.3.1. Industry Cross-section

The 10 interviews included organisations from the following sectors: -

- IT manufacture
- Telecoms equipment
- Power tools & DIY
- Garden power tools
- TV and IT visual products
- Toys & games
- Lighting industry

9.3.2. Role and experience of contact

A lot of effort was put into finding the 'right' contact for each interview. In some cases this meant that up to 3 senior technical staff attended the meetings to provide thorough and detailed information across the various departments involved in material specification and approval. Typical job titles of the interviewees were: -

- Environmental Controller
- Technical Manager
- Quality Manager
- Standards & Approval Engineer
- Social Responsibility Manager
- Head of Product Integrity

Where any information was lacking or gaps in knowledge were found, effort was made to follow-up the interview to resolve the points.

The length of the interviewees' experience in their specialist technical roles or similar functions in the industry was impressive. In total 15 people attended the 10 interviews, most with between 5 and 10 years experience in the job. Four of the interviewees had over 20 years of related industry experience.

In nearly all cases the people attending the interview had been 'living with' the WEEE & RoHS Directives over the past few years and were handling their firm's corporate response to the new legislation.

9.3.3. Types of Polymer most commonly Used

Each of the firms interviewed were asked to state the most commonly used type of polymers in their existing product range. This data is summarised in the table below, which indicates the rough percentage split of the types of plastics used for each of the main product types in question.

Product Type	ABS %	HIPS %	PS %	PC %	PP %	SAN %	POM %	PA %	PET %	PVC %	PC/ABS %	PPE/PS %	Comments
Printers /faxes	2.5	10	80		2.5	5							HIPs is FR grade
Telecoms	80	3-4					3-4				10-15		
Power Tools					80								PP mostly glass filled
Garden tools	60				25			10					
TVs									5		30	60	PET is recycled grade
Toys	60-80	10			10-20			5-10		5-10			Wide spread of types
Monitors /TV s	5	5									90		
Lighting				80									For emergency lighting
Computers	50-60	20-10									50-30		

Table - Summary of polymer types most commonly used by E+E equipment manufacturers surveyed for this project

Note: - Figures are rough estimates quoted by individual firms as percentage of total plastics used.

It can be concluded from this simple analysis that the most commonly used materials in new E&E goods are: -

- ABS
- HIPS
- PS
- PP
- PC/ABS blends

This would appear to represent a good basis for the inclusion of recycled plastics, as this group of materials covers the same range as those commonly found in dismantled WEEE see section 5.1.

Note that many of these manufacturers have components for their equipment manufactured and/or assembled outside the UK, either in Eastern Europe or the Far East.

9.3.4. Number of Components Requiring Flame Retardant Additives & Type of FR Technology being used.

The respondents quote a very wide range for the percentage of components that need to have FR properties. Figures between 10% and 90% are stated depending upon the type of industry in question. As a generalisation, any E&E product where the chassis or frame component is in contact with mains electrical voltage will have to pass a flame retardant test. Many firms quote the 'V0 – V5' standard (Ref UL94) as the basis for their testing regime.

Some of the key data points and comments are :-

Product Type	Percent FR Components	FR additive technology	Comments
Printer for PC	10%	Brominated	BFR-type not banned under RoHS
Telecoms	10%	Non-halogen	FR mostly found in mains transformer casing
Power tools	Most parts	Unknown	Non BFR since 1995
TVs	95%	Non-halogen	Polymer blends used to achieve V0 performance
Toys	Not known	Non-bromine	RoHS compliant specified
Computer IT	70 – 75%	Non PBB / PBDE	Restricted used of brominated FRs since 2002

One observation from this data is that streaming of different WEEE product groupings at the input to any dismantling and materials recycling process will lead to very marked differences in the level of FR-containing plastics found. Such an approach could also lead to increased concentration of the common polymer types for each grouping (e.g. Polypropylene from a power tools stream).

9.3.5. Interpretation of RoHs Directive and Future policy on type of Flame Retardant

The majority of firms interviewed are at a well-advanced stage of implementing the RoHs requirements. Most large, professional organisations already operate a detailed 'Prohibited Substance List' for all their suppliers of materials and components. It has therefore been simple for these companies to incorporate the six chemicals banned under RoHs into these lists. Several firms had already banned brominated flame retardants several years before the start of legislation in response to health and safety concerns voiced in the media.

There is some difference in the 'degree of ban' being applied to flame retardants by different firms, this can be demonstrated by the following statements about acceptable materials:-

- No *halogenated* flame retardants to be used in any supplied item
- No *brominated* flame retardants to be supplied
- BFR types Penta-, Octa-BDE & TBBPA placed on 'Banned List', but Deca-BDE & HBCDD on 'Use with Caution' list, if no suitable alternative can be found to deliver require flame retardant performance.
- Suppliers simply asked to demonstrate 'RoHs compliance'.

Some manufacturers have used the implementation of the RoHs Directive as the catalyst to conduct a thorough supplier conformance exercise for every E&E component used in Europe – a large administrative task. This detailed approach is in the minority, with most making sure that all suppliers have been issued with the latest version of the 'Prohibited' or 'Use with Caution' lists and then placing the onus upon the suppliers to adhere to them. In a few cases there has also been investment in state-of-the-art instrumentation to enable spot-checks to be made on incoming goods regarding detection of brominated compounds in polymer components.

There is a general trend for the OEMs to move away from detailed specification of the actual materials used in plastic parts for E&E goods. In most cases the suppliers are given performance specifications that each individual material must meet when used for a particular component. The suppliers are then 'free' to select a suitable material for each functional component specification as long as they operate within the constraints of the manufacturer's restricted substances lists. For flame retardancy performance there were a range of different testing methods quoted, although the UL94 tests for V0-V5 flammability were the most common⁴⁷.

This means that most of the technical experts interviewed were not aware of the exact type of flame retardant chemical currently being used for their own product range, although most were able to comment on the extent to which

⁴⁷ <http://www.geplastics.com/resins/devprod/flammabilityt.html>

brominated FR-compounds were still present. For example, "Our plastic casings are now all BFR-free, although halogenated compounds are still present in some circuit boards, until a viable alternative can be found".

There was limited knowledge about the actual level of a brominated compound that would be accepted in a 'BFR-free' material. Those interviewed who held an opinion on this subject referred to the '0.1% by weight' limits in the draft legislation, although one firm stated that they were using 80% of the RoHs limit as their own 'maximum acceptable level' in any incoming material.

9.3.6. Current Usage of Recycled Polymers and Company policy in Future

Use of post-consumer recycled polymers in new E&E goods is very limited at present. Only two of the firms interviewed had a specific policy to use recycled plastics, with one of them aiming to reach 20% of material made from recycled sources in next 5 years. Some industries positively exclude recycled material in 'critical parts' citing the perceived risk of contamination and associated product liability risk as the reasons for this (e.g. hand-held power tool casing; children's toys). One company had an upper limit of 15% for the inclusion of recycled polymer, as long as performance was acceptable.

There was a general viewpoint that 'post-industrial' scraps could be used up to levels of ~25%, but this really refers to the common practice of regrinding mould 'sprues' in high volume injection moulding factories where the risk of contamination or polymer mixing is negligible.

With firms tending towards 'performance specification' as the basis for component supply, it is possible that recycled polymers are being used at increasing, but undetected, levels at present, following a natural economic driver to do so. So long as the performance is above the specified limits, E&E manufacturers would find it difficult to detect inclusion of recycled material in place of virgin compounds.

Companies' future policy regarding the use of recycled plastics depends upon their current stage of development towards using such materials. Only the one clear 'future target level' of 20% recycled content was quoted, with others declaring 'an accepted, company wide policy' to increase recycled use. The response of 70% of the interviewees can best be summed-up as: 'no actual policy yet, but have talked about it'. For most firms however, the current focus is upon implementing the RoHs & WEEE Directives' obligatory requirements, so that being '*encouraged to integrate recycled material*' is being given lower priority.

9.3.7. Target Components & Plastic Specifications for Recycled Material

It is not surprising, given the low level of usage for recycled polymers in E&E goods, that the typical components selected for 'first-off' targets to test addition of recycled resins were as follows: -

- Non-critical part
- Hidden from sight in product internals or on base
- Black in colour
- Surface finish not important
- Low mechanical stress

Some of the named parts for possible early testing of post-consumer addition were:-

- Fan shroud in computer cabinet;
- Power Tool carry-case;
- Blade cover for garden trimmer;
- Internal brackets for TV / Hi-Fi.

The examples given from the companies that are currently using recycled material were (i) printer toner cartridge made from polystyrene; (ii) speaker boxes made from PET. This PET was recovered from post-use bottles rather than from E&E equipment.

It is interesting to note that in example (i) a key driver for change was created by the 'green' purchasing policy of public sector buyers actually specifying a requirement for recycled printer cartridges in preference to brand-new OEM consumables. In example (ii), above, problems sourcing sufficient volume of acceptable quality recycled material were stated as a barrier to increasing recycled content.

Some of the interviewed managers had been involved in exercises to test the feasibility of recycling plastics from their own-brand of products (e.g. customer returned goods). This had demonstrated that it was possible to obtain a satisfactory grade of recycled polymer from dismantling, sorting and cleaning the plastic. Obviously the known origin of the polymer resins makes it much easier to achieve material quality standards; however this 'own-brand' post-consumer route does offer a potential opportunity to WEEE dismantlers, who may find it economically feasible to sort some of the

common makes and colours of plastic by manufacturer or product brand-name (e.g. bright orange polypropylene used in 'Flymo' garden tools).

Most of the companies which were interested in including recycled polymers in their products were prepared to consider the idea of sourcing recycled material in Europe for use by their component suppliers overseas.

Several of the companies were able to supply us with material specification sheets for the branded, virgin polymers currently being used in the manufacture of 'target' components. This data is specific to each individual application and polymer type, so is not reported here. However it does provide some benchmark figures that can be used for comparison of the potential performance of recycled polymers.

9.3.8. Main Issues / barriers to acceptance – comments

The experts interviewed during the survey were given an opportunity to voice their own opinions about the main issues regarding closed-loop recycling of WEEE plastics back into new E&E goods.

The responses had some common themes under the following subjects: -

- **Quality**
 - Concern that 'equal to virgin' quality and performance standards could not be achieved with recycled polymer
 - Consistency of supplied recycle quality – potentially more variable
- **Volume**
 - Insufficient tonnage of on-specification recycled resins available in market
 - Potential large-volume WEEE recyclers not geared-up for plastics recovery
- **Location**
 - Collected WEEE plastic may be remote from manufacturing site (i.e. Europe to Asia)
- **Additives**
 - BFR and other flame retardants now on 'Prohibited Lists' of materials for manufacturers based in Europe although many manufacturers in Asia and the Far East continue to use BFRs because they provide an effective and low cost means of achieving fire safety standards.
 - Other undesirable additives in old plastics e.g. cadmium
- **Risk**
 - Perceived increased risk of critical product failures caused by contamination of recycle
 - Only prepared to use known-origin plastic from 'own-brand' recycling loops
- **Legislation**
 - Some industries have several other legal obligations related to the products (e.g. EN50088 – Safety in electronic toys).
 - Position of recycled materials under REACH legislation?
- **Cost**
 - Can cost parity (or better) be achieved for recycled resins
 - Is total energy and monetary 'life-cycle' cost better than virgin raw material?
 - Cost of quality testing on small recycled batches can be prohibitive

The above list of opinions and concerns about the use of recycled resins indicates that the market is still in its early stages of development. It is encouraging to note that 3 of the firms are already beginning to utilise post-consumer material in new E&E products. These 'early entrants' into the recycled raw-material market will gradually overcome the challenges and create a 'pull-through' effect on their competitors.

There are also some significant changes in the economic and consumer environment that create increased pressure to use recycled polymers. Recent increases in oil prices have had dramatic impact upon the cost of virgin plastics and a continued groundswell of environmentally conscious consumers, whose purchase decisions are influenced by the 'green' credential of products, being two examples of such change.

9.4. Conclusions

As a result of the unique opportunity to conduct face-to-face interviews with 15 representatives from 10 leading E&E manufacturers, we are able to draw the following conclusions from this Market Survey:-

1. The most common 4 or 5 types of plastics being used to make new E&E products today are very similar to the range of polymer types found in analysis of WEEE from post-consumer collections. This means that there is a good basis to re-use those polymer types back into new electrical goods.
2. Most OEMs in Europe have already taken steps to cease the use of halogenated flame-retardants over the past 5 – 10 years in anticipation of the forthcoming legislation. These manufacturers tend to produce the larger E&E items.
3. Manufacturers outside Europe continue to use BFRs. This is evidenced by the continuing growth in sales of the major bromine companies. 2004 was an all time high for BFR sales, with most of the growth concentrated in China and the Far East. These manufacturers tend to produce the smaller E&E items where transport cost is less important.
4. Conclusions 2 and 3 above mean there is likely to be a rapidly decreasing concentration of BFR compounds found in plastics from larger WEEE items over the next 5 years. While BFR content of smaller WEEE items is likely to remain high for longer.
5. The responses from different industry sectors concerning the incidence of FR-additives in different product types suggests that selective streaming of the items in WEEE waste could create a concentration of the FR-containing plastics at a dismantling facility. This may mean that segregating plastics from (say) TV and computer equipment will tend to concentrate the BFR-containing polymers into one waste polymer stream.
6. Based upon limited response, it appears that 'an acceptable level' of trace-BFR compound in a recycled polymer for use back into new E&E goods would be the 0.1% level stated in the draft RoHs legislation.
7. The survey shows that the current level of recycled polymer use is still low in the E&E sector. However some of the progressive 'early adopters' are creating a precedent for using recycled resins that, combined with other changes in the business environment, generates a significant driver for their competitors to follow suit.
8. Performance based specification of E&E equipment, instead of strict definition of material types, gives the opportunity for increasing levels of recycled material in plastic components. This opportunity will only be open to those recycling businesses that can deliver high quality material both consistently and at high volume.
9. Sorting of plastic components from WEEE into polymer types of known-origin based upon manufacturer brands could represent a route to deliver an acceptable quality recycled material source for those OEMs who are reluctant to risk using recyclates from bulk mixed waste.



Streaming of WEEE items by product type or by brand could yield more attractive recyclates

10. WEEE polymer compatibility with new EEE polymers

10.1. Introduction

This section of the report provides an overview of the important technical issues to consider when using recycled polymer to manufacture new goods. It includes experience-based knowledge gained from re-processing of the most common WEEE plastic types.

Before describing particular materials and their properties some general points should be considered:

Incompatibility of most polymer types when mixed with each other, resulting in poor toughness of the material and problems with the different processing melt temperatures required for the different components. Many other properties, such as stiffness, have some average value of those of the individual components. Hence it is best not to let the different plastics get mixed up in the first place. If they do then it is usually necessary to separate them.

Colour Plastics are usually coloured and mixtures of different colours usually lead to a dull unattractive shade e.g. a dirty grey or green. Hence recyclate is often pigmented a dark colour (often black) to mask this and to give consistency of colour.

Degradation Recycling involves reprocessing, i.e. heating to melt the material – usually at least twice, once to produce granules suitable for feeding to a processing machine (such as an injection moulding machine) and once for the shaping operation. Each time a plastic is heated and processed (involving high shear) some loss in properties occurs, especially toughness.

However, several investigations at London Metropolitan University and elsewhere on the effects of repeated reprocessing have shown that little loss in properties occurs. Some particular plastics are especially sensitive though. Often heat stabilisers are added to recyclate to minimise problems especially with particularly heat sensitive plastics – mostly PVC and acetal. Material may also become degraded during its normal service lifetime before recycling, especially if it has been exposed to sunlight or high temperatures for long times.

Flow/processability For shaping operations (processing) plastics need to have adequate melt flow. Better flow properties are required for some processes, e.g. injection moulding, than others. For example profile extrusion requires higher viscosity polymer. Especially good flow is needed for injection moulding of products with thin sections and/or long flow paths. As a result not all recyclate can be used to produce all shaped products.

10.2. The Particular Materials

Materials are chosen for the optimum combination of end-use properties and adequate processability at an acceptable cost. Plastics are used in electrical products mainly in housings especially for computers and televisions. The most commonly used materials for these applications are high impact polystyrene (HIPS), acrylonitrile-butadiene-styrene (ABS) and blends of ABS with polycarbonate (PC).

Housings for other consumer products such as carpet cleaners, electric mowers and jug kettles may be made of polypropylene (PP).

More specialist materials, such as PTFE and polybutylene terephthalate (PBT) are often used for electrical components such as connectors and coil formers and for high performance mouldings such as power tool housings.

Any mechanical components such as gears, cams and bearings will most likely be of acetal or nylon. Thus we have to consider a wide range of plastics materials.

10.2.1. HIPS and ABS

- Easily processed materials with good flow
- In effect rubber toughened polystyrene
- Can be of variable composition (especially ABS) but rarely contain glass fibres or mineral fillers
- No particular problems with heat stability, though ABS has a lower heat stability
- Both are tough plastics, especially ABS
- ABS is noted for its ability to produce attractive, smooth glossy surfaces
- Should be no major particular problems on recycling

10.2.2. ABS/Polycarbonate (PC) blend

- PC alone is not often used in electrical products
- ABS and PC are separately compatible with several other plastics as well as with each other
- The PC improves the heat resistance of the ABS
- The ABS improves the melt flow of the PC
- The combination is very tough
- PC needs thorough drying before melt processing
- PC is more expensive

10.2.3. Polypropylene

- Often the first choice for injection moulding due to its low cost and reasonable end-use properties
- No particular problems but is sensitive to atmospheric oxidation resulting from exposure to high temperatures or sunlight. Thus recycle may need addition of appropriate stabilisers if it is to be used for products which are exposed to these conditions
- Frequently reinforced with glass fibres to improve mechanical properties, especially stiffness, including in some electrical products, but not usually in housings

10.2.4. Nylon

- Several different types, but usually nylon 6 or nylon 66 and they are very similar
- Very water sensitive absorbing large quantities (up to 8%) from the atmosphere, therefore must be thoroughly dried before processing

10.2.5. Acetal

- Similar end-use properties to nylons, both very often being used for similar products
- Sensitive to heat degradation during processing, so must be stabilised. Degradation catalysed by acids, so must never be used in machines used for processing PVC or used with halogenated fire retardants since both produce acids when heated. Must be flame retarded with phosphorus materials.

Typical values of the properties of these plastics are shown in section 10.3.4.

10.3. Particular Properties

10.3.1. Processing

Flow The plastic melt must flow sufficiently easily under available machine pressure to fill a mould or extrude easily. This aspect of “processability” is indicated by the melt flow index (MFI) [also called the melt flow rate – MFR]. The lower the MFI the less easily the material flows.

The different grades of any particular plastic are available for the different flow requirements. In general, high MFI is used for injection moulding especially if the section is thin or the flow path long.

Recyclate may have a higher MFI than it had originally because of shear-induced degradation during reprocessing. MFI may be adjusted by blending different grades of the same material.

Temperature A melt temperature is used at which adequate flow occurs with available machine power. This can vary considerably with different materials. This may cause a problem with mixed plastics recyclate, when the different components have different temperature requirements.

Degradation Some materials have low heat stability and decompose (degrade) if overheated. These include, particularly, PVC and acetal. Some halogenated fire retardants similarly have poor heat stability and decompose if overheated. Recent trials have demonstrated that certain flame retardants such as TBBPA and brominated epoxy oligomer can improve the recyclability of WEEE polymers⁴⁸.

Shrinkage Like all materials, plastics expand when heated and shrink when cooled, only much more so. Shrinkage varies with different materials. Crystalline plastics (PP, nylons, acetal) shrink much more than non-crystalline (amorphous) materials (PS, HIPS, ABS, PC).

10.3.2. Compatibility

The chart below⁴⁹ indicates the compatibility of typical polymers found in E&E equipment:

Polymer compatibility matrix Source: Dow Plastics	Ethylene Copolymers														
	LDPE	LLDPE	ULDPE/ULDPE	HDPE	PP	EPDM/EPDM	PS (gen.purpose, high impact)	SAN	ABS	PVC	PA	PC	PMMA	PBT	PET
LLDPE	1														
ULDPE/ULDPE	1	1													
Ethylene Copolymers	1	1	1												
HDPE	1	1	1	1											
PP	4	2	(1)	2	4										
EPDM/EPDM	4	4	(1)	3	4	1									
PS (gen.purpose, high impact)	4	4	4	4	4	4	4								
SAN	4	4	4	4	4	4	4	4							
ABS	4	4	4	4	4	4	4	4	1						
PVC	4	4	4	(2)	4	4	4	4	2	3					
PA	4	4	4	(1)	4	4	(1)	4	4	4	4				
PC	4	4	4	4	4	4	4	2	2	4	4				
PMMA	4	4	4	(3)	4	4	4	2	2	2	4	2			
PBT	4	4	4	(2)	4	4	4	4	4	4	4	1	4		
PET	4	4	4	(3)	4	4	4	4	4	4	3	1	4	3	
SBS	4	4	4	4	4	4	1	3	2	3	3	4	4	4	4

Key: 1 = Excellent
 2 = Good () = compatibility depends on composition
 3 = Fair
 4 = Incompatible

⁴⁸ Comparison of the Recyclability of Flame Retarded Plastics, Imai T, Hamm S, Rothenbacher K, Journal of Environmental Science and Technology, 2004

⁴⁹ Dow Chemical, 2004

10.3.3. End-use

Here we are most importantly concerned with mechanical properties, since these are of relevance in most products, but also because it is in this area that plastics perform badly compared to other materials.

Stiffness Indicated by the tensile or flexural modulus (E). Plastics lack stiffness, the basic polymers having values in the narrow range of 1-3 GPa for most plastics. Stiffness is very effectively increased by incorporating glass fibres (E about 70GPa) and is the usual reason for using glass. Stiffness does not usually suffer from recycling

Toughness The most common mode of failure in plastics products is brittle fracture. Toughness is usually indicated by a the result of a pendulum-type impact test (Izod or Charpy type). Values vary widely between different plastics and also between different grades of the same plastic, reducing as MFI increases. Many factors affect impact strength especially the inclusion of particulate additives which often reduce it, especially if the particles are large. Toughness is usually improved by the incorporation of a rubbery impact modifier, as used in HIPS and ABS. Recycling may reduce impact strength.

Softening Plastics properties are very temperature dependent. In particular, they soften at low temperatures, as indicated by a heat distortion temperature (HDT) or Vicat temperature. Should not be affected by recycling.

Burning Most plastics burn readily although the high chlorine content of PVC reduces its flammability significantly. The flammability is indicated by either the simple UL94 result – HB, V1, V2 or VO, or by the limiting oxygen index (LOI). Flammability decreases as LOI increases. Flammability should not be affected by recycling.

Values of these properties for plastics used in electrical products are shown in section 10.3.4 below.

10.3.4. Typical properties of plastics used in electrical products

Property	HIPS	ABS	ABS/PC	PP	Nylon 66	Acetal
Flexural modulus/GPa	2.1	2.7	2.8	1.5	1.2	2.6
Notched Izod impact strength/kJm ⁻¹	0.1	0.2	0.55	0.07	0.11	0.07
HDT@1.80MPa/°C	75	89	122	65	100	110
UL94 Flammability	HB	HB	HB	HB	HB	HB
LOI/%	18	19	19	17	22	15
Melt temperature/°C	210-270	230-270	245-275	210-290	280-300	190-210
Shrinkage/%	0.5	0.6	0.7	1.5	1.5	1.8

10.4. Conclusions

- Polymer types are generally incompatible with each other, leading to melting problems and reductions in toughness when they are mixed together. It is therefore important that recycling processes ensure good separation by polymer type
- The following polymer properties are unlikely to be affected significantly by recycling and will produce an average property when recyclates and virgin materials are blended:
 - Stiffness
 - Softening point
 - Flammability
- Most WEEE polymer types do not suffer major degradation in mechanical recycling processes and can therefore be re-used or mixed with virgin material without significant loss of physical properties.
- Some halogenated flame retardants and certain polymers such as acetal and PVC have a tendency to suffer thermal degradation if subjected to multiple thermal processes. However recent trials with the brominated 'backbone' flame retardants TBBPA and brominated epoxy oligomer have demonstrated that these flame retardants can improve the recyclability of some polymers.

11. Methods to detect and measure BFR type and concentration in WEEE polymers

11.1. Introduction

The WEEE Directive requires recyclers of plastics from WEEE to identify the presence of BFR in plastics to be recycled. Any technique used must be suitable for implementation on a practical recycling line.

This section of the report reviews the techniques available for identification of polymer types and whether or not polymers contain brominated flame retardants (BFRs). It then identifies which of these techniques may be suitable for use on automated sorting lines and reviews the capabilities of a selection of commercially available 'state of the art' polymer identification and BFR detection instruments.

This background information will help to inform the bulk separation process designs proposed in Chapter 13 of the report.

11.2. Existing labels and markings

The problems associated with plastics identification for recycling were highlighted in a recent exercise in which six 1m³ bags of real computer WEEE were transported from Associated Polymer Resources Ltd⁵⁰ to the University of Southampton for analysis. The bags contained a large quantity of plastic housings from CPU's, monitors and keyboards in various states of completeness. Most of these pieces were marked with a material identification code and the load in total comprised some 12 different types. The markings were as follows:

PS
ABS
PVC
HIPS
PS-HI
PC+ABS
ABS-FR
ABS+FR(17)
PC+ABS-FR
PC+ABS FR(40)
NORYL
PPO-94VO

The assumption is that the denotation FR refers to the presence of flame retardant but with no indication of type or concentration. It can not be assumed that those without the FR abbreviation do not contain BFR. Indeed, recent experiences have shown that markings cannot always be trusted as engraved or stamped moulds are known to be shared for different plastics.

⁵⁰ Associated Polymer Resources Ltd. West field House, Knowle Hill, Allbrooke, Eastleigh, Hants. SO50 4LZ. UK

11.3. Techniques for the detection of BFR's

Due to the relatively low levels of BFR in plastics and the way they are incorporated into the structure of the material it has been determined that with one exception only those methods based on spectroscopy can be practically used for their detection. The 'COMBIDENT' report⁵¹ lists ten different identification techniques:

- Near infra-red (NIR) spectroscopy
- Mid infra-red (MIR) reflection spectroscopy
- MIR pyrolysis spectroscopy
- Raman scattering spectroscopy
- Mass pyrolysis spectroscopy
- Sliding spark (spark ablation) spectroscopy
- X-ray fluorescence spectroscopy
- MIR Acousto-optic tunable filter (MIR AOTF) spectroscopy
- Laser induced thermal impulse response(TIR)
- Laser induced plasma spectroscopy (LIPS) spectroscopy

TIR is a non-spectroscopic technique and analyses the macroscopic heat produced by the sample surface. The COMBIDENT report suggests that from the above list MIR AOTF, TIR and LIPS are best suited to an automated line due to (a) sampling speed and (b) ability to work on black plastics. Section 3.2 of the COMBIDENT report tabulates the relative performance of each of the three techniques.

The above report also comments on the presence of surface treatments, coatings and contamination which can greatly affect the accuracy of some of the identification techniques. The method found to be most successful was blasting with plastic powder or grinding media. Commercial equipment is available to perform this although it is expensive and requires a long treatment time. In the end the prototype line for the COMBIDENT project used industrial brushes including silicone carbide to abrade the plastic surfaces.

11.3.1. Thermal impulse response (TIR)

A CO₂ laser (10.6µm) is used to heat a small area of the sample surface. Depending on the materials properties such as absorption coefficient, thermal conductivity etc. a specific time-dependant temperature distribution is generated. This is detected by means of an infra-red thermographic system. Since the temperature distribution is likely to be influenced by the presence of flame retardants this method is feasible however the detection of low levels of BFR and the ability to distinguish between different types has not been proven.

A major disadvantage of this technique is that it does not work with black plastic and this lead to it being dropped from the prototype identification line developed in the COMBIDENT project.

11.3.2. X-Ray Fluorescence Analysis (XRF)

Drinks bottles are commonly made of PVC or PET. These items are often collected under recycling schemes. The requirement for very low levels of PVC in a PET product led to the development of automated sorting systems based on identification of PVC using XRF in the 1980s. Systems were developed by National Recovery Technologies (NRT) Inc., Magnetic Separation Systems, Asoma and Govoni.

When x-rays bombard the surface of a material secondary x-rays are generated which have wavelengths characteristic of the elements contained within the material. The production of x-rays from excited chlorine atoms is used to identify PVC. Following identification a computer controlled air ejection system can be used to remove the PVC bottles from a mixed plastic waste stream⁵². The separators, with multiple analyses (up to 200 per second) on each bottle, are capable of highly efficient removal of PVC. The detector must be close to the bottle because of the attenuation of x-rays in air. Failure to detect the characteristic x-rays can result from the 'sandwiching' of a PVC bottle between other polymer types. This may be caused by a failure to deliver a single bottle stream through the unit and is more likely to occur when the feed material has been compacted. Labels on PVC bottle are also reported to cause reduced transmission and hence reduced efficiency.

⁵¹ COMBIDENT Final Technical Report, EU Contract No BRPR-CT98-0778, December 2001

⁵² Summers, Mikofalvy & Little. 'Use of X-ray fluorescence for sorting vinyl from other packaging materials in municipal solid waste'. J.Vinyl.Tech. 12, No.3, Sept. 1990, 161-164. 411966

The NRT 'VinylCycle' separator⁵³ was installed at the Reprise plant near Blackpool, England in 1990 and operated at a sorting rate of 20,000 bottles per hour, equivalent to 1 tonne per hour. NRT also supply a separator with a higher throughput of 2.27 tonnes per hour.

Spectrometers based on energy dispersive X-ray analysis (EDAX) are traditionally laboratory based systems. Their cost and complexity plus the issue of exposure of the work force to X-rays do not make them ideal for an industrial recycling line. Furthermore there is little evidence to show that they are efficient in detecting BFR's. The US company Niton make a hand-held unit specifically designed to identify plastic additives.

11.3.3. Near Infrared (NIR) Spectroscopy

According to Krummenacher et al⁵⁴ NIR spectroscopy (700-2500 nm spectral range) is the most widely used identification method for automated plastic sorting. The infra-red irradiation is absorbed by overtone and combination vibrations that are characteristic of particular functional groups, such as O-H, N-H and CH. Different polymers can be readily identified provided that the objects do not contain additives such as carbon black, which cause excessive absorption of the radiation. Advantages of NIR compared to mid infrared spectroscopy (see below) include shorter response times, improved detection ability of the NIR photodetectors (germanium, indium arsenide or indium gallium arsenide) and the ability to use inexpensive quartz fibre optics with low attenuation.

The Fraunhofer Institute of Chemical Technology has developed a fast on-line identification system for plastics using a NIR spectrometer with an acousto-optic tuneable filter (AOTF)^{55 56}. Spectrometers used with an AOTF allow scan speeds of 200 nm per millisecond at a wavelength resolution of 2-5 nm in the region 1000-2500 nm. The Fraunhofer Institute have also developed a hand-held mobile diode-array grating spectrometer or Mobi-DAGS for the identification of plastics but it is not appropriate for BFR detection.

Manufacturers of NIR sorting systems include National Recovery Technologies Inc. (NRT) which claims to have a high-speed IR separator called Flake Analyzer⁵⁷ that can identify additives down to ppm levels but does not mention BFR's. NRT supply units for whole plastic bottles (MultiSort) or flaked material (FlakeSort) giving throughput rates of up to 2.3 tonnes per hour. Other companies include Binder AG in Austria, and Integrated Recycling Systems (IRS) in England. MSS Inc. has recently developed a NIR sensing system that can identify polyethylene naphthalate (PEN)⁵⁸. LLA in Germany also manufacture a plastics ID system based on NIR⁵⁹. None of these companies make claims regarding BFR.

11.3.4. Fourier Transform Mid Infrared Spectroscopy

According to Morley⁶⁰ Fourier transform mid infrared spectroscopy (2,500-5,000 nm) is the most widely used system for identifying plastics. Instruments generate spectra in the 'fingerprint' region, which contains the fundamental vibration frequencies of the functional groups within molecules. The technique can be used to identify blends and fillers, and can identify dark objects. It is proven that this technique can detect the presence of BFR's because they produce small differences in the reflected spectra.

Most new infra-red spectrometers use a specular reflectance technique in which infrared light that is reflected from the surface is analysed. The surface of the object should therefore be relatively flat (a potential disadvantage in some systems but unlikely to be a problem in manual WEEE recycling). Analysis times greater than 1 second are commonly used. As the object has to be held stationary at the detector the technique does not lend itself perfectly to automated sorting. To improve the accuracy of identification the technique may be combined with pyrolysis units such as 'Sliding Spark' and LIBS, which analyse vapours derived from heating of the surface.

Suppliers of bench top analysers include Bruker Optics and ThermoNicolet. The reflected spectrum is compared against a library of polymers which can include many hundred spectra and identifies the closest match, and (if required) the 'next best hit'. Measurement and identification take approximately 1-5 seconds depending on the number of surface scans,

⁵³ Ottewill S., The Chemical Engineer, 15th Nov. 1990. p.19

⁵⁴ Krummenacher, Peuch, Fischer & Biddle. 'Automatic Identification and sorting of plastics from different waste streams – a status report'. APME, Brussels, 1998.

⁵⁵ R 95 – Recovery, Recycling, Re-Integration. Vol III: Mechanical Processes, Logistic Networks, Separation Tech. Conf. Proc. Geneva 1-3 Sept. 1995. III 230-235. 8(13).

⁵⁶ Eisenreich, Herz, Kull, Mayer & Rhoe, 'Fast on-line identification of plastics by near-infrared spectroscopy for use in recycling processes'. Antec 96. Vol. III Conf. Proc. Indianapolis 5-10 May 1996. 3131-3135. 609107

⁵⁷ www.nrt-inc.com/flakeA.htm

⁵⁸ www.magsep.com/PprNP97.htm

⁵⁹ www.lla.de/index.php

⁶⁰ Morley N., 'Current state-of-the-art in Sorting and Identification of Mixed Plastic Waste'. Polmer Recycling 3, No.3, 1997/98, 217-226. 736640

the size of the library and the computer speed. The PolyAna purpose built plastic ID system is based on the ThermoNicolet spectrometer.

Mid infra-red spectrometry for high-speed analysis of materials is often used with AOTF. These devices control the IR beam intensity and enable the beam to be rapidly switched on and off⁶¹.

11.3.5. Raman Spectroscopy

Raman spectroscopy of inelastic light scattering is a technique that has until recently been restricted to the research laboratory, but has now been applied to plastics identification. Knights⁶² described the operation of the Rapid Plastics Identification System RP-1 supplied by SpectraCode Inc. A laser gun is placed on the object to be identified and a push button fires the laser at the object. The laser penetrates 100 µm into the object, so that thin coatings and irregularities should not affect the identification. Certain photons from the laser light will change frequency when they encounter the polymer molecules, whilst others do not. Holographic optical elements distinguish which photons have interacted allowing a Raman 'molecular barcode' to be generated. This information is transmitted to a computer console which has a software library of 'molecular barcodes' which can be compared with that produced by the object.

SpectraCode⁶³ claim that almost 100% accuracy is possible for a 1 second analysis time. Darkly pigmented materials can be identified, although it is reported that the system is somewhat sensitive to the presence of carbon black, which can reduce the reflection back to the detector.

Raman spectroscopy has potential for automated sorting due to measurement times as low as 50 milliseconds.

11.3.6. Laser Desorption-Ion Mobility Spectroscopy - LIBS, LIPS & LIMES

Laser Induced Breakdown Spectroscopy (LIBS) (also known as Laser Induced Plasma Spectroscopy (LIPS)) and Laser Induced Multi Emission Spectroscopy (LIMES)⁶⁴ are simple, relatively inexpensive analytical techniques to determine the elemental composition of a sample, regardless of whether the sample is a solid, liquid or gas. A powerful laser is focused onto the sample and hot plasma is formed. Light emitted by the plasma is composed of spectral lines characterising the element present in the sample.

This technique is sensitive to all elements, with typical limits of detection between 0.1-200 parts per million (depending on the sample and the element of interest). Minimal sample preparation is needed making it quick and easily adaptable to automated chemical monitoring equipment or portable units. The technique can be used in a variety of more complex analyses such as determination of alloy composition, origin of manufacture (by monitoring trace components), and molecular analysis (unknown identification). There is also the option for use in man-portable or robotics applications.

Simpson et al⁶⁵ used a relatively low powered laser to ablate organic material from the surface of a plastic. The vapours generated by the laser were transported using a carrier gas (air, argon or helium) to an ion, mobility spectrometer. Within the spectrometer the charged organic species are separated in a drift tube, with different species having characteristic drift times. The result from ion mobility spectrometry is a series of peaks at specific drift times. Testwork conducted with low-density polyethylene (LDPE), HDPE, PP, nylon 66, ABS, PET and PVC revealed that all the polymers exhibited characteristic outputs except PET. The lack of 'signature' with PET was attributed to insufficient attenuation of the laser beam, and resultant lack of ablated material from the highly transparent sample. The method is reported to be well suited for the identification of other materials within a plastic, such as fillers, reinforcing agents and pigments. LIPS (LIBS) is claimed by the COMBIDENT report to work well in identifying the presence of BFR's.

Variation in the laser operating conditions, such as increased power, will cause a variation in the type of molecules generated at the surface and the 'signature' for a particular polymer will change. The technique therefore needs well-controlled operating conditions for consistent identification. The time taken for spectrum acquisition of approximately 0.1 to 1 second suggests the technique is applicable for the identification of plastics on a recycling line.

⁶¹ www.sciner.com/Acousto-Optics/AOTF.htm

⁶² Knights M., 'Laser eye quickly identifies plastics in waste' *Plastics Technology* 43, No. 12, Dec. 1997,24-25. 664147

⁶³ www.spectracode.com

⁶⁴ www.ltb-berlin.de/limes.html

⁶⁵ Simpson, Anderson, McLeod & Cooke, 'Polymer characterisation using laser desorption-ion mobility spectrometry'. *Analyst* 118, No.4, April 1993, 449-451. 478440

Stepputat & Noll⁶⁶ ran a conveyor line at 0.5m.s-1 and using LIBS with an auto-focusing system identified the metals Cr, Hg, Cd and Pb in plastic samples with an accuracy of 84-95%. They had more difficulty with Br relying on determining the presence of BFR's in the plastic by identifying Sb in the synergist compound Sb2O3.

In the laboratory, they could detect Br directly at levels down to 1.5% by weight of plastic. This is sufficient to detect BFR in plastics which normally occur in concentrations exceeding 3% wt.

11.3.7. Spark Ablation (Sliding Spark)

Sliding spark technique works in a similar way to LIBS but uses an energetic spark discharge to ablate the surface. The effectiveness of this system is similar to the LIBS technique and commercially available equipment such as the SlideSpec-S2 is specifically designed to identify BFR's (see next section).

⁶⁶ Stepputat & Noll, 'On-line Detection of Heavy Metals and Brominated Flame Retardants in Technical Polymers with Laser-induced Breakdown Spectrometry'. Applied Optics Vol. 42, No. 30, Oct. 2003, 6210-6220

o Automated Sorting Systems

Automated sorting systems for plastic containers are commonly found in many parts of Europe, although few systems have been installed to date in the UK. The increase in the amount of recyclable material that requires sorting over the next decade should result in the increased use of this technology. Identification of the polymer type and additives is a key component of all automated sorting systems. A comparison of the application of the various polymer identification systems is given in Table 2.

The efficiency of an automated sorter will depend on its ability to present an object singly to the polymer identification system. The objects may be fed and spread at a controlled rate onto a moving conveyor. In order to help singularise the objects the conveyor may be grooved or vibrated. To move the objects apart they can be passed down a steeply inclined chute or may be dropped onto a high-speed moving belt.

Many automatic sorters use similar technology for object separation once the polymer has been identified. The measurements based on transmitted or reflected spectra are compared against standard values. This information determines whether to initiate the object removal system. Typically this involves actuation of a compressed air blast which can either blow or suck objects away from their normal trajectory. The air blast is timed to occur when the object passes the ejection area, calculated from the expected particle velocity.

† Table 2. Comparison of the identification systems of automatic sorters

† Identification Method	† Advantages	† Disadvantages	† Applicable to BFR detection?
Thermal Impulse Response (TIR)	Simple in essence.	Does not work with dark plastics.	No. Dropped from the COMBIDENT project.
X-ray Fluorescence (XRF)	Proven technology for the identification of PVC	Slow sampling rate for some materials. Question of X-ray hazards. Quite expensive.	May detect BFR but yet to be conclusively proven as a practical recycling technique.
Near Infrared (NIR)	Fast. P-detectors have short response times. Suited for transparent or lightly coloured objects	Unsuitable for dark objects such as those containing carbon black which absorbs and scatters at NIR frequencies	Yes but with limitations.
Mid Infrared	Proven Technology. Can identify dark plastics. Purpose built for recycling apps.	Not applicable for very high speed lines. Requires relatively smooth, clean surface.	Yes but yet to be fully evaluated with BFR.
Raman	Fast sampling time. Designed specifically for element identification.	Accuracy for BFR identification unknown. Raman signals are weak leading to possible inaccuracies. Very expensive	Unknown.
LIBS, LIPS LIMES	Fast sampling time. Proven application in COMBIDENT Project.	Not perfectly accurate. Expensive. Designed for lab rather than industrial use.	Yes.
Spark ablation (sliding spark)	No problems with black samples. Speed and simplicity of operation. Purpose built for recycling apps.	Requires sample prep. Some uncertainty as to whether some plastic types can be identified. Quite expensive. Shock and fire hazards from EHT spark.	Yes. Accuracy claimed but yet to be fully evaluated.

11.4. Commercially available systems suitable for use on manual dismantling lines for WEEE

11.4.1. PolyAna Avatar



PolyAna Avatar available from Wolfson Electrostatics⁶⁷ at the University of Southampton

The PolyAna Avatar uses FT-IR reflectance spectroscopy operating in the spectral range 3-20 μ m. The blue section contains the special optics to bring the IR beam to the sample held at the nozzle. Cost is £22,000 including computer and various databases.

The PolyAna is based on the original Millennium-Award-winning technology designed at the University of Southampton in collaboration with the Ford Motor Company⁶⁸. It is specifically designed to provide a quick and accurate identification of unknown materials and will detect BFR's in plastics. It can be used on large items (VDU housings, mouldings etc.) and small objects down to about 10mm. The test is non-destructive and does not require modification or treatment of the sample in any way. It is designed to be operated in an industrial environment by non-technical personnel and can be programmed to identify or distinguish between a large variety of materials. The PolyAna Avatar has already achieved good results in industrial trials providing a good level of accuracy with a measurement time down to 2 seconds.

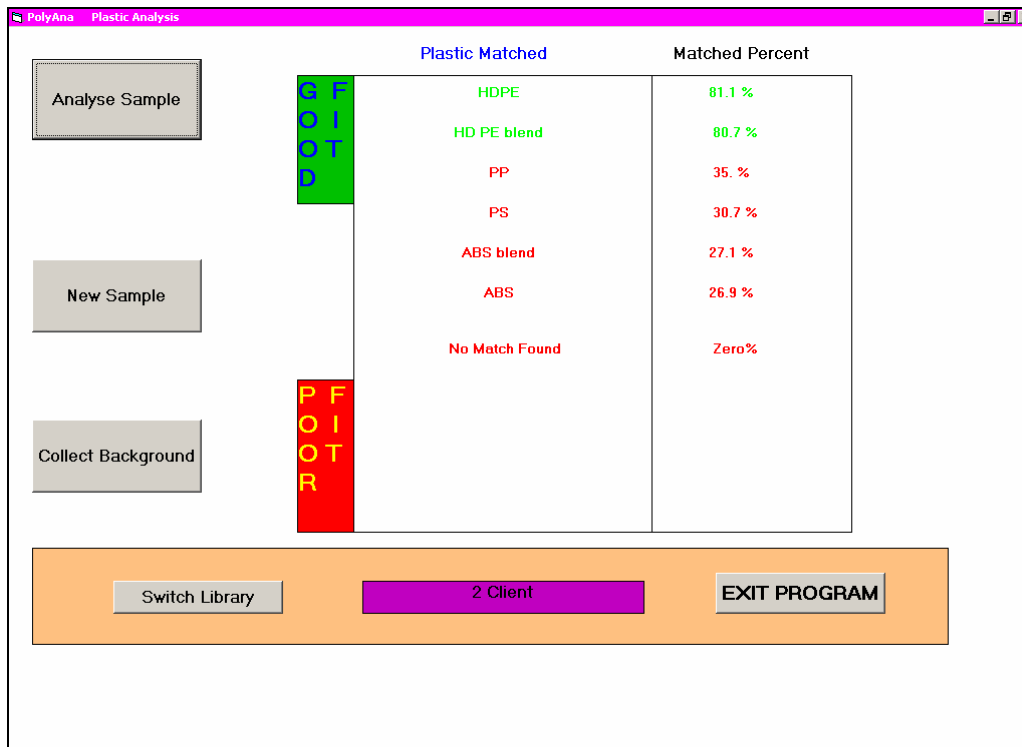
The PolyAna is based around the latest generation Nicolet Avatar Spectrometer with an integral optical cell and a supporting computer. The spectrometer uses a beam of mid infra-red wavelength light fired at a sample of unknown material to produce a spectrum from the reflected radiation.

The infra-red beam is directed to the sample by means of a series of mirrors within the optical cell. The reflected light is similarly directed to a detector also housed in the spectrometer. The computer then compares the spectrum of the reflected light with a database or 'library' of pre-programmed spectra stored within the computer. Different libraries are available for different applications, and a 'custom' library can be easily set up by the user in order to deal with specific materials of interest.

The PolyAna Avatar runs with MS Windows XP software. When presented with an unknown material the computer rapidly scans the spectrum of each of the plastics stored in the library and produces a list of the best matches with the sample together with their percentage fit.

⁶⁷ Wolfson Electrostatics, Dept. of Electronics & Computer Science, University of Southampton SO17 1BJ England. Tel: 02380 552266/594995. Fax: 02380 593015. email: wolfson@soton.ac.uk www.soton.ac.uk/~wolfson

⁶⁸ Ford Motor Company Research & Engineering Centre, Laindon, Basildon, Essex SS15 6EE England



PolyAna display. Click on 'Analyse Sample' or use foot switch. Various libraries can be programmed into the device containing up to several hundred materials

Advantages:

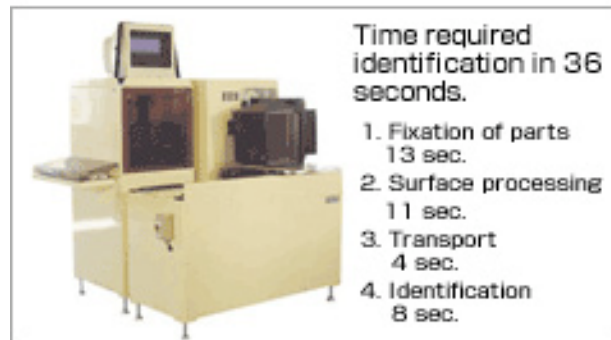
- Requires little or no sample preparation
- Speed and simplicity of operation
- Compact rugged construction proven on recycling lines
- Relatively low cost compared with other spectrometer based techniques

Disadvantages:

- Unproven on the full range of BFR's and additives
- Likes flat, smooth light coloured surfaces
- Still quite expensive for the recycling industry

11.4.2. Sony Plastics Identification Device

Using mid-infra red reflectance spectroscopy and new algorithms, a 99% accuracy rate has been achieved.



Sony Plastics ID system

This device makes it possible to locate black plastics and plastics with flame retardants, formerly difficult to distinguish. Using mid-infra red reflectance spectroscopy and new algorithms, a 99% accuracy rate has been achieved⁶⁹.

Advantages

Very high accuracies claimed
'Reputable' manufacturer

Disadvantages

Cumbersome
Expensive
Sampling time of 35 seconds impractical for recycling line

⁶⁹ www.sony.net/SonyInfo/Environment/recycle/development/02.html

11.4.3. Sliding Spark



The SlideSpec-S2 sliding spark spectrometer (left) and typical screen display (right)

The SlideSpec-S2⁷⁰ uses an electrostatic spark to vaporise the surface of the plastic under test and sampling the emissions.

Paints or contamination on the surface can be automatically removed by pre-sparking. Additive detection is performed by measuring simultaneously the characteristic emission lines of the elements of additives in the spectral region of approx. 210-500 nm. The intensities of selected spectral lines are compared with preset threshold values. After calibration with known samples, the system enables semi-quantitative analysis of inorganic contents down to the sub-%-region. A measurement time of 1 second is claimed.

The basic principle of the method is the thermal vaporization of a small amount of the material surface using a train of defined high-current sliding sparks. The material components in the spark by plasma are vaporized, atomized and, activated to emit radiation.

For analysis the sparking pistol is simply pressed on to the sample. The measurement begins by pressing the start button on the pistol grip. After sparking-off an integrated TFT-colour-screen displays the result.

The hand measuring head is connected with 3 m protection conduits to the instrument. Optical signals are coupled via fibre optics to the spectrometer system. The portable device includes the CCD spectrometer unit, the spark generator and a computer, which steers and evaluates the identification process.

The use of the software can be done by an integrated Touch Panel or by an external keyboard. Intensity data are saved in flat ASCII-format. The serial interface using a link program allows external data transfer (dimension in mm: 364x195x316, weight: 10 kg, electric power supply: 230 Volt-/50 Hz). Setting of different sparking conditions as well as the detailed spectra view and evaluation of the out coming atomic emission spectra enables to develop easily own applications (screening of woods, glasses, ceramics, textiles, leather goods, dried sludge, varnishes, paintings etc.).

Advantages

No problems with black samples
Speed and simplicity of operation

Disadvantages

Requires some sample preparation
Some uncertainty as to whether some plastic types can be identified (ie. HIPS from ABS, PE from PP etc)
Potential shock and fire hazards from high voltage sparks.

⁷⁰ www.iosys-seidel.de/slidespec_e.htm

11.4.4. Niton XLt

The Niton portable XLt Plastics Analyzer is an X-ray tube-based system which is claimed to be the first hand-held XRF (X-ray fluorescence) instrument for the plastics industry.

According to the manufacturer the device accurately covers a wide range of plastic samples used in manufacturing and comes calibrated for the quantification of cadmium (Cd), lead (Pb), chromium (Cr), antimony (Sb), tin (Sn), mercury (Hg), bromine (Br) and other potentially toxic metals. Additionally, chlorine (Cl) analysis is available for the sorting of PVC materials in recycling and waste streams.

The portable XLt can also be used anywhere it is needed, according to Niton, including on the assembly line, in the warehouse, on the back of a truck, or on supplier trips around the globe. It has also been engineered to be environmentally sealed and rugged, so it can withstand rain, dust and other harsh industrial and field conditions



The Niton XLt incorporates a hand-held X-ray tube

Advantages

Claimed accuracy for detecting BFR
Purpose built, compact and rugged
Competitive price (£25,000)

Disadvantages

Sampling times may be slow for some materials
Potential hazards from X-rays
Quite expensive for recycling industry

11.4.5. Spectracode RP-1

The Spectracode RP-1 uses Raman spectroscopy.

The Spectracode RP-1 can, it is claimed, identify BFR in plastics although the manufacturers admit that the accuracy of identification is unknown. It is also claimed that the acquisition time for sampling a plastic is 1 millisecond and assuming rapid processing and display of information is certainly fast enough for most recycling lines.

The RP-1 Console houses a high-resolution imaging spectrograph, large-area charge-coupled device detector and high-powered diode laser. The RP-1 data system employs a 233 MHz Pentium Processor loaded with image processing software, and user expendable libraries for a variety of applications in product testing and quality control as well as post-consumer, post-industrial, durable goods, and fibre recycling.

The equipment identifies plastic components, fibres, and scraps accurately using point and shoot. The RP-1 uses a fibre optic laser probe to read the Raman molecular bar code that distinctly identifies every polymer material. The RP-1 probe is lightweight, internally rugged and protected by Teflon impregnated coating designed for industrial use. A fifteen foot armoured umbilical connects the hand held probe to the console. Fibre-optics carry laser light to the sample, and return the Raman signal to the spectrograph.



The Spectracode Raman ID instrument

Advantages

Fast sampling time
Designed specifically for material identification

Disadvantages

Accuracy for BFR identification unknown
Raman technique works on very weak signal levels
Expensive

11.5. Conclusions

The following broad conclusions can be drawn from this review:

Because of the way flame retardants are incorporated into plastics and the concentrations in which they are present the methods for their detection are limited to around 9 techniques all based on spectroscopy. BFR detection in recycling is in its infancy and many of these techniques have been developed for the laboratory rather than a recycling line. This means they are generally expensive, relatively fragile and not particularly user-friendly.

Other current recycling techniques based on macro-physical properties of plastics such as density separation, surface hardness, electrostatics etc. will not identify the presence of BFR's. Thermal Imaging Response (TIR) which monitors the heating of the surface in response to an incident CO₂ laser beam may detect BFR's in similar light coloured plastics.

Bromine is not the easiest element to detect using spectroscopy and the LIBS technique for example identifies the presence of BFR by detecting Antimony (Sb) in the Br synergist compound Sb₂O₃. This also probably applies to the Sliding-Spark technique. Another technique FT-IR is less specific in the way it detects BFR; in this case relying on a small but significant shift in the spectral pattern of reflected radiation between BFR and non-BFR plastics. Neither of these points are important however for recycling applications since a simple streaming of BFR and non-BFR is all that is required.

Of the nine techniques, surface ablation by LIBS or sliding spark and FT-mid IR appear to be the most suitable for BFR detection with X-ray fluorescence in third place. It is no surprise therefore that it is these three methods which have produced purpose-built commercial instruments aimed both in terms of cost and practicality at the recycling industry. The instruments in question; SlideSpec, PolyAna and Niton XLt are similar in many ways and currently appear to set the benchmark for this application. They are similar in size, cost, sampling speed and ergonomics of use. (Note. It is assumed that the SlideSpec is similar in cost to the other two. Three attempts to obtain a price from the company were unanswered).

LIBS equipment is generally available but appears more complex and expensive. Recent attempts to run LIBS on a recycling line resulted in a reduction in accuracy compared with its operation in the laboratory. We are not aware of any 'stand-alone' LIBS system specifically targeted at BFR detection for industrial recycling although it is hinted in the scientific press that such hardware is on its way⁷¹.

The PolyAna FT-IR instrument has already been used on IT recycling lines and has successfully segregated manually-dismantled computer casings into streams with and without BFR. It is dependant however on having reliable known samples in its library for comparison of spectra.

The claims in the SlideSpec-2 sliding spark instrument literature that it can detect the presence of BFRs must be acknowledged although the authors have no direct experience with this equipment.

Information relating to the performance of the Niton XLt X-ray analyser is less specific with regard to BFR detection. Enquiries to the UK agent for this instrument produced responses for example with regard to sampling times where 'seconds to minutes' were quoted.

⁷¹ http://fw.pennnet.com/Articles/Article_Display.cfm?Section=ARTCL&ARTICLE_ID=185735&VERSION_NUM=2

12. WEEE polymer identification and separation trials

The work carried out under phase 2 of the project was focused upon the two main formats of plastic feedstocks that will become available as WEEE treatment facilities come on-stream in the near future:

- Whole plastic components from manual dismantling operations
- Shredded, mixed plastic from large scale fragmentation plants

12.1. Identification and analysis techniques

The work carried out to investigate manual identification and sorting techniques was conducted with the co-operation of the Hampshire Natural Resources Trust (HNRT), utilising the WEEE demanufacturing facility that has been built in Portsmouth by HNRT with funding from Onyx Environmental Trust. Samples of plastic components were also supplied from Remploy, Sheffield as part of their work on dismantling WEEE.

Following the conclusions from the review of available identification techniques for polymer types and BFR content from the first interim project report, it was decided to make a practical, working comparison of the following instruments:

- FT-IR reflective spectroscopic instrument – PolyAna Avatar
- NITON hand-held XRF device
- SSS3 Sliding Spark Detector from Iosys

These units were set up on a single workbench and a range of different plastic components was tested with each device over a 2 week period. The results in terms of both detection accuracy and user-friendliness are summarised in the table below:

Name:	PolyAna Avatar	Niton XRF	Iosys SSS3
Web address	www.soton.ac.uk/~wolfson	www.nitonuk.com	www.iosys-seidel.de
Instrument Type	FT-Infra Red Reflectance	X-Ray Fluorescence	Sliding Spark spectral analysis
Prime Function	Detect polymer type + some additives	Detect and quantify additives	Detect + quantify bromine and chlorine
Method of operation	Measures absorption of range of IR light wavelengths on sample surface and compares with library of known reference samples to give % fit to ID type.	Low power X-ray penetrates ~10mm into sample, detector measures distinct energy peaks from fluorescence of a range of elements to give ID and % conc. of additives	High voltage spark on surface creates plasma of vaporised material. Light spectra analysed for know peaks at Br and Cl wavelength to estimate % conc.
Approx Cost GB£	£22,000	£25,000	£3,200
Size	Benchtop box approx 1000 x 500 x 200mm	Handheld, bulky gun	Hand-held detector with small bench-top box
Weight approx	25 kilos	1.7 kilos	0.75 kilo (gun)
Portability	Zero – needs firm stable worktop + separate laptop PC	Excellent – battery powered, no cables.	Okay – light to carry, but needs mains power.
Ruggedness	Low – treat as laboratory equipment	Excellent – built for on-site use in scrap-yards	Good – but care needed for fibre optic cable
Start-up speed	Slow, 15 minutes to calibrate etc	Okay – 2-3 mins	Fast - < 1min
Operator manual	Basic	Good	Very good

Name:	PolyAna Avatar	Niton XRF	Iosys SSS3
Instrument Type	FT-Infra Red Reflectance	X-Ray Florescence	Sliding Spark spectral analysis
Ease of use: 1 – ergonomics	Poor - Fixed position nozzle	Easy – but care to point away from user	Easy – but low flex cable to gun
2 – sample presentation & speed	Difficult with big samples and must keep still for 30 seconds	Easy – hold gun on sample for 15 – 30 seconds	Very easy – 1 second to 'fire' spark
3 – Read-out	Good – degree of 'fit' to reference sample for ID	Okay – but need to interpret ppm numbers on screen	Simple & clear
4 - Adjustment	Tricky – need background measurement and to re-align laser unit	Not a problem	Easy to adjust base level reading to remove noise. Simple sensor cleaning method.
Sample preparation	Flat non-shiny surfaces best. Dark colours more difficult, surface coatings a problem	Thicker samples better (> 5mm). Will detect surface contamination & coatings. Good for granular plastics.	Clean surface required and flat area for good spark contact. Will detect dirt and coatings on surface.
Measurement - - Accuracy	Depends on closeness of match to library samples	Very good – ppm levels of elements	Sufficient – to nearest 1% on Br / Cl concentration
- Repeatability	Good if high match level	Excellent	Good – some noise around 0-1% level
- Reliability	Average	Very good	Very good
- Speed	Slow – 30 secs	Slow 15-30 secs	Fast – 1 sec
- User confidence	Average – needs degree of judgement	Good on primary elements, lower on chlorine.	High – except at 1% conc'n. level
Operator Skill level required	Good technical / laboratory person	Technical operator to interpret results	Factory operator with basic training

Conclusions from comparison of instruments:

- These three units have been designed to do different jobs, so this is not a like-for-like comparison.
- The focus of the trial was to assess each unit from the point of view of a plastics recycler, with the specific need to identify polymer type and the presence of brominated flame retardants.
- **The PolyAna** is the only device from the three tested that gives an identification of unknown plastic sample by type of polymer. The nature of its operating methodology means that the result is a 'percentage fit' of the spectrum collected from the unknown sample, to the spectra stored in its library of reference samples. It is thus susceptible to making wrong ID's (or giving 'no match') if the level of IR reflectance is low (as with dark colours or coated surfaces). Polymers with similar chemical structure and blends of polymers are more difficult to identify using this instrument (e.g. ABS from PS; or PC/ABS blends). However, it was generally found to give a reliable method to 'screen-out' unwanted polymers such as PVC or POM from a stream of mostly ABS & PS components.
 - The Polyana did not prove reliable in the identification of brominated additives in the samples tested
 - There was a good correlation between the Polyana's identified polymer type and that marked on the sample by the original manufacturer. This means that it is viable to use the 'moulding marks' as a method to sort out components, with the Polyana (or similar device) being utilised to provide a statistical level of quality checking and for I.D. of unmarked plastic components.
 - As the summary table indicates, the Polyana is a development of a laboratory instrument and is thus not suited to the rough industrial environment found in many recycling operations. It needs the attention of a technically competent person to ensure proper set-up and re-calibration, although an unskilled operator can use it to process a lot of similar samples, under remote supervision.
 - Each measurement takes around 30 seconds and access to the fixed detector nozzle with large components (e.g. back of TV casing) is difficult.
 - The Polyana is not suitable for continuous, at-line analysis of a flow of plastic samples past a sorting station. It is however useful as an off-line analysis tool in a QA role.

- The **NITON XRF** unit has been designed for use in a rugged environment and it is fully portable with no power cable required in use.
- The claimed 'plastics ID' software only uses detection of a high chlorine content to infer that the sample is PVC. No other polymer-type ID is possible. It detects a range of specified elements from the periodic table for atomic number of 13 and above (so C-H-O molecular substances such as plastics are not detected).
- It is a very accurate method that gives quantitative measurement of the important additives throughout a depth of approx 10mm into the sample. So cadmium, lead, titanium, antimony, chromium, bromine, chlorine, etc can all be assessed accurately. Levels of a few ppm can be measured in around 15 – 30 seconds per reading.
- This instrument is better suited for use in a 'policing' role for the detection of RoHS banned substances and other unwanted additives at a manufacturer's goods-in warehouse. It could also be easily taken on supplier QC visits to randomly inspect components or even bulk raw materials for unwanted additive content.
- Slow speed of measurement makes it not suitable for rapid on-line testing of a continuous flow of samples.
- **Iosys SSS3 Sliding spark detector** – this simple, low-cost machine does one job very well.
- The no-frills design and ease-of-use make it very good for quickly sorting components by Bromine or Chlorine content, with each measurement taking just 1-2 seconds.
- It can measure bromine or chlorine in discrete components over about 20mm size but not in granular material
- It can be used at-line to screen out Br & Cl containing plastics from a stream of components.
- The results for %Br on the sliding spark unit showed good correlation with the more accurate measurement of the Niton XRF machine.
- For any recycler wanting to sort brominated additive containing components from a mass of plastic parts, this unit represents the lowest cost and simplest unit for the job.

Recommendations

Dismantlers of electrical equipment are likely to find that 20 – 40% by mass of their material output streams will be plastic components. Most of that mass will be concentrated in the larger plastic moulded parts (e.g. TV rear casing; printer cover; photocopier paper-tray).

Value can be added to that mixed stream of polymer components by good sorting techniques to stream the material into groups of known plastic types. As few as 4 different polymer types will cover the majority of plastic found within each of the main streams of WEEE (e.g. PS; ABS; PC; 'other' for IT plastic parts).

In many cases the use of the 'moulding mark' can be reliably used to sort by polymer type. However the marking of components for brominated additives has been found to be very unreliable, with either no indication of flame retardant being given or a 'XX-FR' code used that relates to a non-halogenated flame retardant compound.

The value and range of re-use applications for recycled polymer can also be increased by thorough separation and removal of the brominated (and chlorinated) additives. This sorting process demands rapid and simple detection techniques that can be applied in an industrial environment by low skilled operators. The SSS3 sliding spark detector offers the right mix of robustness, speed and cost to make it suitable for this task.

In these trials the **Infra Red spectroscopy** method used to verify polymer type was able to give a close match to the 'as marked' polymer type on the majority of components. Differences between the 'marked' polymer type and the detected polymer were often due to similar IR absorbance profiles of like plastic compounds (e.g. HIPS detected for part marked as PS). The type of plastics that would definitely need to be screened out were always reliably identified (e.g. POM and PVC parts).

The particular instrument used in these trials was too much of a 'laboratory-developed' tool to make it suitable for general industrial use. The level of operator skill, time for each reading and slow start-up made it less suited to an industrial environment. Recycling firms are likely to want higher reliability and more rugged design from an instrument costing over £20,000 UK sterling.

During the course of this work programme, Axion visited the premises of IOSYS in Germany (the supplier of the SSS3 sliding spark unit). IOSYS have a full range of infra-red and sliding spark plastics identification tools that have been designed for specific industrial applications. During the machine demonstration the NIR unit was able to correctly identify a set of known polymer samples and reliably pick out those that contained BFR additives. The machine that offers a combined NIR and Sliding spark detector in one unit (the Mirospark) should be able to do all the identification of polymer type and additive sorting tasks that a plastics recycler is likely to need. This unit costs around €25,000 (approx £17k) and was seen to give rapid and accurate results.

For rapid on-line sorting of polymer components IOSYS have developed a suspended unit called 'Siroline' that focuses a beam of IR light onto a work-top or conveyor. Any piece of plastic placed in the 'pool of light' is rapidly identified and indicated by a row of LED lamps marked with the polymer type. This enables rapid, hands-free polymer sorting and could easily be linked to an automated plastic sorting mechanism.

It must be noted that a one-off demonstration during a single day visit does not give the same level of in-use assessment that has been possible with the practical trials of the other instruments.

Other instruments tested :

- **Tribopen** – (www.soton.ac.uk/~wolfson) A simple hand-held instrument that uses differential charging between the sensor head and the test sample, caused when the 'pen' is drawn across the sample surface. A red or green indicator light tells the user if the test sample is above or below the sensor head material in the triboelectric series. This instrument has been used in practical trials at the Hampshire Natural Resources Trust pilot WEEE demanufacturing project and has demonstrated that it can distinguish between PVC and other polymer types.
- **RF Sensors** – (www.oxfordrfsensors.com) uses attenuation of radio frequency as the basis to differentiate materials. Await full results from Oxford RF Sensors Ltd, although early indications are that polymer type can be identified. Some success has also been shown in differentiating between BFR and non-BFR polymer compounds. This is an early stage development, that is a long way from a commercial application. There may be fundamental problems with obtaining adequate penetration of RF signals into polymer samples.

Results of Polymer Component Analysis Work

This work was carried out in order to give some answers to the following questions about WEEE plastics and the BFR content of those streams:

1. How many plastic components DO contain brominated compounds?
2. How does the incidence of BFRs vary between different product groupings?
3. What are the most common types of plastic found in each group?
4. Is the quality of type-sorted polymer recycle suitable for re-use in new E&E goods?

A wide range of plastic component samples have been tested using the FT-IR Polyana instrument and the Sliding Spark meter over a 4 month period. This work is labour intensive but it does build-up a picture of the following items on a group by group basis:

- The range of polymer types found in each grouping of WEEE
- The frequency and level of Br or Cl compounds found
- The mass of typical components
- The average mass concentration of Bromine (or Cl) compounds
- The typical age profile of plastic parts
- Brand / manufacturer name – where marked
- Part description and colour

The following samples have been tested:

Grouping of source plastic material	Number of samples tested
TV casings	134
VDU casings	187
Telephone casings	67
Mixed IT – sample 1	207
Mixed IT - sample 2	194
Photocopier parts	83
Washing machine parts	295
Vacuum cleaners	176
Lawn mowers + other garden eqpmt.	41
Small Kitchen appliances	76
Total Components Tested	1,460

From the above testing programme the following main observations can be made:

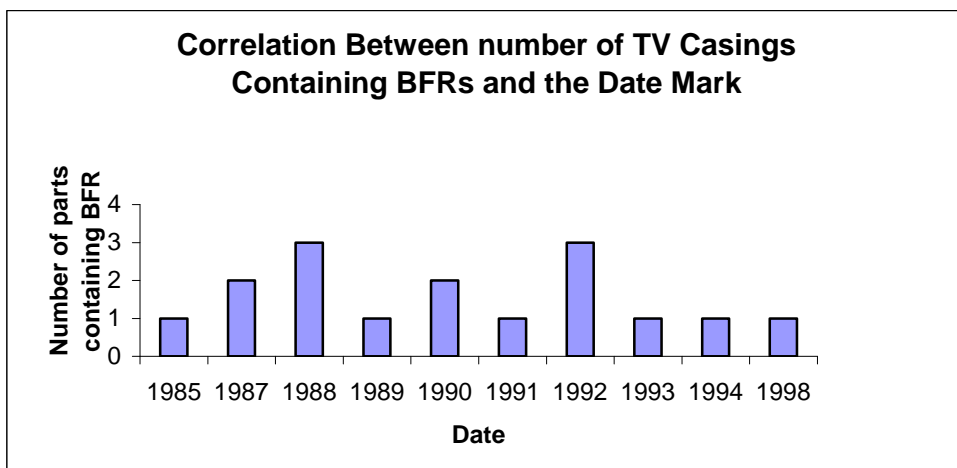
1) TV Casings – Two sample groups were tested:

TV Casing sample 1 – 30 casings - these were mostly rear casings from large sized black/grey televisions. Weights were in the range of 1.0 – 3.6 kilos per part and date of manufacture ranged from 1992 – October 2000, as marked. The polymer type was shown on nearly all casings as PS (polystyrene), with additional marking to indicate 'HI' – high impact on 4 of the 29 samples. Three casings were marked as –FR, one as 'V0'; 2 as UL94; 2 as 94HB – it was assumed this referred to some type of flame retardant additive.

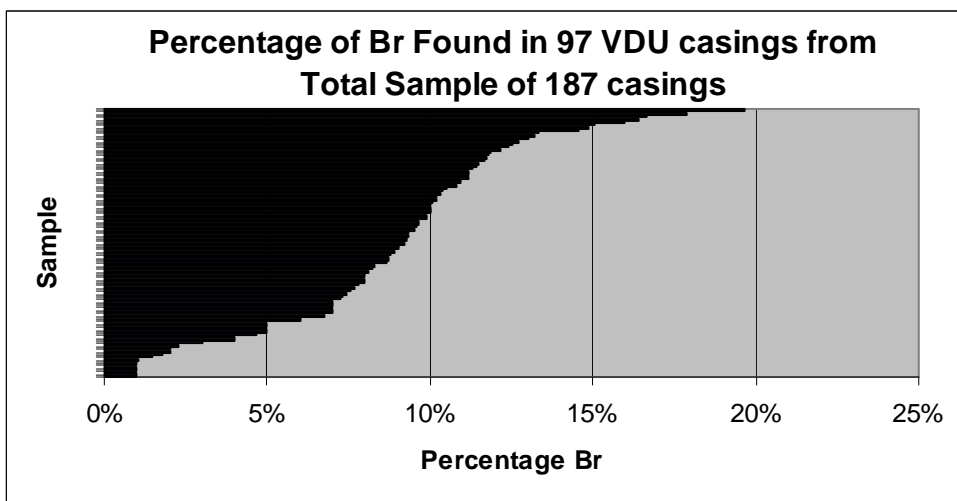
The NIR testing confirmed the polymer type as PS in all but 2 cases, but surface finish and coatings caused some difficulty in getting good readings. Bromine content was only found in 3 parts using the Niton XRF and this was confirmed with the sliding spark device (Br 12% and 11%, with Sb detected in each case). One casing showed Chlorine content of 13% on the sliding spark unit, but only Sb (antimony) was detected on the XRF.

On the basis of the complete sample weight of 53 kilos of PS material, we found 11% of the mass to contain either Br or Cl additives. If the whole sample was granulated en-mass the resulting bromine concentration would be approximately 1.1% by mass.

TV casing sample 2 – A larger sample was tested of 104 casings with an age range 'as marked' of 1985 – 1998. The average mass of the casing parts was 1600g. In this sample not many casings were marked with polymer type. Bromine additives were detected in 33 of the items (31% of the sample), with levels from 8 – 12% being found using XRF measurement. If the whole sample was ground into a homogenous mass of mixed polymer chip, then the bulk average bromine level would be 3.4%. The graph below shows that the distribution of bromine containing polymers across the age range of the Group 2 sample shows little change with year of manufacture.



2) VDU Casings – A sample of 187 dismantled VDU casings were tested at Remploy Sheffield using XRF to detect additives. Average moulding weight was 0.96 kilos and 97 of the tested items (52%) showed bromine content. The bromine level ranged from 2 – 18% with an average level of 9% (see graph below). This represents 3.9% bromine on a 'whole sample' mass basis. Polymer type was noted from the moulding stamp – of the 100 which were marked with polymer type, 52 casings were ABS, 20 PVC, 8 PS, 4 PPE and 3 PPO + other.



3) Telephone Casings – A first sample group of 40 casings from desk-top telephones were taken from a large pallet-box of stripped parts. Date marks ranged from 1993 to 2001 and the colours were mixed, with a majority of cream / white. Average weight per moulding was 100 grams. These were all identified as ABS and there was nil incidence of Bromine compounds. The keys from the telephones were identified as POM however, so these would need to be separated from the main casings before re-compounding could be considered. (40grams of keys were removed from one 100gram casing).

A second sample group of 27 telephone casings from a different dismantler showed similar results. No Bromine detected, primarily ABS plastic type and average mass of 145 grams per item, with a date range of 1991 – 2000 as marked.

4) Mixed IT Plastics 1 – This sample was taken at random from an IT dismantling facility. 207 items were tested and of these 33 parts (16%) were found to contain Bromine (in the range 2% - 11% Br as detected). The most common polymers are ABS, PS, HIPS and PC (with just 4 PVC parts and one POM). Dates ranges on those marked were from 1993 to 2003.

5) Mixed IT plastics 2 – A similar random sample of stripped IT parts taken from the same IT dismantling plant, but on a different day. From the 194 items tested 51 showed some Bromine content (26% of parts). In this sample there was a higher incidence of PC/ABS blend polymers, a lot of ABS and some PC material. A lot more of the parts were marked as

'XX-FR' than seen in sample 1, although many of these did not contain bromine. Judging from the description of the plastic parts in this sample it appears that there was higher incidence of printers and laptops than seen in sample 1, which reflects the mix of product being dismantled on the day the sample was taken.

6) Photocopier Parts – A sample of 83 parts was obtained from a dismantler of commercial photocopiers, mostly light grey in colour. Polymer type was marked on 95% of parts :- 31 were PC+ABS ; 26 PC+PS; 20 PS – with a high incidence of (FR) markings across all grades. Average mass of item was 170 grams and only 12 parts displayed bromine content (average 4% level). This indicates that a large proportion of the items marked as FR containing are using non-Bfr flame retardant additives.

7) Washing Machine Parts – A sample of 295 parts from dismantled washing machines was analysed. About half of the parts were made from PP and a third from ABS. POM, PA66 and PC making up the rest. Many of the PP parts are marked as containing fillers (e.g. PP-GF = glass filled). There were only 5 parts (1.7%) found to contain Bromine (in range of 2 – 7% Br detected).

6) Vacuum Cleaners – Two sample groups were tested. Sample 1 – 132 parts from a range of brands (Hoover, Dyson, Electrolux etc). Average mass of component was 385 grams and the date range of items was 1992 – 2000. Nil bromine content was found in any parts. ABS was the most common polymer (72% of marked items) with PC and PS being the other main types, plus some PP items. Sample 2 – 44 parts were tested from a different source. Again nil bromine was found in any parts. 18 of the parts were marked with polymer type, 17 of these being ABS. Average moulding weight was 720 grams. The handheld XRF was used to look at a range of additives – with traces of Cadmium being found in 2 parts (at ~0.15% level) and 3 parts showing some chromium content (~0.17% Cr level). Titanium traces display in about 2/3rds of parts with levels up to 5% by mass.

7) Lawn mowers – 41 Parts were sampled from a range of lawnmowers and other garden equipment. The bright 'Flymo orange' was a common colour, with green and dark grey parts also present. The most common plastic type was ABS (~90% of parts), with PS and PP making up the rest (except for fan mouldings which were nylon PA66). Average part weight ranged from 200 – 550 grams. Date stamps were from 1994 – 1999. No bromine was detected in this sample.

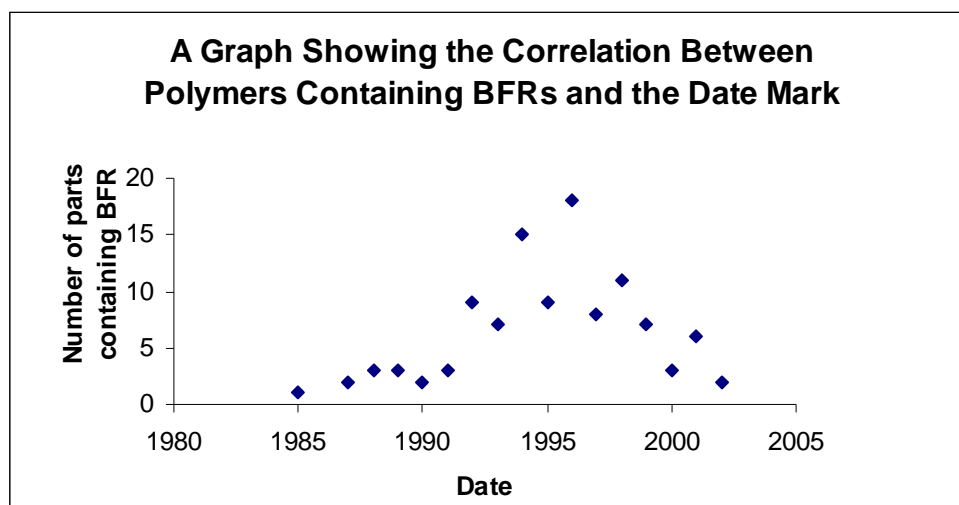
8) Small household – consumer / kitchenware – A varied collection of parts from kitchen equipment was tested – ranging from toasters, kettles, irons, mixers, blenders, etc. A lot of white colours or dark browns were seen. Average mass of part was 125 grams with PP being the most common plastic type (~70%). ABS; PS and PC were also present. This sample was not tested for Br content.

9) Hi-Fi consumer parts – Approximately 100 – 150 parts from old Hi-fi equipment and radios was sorted by polymer type, and quickly scanned for bromine content. Approx. 75% of parts were ABS with PS being the next most common. No bromine was detected with the sliding spark unit.

The results of the polymer component testing work is summarised in the following table:

Grouping of source plastic material	Number of samples tested	Average Weight of Component grams	Most common Polymer type	Other polymers found in sample	Percent of parts with Bromine	Average Bromine level (in Br parts)	Bromine level as percent of whole sample mass
TV casings - sample 1	30	1750	PS	HIPS	10%	11%	1.1%
TV - casing - sample 2	104	1600	PS	-	31%	10%	3.4%
VDU casings	187	960	ABS	PVC;PS;PPE	52%	8%	3.9%
Telephone casings	67	120	ABS	PS;POM	Nil	0%	0.0%
Mixed IT – sample 1	207	255	ABS	PS;PC;PVC	16%	5%	1.3%
Mixed IT - sample 2	194	130	PC/ABS	PS;PC	26%	6%	1.4%
Photocopier parts	83	170	PC/ABS	PC/PS;PS	14%	4%	0.8%
Washing machine parts	295	125	PP	ABS;POM;PA66	1.7%	3.5%	0.02%
Vacuum cleaners 1	132	385	ABS	PC;PS	0%	0%	0.0%
Vacuum cleaners 2	44	720	ABS	PP	0%	0%	0.0%
Lawn mowers + other garden equipment.	41	325	ABS	PS;PP	0%	0%	0.0%
Small Kitchen appliances	76	125	PP	ABS;PS;PC	----	---	---
Total Components Tested	1,460						

Where date stamps were marked on the casings the date of the moulding was recorded in each case. For the 144 casings that were date marked and also contained BFRs the distribution of ages is shown by the graph below:



Polymer Properties of Sorted Materials from Component Testing

During the material testing programme described above, the components were sorted into individual polymer types under the different source groupings. Samples of the non-BFR components have been processed into 'raw' recycled pellets by London Metropolitan University Polymer Centre in order to assess the material properties of the plastics. This exercise enabled a comparison to be made with the typical physical properties of virgin polymers as a measure of the re-usability of the untreated recyclates.

The full results from the polymer testing are attached at Appendix D.

As an example, results for a sample of post-use ABS telephone cases are presented below

Starting sample prior to granulation



Sample after granulation



Finished extruded resin



Material Properties – Sample Axion006 – ABS ex Telephones

Test	Axion006	Commercial grade
IZOD Impact Notched (Kj/m ²)	10.52	13 – 26
Heat Deflection Temp. degC	82	82 - 103
Tensile Strength at Yield (Mpa)	45.7	43 - 55 (medium impact)

Conclusions of the test work and subsequent review of the results by Peter Cracknell of London Metropolitan University are:

- Well sorted plastics from injection moulded electrical goods do make good quality recyclates with material properties that are good enough for most injection moulding applications
- Compatibiliser and antioxidant additive formulations are available which should be able to upgrade the performance of recycled polymers of the type tested in these trials close to equivalent virgin polymer specification at modest additional cost.
- The recycled material could also be blended with virgin polymer to make, say, 40% recycled grade resin in order to reduce physical property variation risk for injection moulders.

12.2. Bulk separation techniques

A large sample of 3 tonnes of mixed plastic from shredded post-consumer household WEEE was obtained from a leading UK shredder and metal recycling company. It was not possible to make any analysis of the mix of items that had generated this plastic sample, other than from a visual impression of the infeed WEEE 'mountain':



Typical household WEEE – prior to shredding and metal recovery

The above infeed WEEE produced plastic that appears as follows, after the vast majority of the ferrous and non-ferrous metal has been extracted by large scale processing. This material would represent a large fraction of the infeed to any WEEE plastics sorting plant (along with plastic from fridge recyclers and bulk shredded IT plastics).



Example of plastic pieces ex shredder & post metal removal

In order to prepare this material for a range of bulk separation trials, it was further shredded down to a particle size of 20mm. The material was then passed over a combined rare earth and eddy current machine (Master Magnets Ltd – www.mastermagnets.co.uk) in order to check for any metals that may have been liberated by the shredding, there was virtually nil metal in the sample.

Some of the above sample was further reduced down to 5-8mm granule chips to be sent off for various separation trials.

The following set of separation trials were carried out in order to determine which was likely to be most suitable for :

- The separation of bromine containing polymers from the bulk
- The sorting of the primary polymer types within the sample mix
- Removal of contaminants and minor plastic fractions
- Producing a high yield of commercially viable pure plastic

List of Processes in Bulk Separation Trial

- PHB Holland – Commercial scale process used for separation of plastics from refrigerators and other mixed stream.
- Deltex Pro - Jigging Rig for liquid phase density separation, full-scale plant unit (at Recycling Avenue, Holland)
- Axsia Mozley – Hydrocyclones for liquid phase density separation
- Titech Autosort – commercial scale NIR automatic sorting machine
- Hamos – Triboelectric separation machine, full-scale unit.
- Sortex Optical colour sorting equipment – short test
- X-Ray Transmission unit at T U Delft

For the purposes of this report, a summary of these trials is presented in a tabular format below.

Process	Developed by	Outline description	Trial Size	Summary Results
Full-scale, multi-unit commercial process	PHB (Envirotec) Waalwijk, Holland	Series of size reduction, dust removal, liquid phase separation and final refining unit operations developed over several years. Claims to remove heavier Bfr plastics.	1450 kilos of 20mm mixed shred	Produced high yield (>55%) of clean, dry 5mm granulate product – ABS/PS (97.6% purity) with low bromine (0.03%), from feedstock of average 0.14% Br. Heavies product contains 0.65% Br; floats product – was 78% PP/PE at 0.04%Br
Water Jigging Rig – Deltex Pro	Recycling Avenue, TU Delft, Holland	Three-way density split of infeed plastics created in water tank by means of a pulsed bed of fixed density spheres, suspended on mesh. Heavy fraction must pass down through 'jigging' bed of spheres, middle fraction 'sinks' in water, but 'floats' on spheres of 1.1 density.	250 kilos	Gave 60% yield of ABS/PS rich (97% purity) product with low Br at 0.07%. Heavies fraction was 1.8% Br, floats fraction 0.037% Br. Floats was mixed with 45% PS in PP/PE mix due to poor wetting at surface sink/float point.
Water Hydrocyclones	Axsia Mozley, Gloucester UK	Full-scale test rig used to demonstrate 3 stage separation of input material to deliver 3 density fractions. Dry sieving was used to remove around 20% fines and dust from the feed sample.	100 kilos	High throughput of liquid gives dry solids feed-rate equal to 3.7 tonne/hr. This was split into 86% ABS/PS rich fraction; 12% PP/PE rich; rest heavies >1.1 SG.
NIR auto-sorter machine	Titech 'Polysort' detect / eject system	Full scale machine fed with 20mm nominal sized pieces. NIR reflectance used to sort by polymer type – some limitations with dark colours.	60 kilos	Poor separation achieved due to high proportion of coloured components in feed material
Triboelectric sorting machine	Hamos GmbH Penzberg Germany	Particles of plastic are charged by vigorous vibration in a metal chamber. These then pass along a belt to fall through a high voltage electric field. Gives 3 way split of +ve, uncharged and –ve particles.	5 x 10kg samples mixed plastics.	Not able to generate a significant separation with 4 of the samples. One sample did give an 80/20 concentration of material – Dark colour HIPS+BFR mixed with light ABS material, but not a pure split.
Optical Colour Sorting	Sortex Ltd, London	Rapid image analysis in visual light range used for high speed sorting of falling cascade of small particles (e.g. rice grains).	2 x 10 kilo samples mixed colours	One sample of ABS from IT which was approx 30% dark/blue granules mixed with cream colour, was sorted to 99.99% purity of light in single pass at 2 tph. Telephone ABS mixed colours with light single pass gave 98% pure light; 2nd pass 99.99%.
X-Ray Transmission Sorter	Tako De Jong T U Delft Holland	Normal airport X-Ray machine used with novel analysis software to measure transmission of X-Rays through sample pieces at two energy levels. Enables identification of material by average atomic number and presence of contaminants (e.g. screw insert). Can be linked to full-scale sorting system at commercial scale.	2 x 10 kilo samples. One post consumer; one shredded IT plastic.	Laboratory rig used to demonstrate the analysis only, not seen linked to auto sort air-jets. Impressive ability to rapidly compare transmission level to a reference material and produce groupings of individual pieces on a graph, linked to the different polymer types or additive content. Software can be programmed to perform a range of sort criteria depending upon required output. (e.g. pick ABS+BFR from normal ABS etc).

12.3. Observations and conclusions from the bulk trial programme

- Density separation DOES appear to remove brominated plastic compounds from a bulk shredded sample.
- By careful selection of the density split point between 'product' and 'heavies', it is possible to generate a reasonably high yield of ABS/PS polymer mix with average bromine content well below the RoHS maximum allowed concentration of 0.1%. In these trials, input material of mixed post-consumer WEEE plastic with 0.14% average bromine content was reduced to a 'product' bromine level of 0.03%. The majority of the bromine containing particles being concentrated into the 'heavies' fraction (SG>1.1).
 - In these trials the 'reject' heavy stream was approximately 10-15% of the infeed material tonnage.
 - It is this mixture of brominated styrenics, PVC, PC, POM, metal, wood, rubber and stones etc that would become the feedstock to any chemical BFR extraction plant. This is far removed from the model 'golden samples' that have been used in laboratory BFR extraction tests.
 - The full scale commercial process at PHB Holland gave the best performance in terms of saleable product yield, because both the PP/PE floats (SG<1.0) and the ABS/PS product (1.0<SG<1.1) were of a high purity.
 - The Deltex Pro jiggling rig provided a more accurate density split in the 1.0 –1.1 SG range, but did not yield a very pure floats fraction. This unit is still in the later stages of process development.
 - A continuous process based upon the best of the above density separation methods could be controlled to remove just enough of the halogenated compounds by fine-tuning of the lower density split point (i.e. somewhere near 1.1SG). The concentration of bromine in the bulk product could be rapidly & accurately measured at-line using a hand-held XRF instrument, such as the NITON unit. This would enable the process to give maximum yield of ABS/PS product that still achieved the required 0.1% maximum Br concentration.
 - Triboelectric separation did not appear to give a reliable basis for sorting of BFR compounds from non-BFR compounds during these tests.
 - The X-Ray transmission machine offers a very specific means to sort individual pieces of BFR-plastics from non-BFR compounds. The technology is not surface dependent (unlike NIR) and can be configured to remove other unwanted additives (e.g, lead, cadmium, metal inserts) in the same pass through an automated sorting machine.

13. Reprocessing options for plastics containing BFRs

13.1. Methodology

The aim of Phase 2 of the project was to prepare outline process designs for the BFR removal process options that were short listed during Phase 1 of the project and to compare the commercial potential and environmental impact of these options against the alternative treatment options of incineration and landfill.

There were three components to the work carried out:

- Laboratory trials of the most promising BFR extraction processes
- Process design for the 6 BFR polymer treatment processes to be evaluated
- Commercial and environmental evaluation of the 6 BFR polymer treatment processes

In Phase 3 of the project the two most promising process options that were identified during Phase 2 (Creasolv and Centrevap) were tested in a series of larger scale trials and their process designs were optimised further. Some of this more detailed design work is confidential to WRAP and the Fraunhofer Institute in Germany but will be made available to commercial users of the process under license.

13.1.1. Laboratory trials of BFR extraction processes

Prior to finalising the list of candidate processes for full assessment some initial process design work was done to estimate rough capital and operating costs for each of the options and two brainstorming sessions were held to identify any further novel process options that should be considered as a result of the literature review and to assess the laboratory work that should be done to validate each of the chosen process options. These sessions involved Dr David Pyke, an expert in brominated flame retardant chemistry and process engineers and chemists from Axion Recycling, Manrochem Ltd, Fraunhofer IVV in Munich and Nottingham University.

The brainstorm sessions identified two new process ideas for evaluation; Centrevap and Antisolv. Two process options (Haloclean and Mitsubishi) were eliminated at the brainstorm stage prior to practical testing because the expected capital cost compared to likely revenue would be prohibitively expensive.

The laboratory trials for each process option were designed to generate maximum useful process design information for minimum research cost in order to make the best use of the available research budget. The trials did not therefore test the full process route for each process option. Instead tests were designed which targeted only specific unknowns in the process design.

In order to avoid introducing extra variables into the experimental work a set of six 50Kg 'golden samples' of polymer were produced by a commercial compounder, MAKSC, in Germany for use in the laboratory trials. The composition of these samples was chosen carefully in discussion with experts from the bromine industry and the polymer recycling sector to reflect the likely composition of WEEE polymers that will be collected in the UK over the next few years.

The sample compositions were as follows:

Sample	Polymer	BFR	Antimony trioxide	Stabiliser	Colour
HIPS	Atofina 7240			0.05%	Green
HIPS-FR	Atofina 7240	10% Deca BDE	4%	0.05%	White
ABS	Bayer Novodur P2HT			0.05%	Grey/Blue
ABS-FR	Bayer Novodur P2HT	5% Octa BDE 5% TBBA 0.5% TBPE 3% Deca BDE		0.05%	Light Brown
ABS/PC	PC/ABS (Dow Pulse A35-105)			0.05%	Blue
ABS/PC-FR	PC/ABS (Dow Pulse A35-105)	7% TBBPA	3%	0.05%	Cream

The compounder accidentally left antimony trioxide out of the blend for sample ABS-FR. They were not asked to repeat this batch because it was decided that it would be useful to have a sample containing bromine but free of antimony trioxide synergist for some of the polymer identification and bulk sorting trials.

The homogeneity of the compounding process was checked at the laboratory of Fraunhofer IVV near Munich by testing multiple samples from each of the HIPS-FR and ABS-FR batches by X-Ray fluorescence spectroscopy for bromine and antimony trioxide. These tests confirmed good sample homogeneity as follows:

HIPS-FR: 7.75 ± 0.077 % for Br and 2.37 ± 0.14 % for Sb (35 samples)

ABS-FR: 11.9 ± 0.29 % for Br (10 samples)

13.1.2. Process design

A flowsheet, mass balance and capital cost estimate was produced for each of the BFR polymer treatment process options selected for final evaluation.

In order to ensure a valid comparison between process options the same fundamental assumptions were used for each of the process designs. The key assumptions are listed at section 6.

The target performance set for the BFR extraction processes was to produce a clean polymer in granule form:

- free of all contamination below 50 micron particle size
- with a maximum volatile solvent content of 1% (this is the practical limit for easy processing in unvented single screw extruders)
- containing a maximum 0.1% of the flame retardant decabromodiphenylether (decaBDE)

For the process options which destroyed the original polymer to produce either chemical feedstock or energy the target was to maximise feedstock or energy recovery and conform to UK emissions legislation.

13.1.3. Commercial and environmental evaluation

Having evaluated the technical potential of the various disposal options they were compared in terms of both their commercial potential and their likely environmental impact.

The commercial evaluation was conducted by compiling a business model for each disposal option at the target throughput of 10,000te/year.

In each case the business model comprised financial projections for a new plant built in the UK on an existing chemical site. The financial projections included profit and loss, cash flow and balance sheet forecasts. They included a similar mix of equity and loan financing in each case.

To ensure a fair comparison the same detailed assumptions were used for each option. These are listed at Section 14.

Two separate environmental impact assessments were made for each option.

White Young Green Consultants, an engineering consultancy with general expertise in environmental impact assessments was engaged to conduct:

- a) A qualitative comparison of the environmental impacts of the different options across all impact categories
- b) A quantitative comparison in terms of global warming potential (CO₂ production), the most relevant impact category for polymers containing brominated flame retardants

The project steering group also recommended that Dr Jaco Huisman of Huisman Recycling Research in the Netherlands should be engaged to conduct a quantitative QWERTY eco-efficiency assessment of each of the disposal options. Dr Huisman's rigorous QWERTY analysis technique is rapidly becoming the standard across Europe for assessment of WEEE recycling processes.

The results of these analyses are presented in Section 21 of this report.

13.2. Process shortlist

Prior to finalising the shortlist for practical trials 13 candidate processes were considered in detail:

Process	Developed by	Outline description	Rejected/selected	Reason for rejection/ selection
Haloclean feedstock recycling	Forschungszentrum Karlsruhe, Germany and SEA Marconi, Italy	Depolymerisation of polymer in indirect heated rotary kiln at high temperature followed by gas treatment in polymer melt bath to debrominate.	Rejected	Expensive to develop process further. High capital cost at target scale
RGS90 Stigsnaes hydrolysis	RGS90, Denmark	Reaction of bromine compounds with sodium hydroxide solution at high temperature followed by high temperature pyrolysis in indirect-heated rotary kiln	Selected	Process already constructed at 40,000te/yr scale in Denmark for waste PVC. Potential to process BFR polymers alongside PVC
Potassium hydroxide debromination	Axion for WRAP and Fraunhofer IVV	Debromination of BFRs in polymer solution by reaction with potassium hydroxide and octanol to produce octyl bromide	Selected	Other workers have demonstrated debromination by this route. Easy scale-up. Octyl bromide is a useful chemical intermediate.
Mitsubishi debromination	Mitsubishi, Japan	Extraction of BFRs from polymer by special solvent in heated compounder/extruder just below polymer melt temperature	Rejected	Difficult to scale up. High dioxin formation likely. High capital cost at target scale
Creasolv	Fraunhofer IVV, Germany	Solvent extraction of BFRs using combination of special solvents. Precipitation of polymer from solution followed by extrusion of finished pellets	Selected	Process already developed at small technical scale. Low energy consumption. Simple process equipment and easy scale-up.
Ionic liquid	Brunel University, UK	Solvent extraction of BFRs using tailored ionic liquid solvent	Selected	High efficiency, low boiling, highly specific solvent. Potentially simple process equipment and easy scale-up
High pressure hot water debromination	Critical Processes, Leeds, UK	Very high temperature hot water used as a solvent to extract bromine compounds and other additives from polymer melt	Selected	Water is a clean solvent which is easy to treat after extraction. Potentially simple process design.

Process	Developed by	Outline description	Rejected/ selected	Reason for rejection/ selection
Supercritical carbon dioxide extraction	Nottingham University Chemistry Department	High pressure supercritical CO ₂ used as a solvent to extract bromine compounds and other additives from polymer granules	Rejected	Supercritical CO ₂ unlikely to dissolve BFRs in commercially viable amounts
Filter BFR removal	Axion	Dissolve polymer in a solvent which does not dissolve target BFRs. Filter to remove undissolved BFRs and any other additives. Recover polymer from solution by evaporation or anti-solvent precipitation	Selected	Relatively simple process technology. Flexible process. Potential to remove other insoluble additives in addition to BFRs.
Centrevap	Axion	Process details currently confidential pending possible filing of patent application by WRAP	Selected	High throughput and relatively simple process technology. Flexible process.
Supercritical CO ₂ antisolvent precipitation	Nottingham University Chemistry Department	Supercritical carbon dioxide used to precipitate polymer from conventional solvent after treatment of solution to remove BFRs by one of the above techniques.	Selected	Supercritical CO ₂ is a clean, relatively low cost solvent which is easy to disengage from primary solvent by reducing pressure. Potentially clean, high throughput process.
Conventional anti-solvent precipitation	Nottingham University Chemistry Department	Conventional solvent such as methanol or hexane used to precipitate polymer from primary solvent after treatment to remove BFRs. Precipitate dried then processed in vented extruder to remove residual solvent	Selected	Potentially low energy cost. Relatively simple process technology. Easy scale-up.
Incineration with energy recovery	Well-established	Burn BFR polymer in conventional large scale waste incinerator alongside municipal solid waste. Energy recovered as electrical power. Dry-type air pollution control system as used in most UK incinerators	Selected	Well-established technology. Plenty of existing municipal waste incineration capacity in UK, although it may be difficult to get permission to burn BFR-containing polymers in UK municipal waste plants under current waste incineration legislation. There is very little available capacity for incineration of other wastes in UK.

13.3. Summary of practical process trials

Most of the process options selected for further investigation were tested at laboratory scale or larger in the course of this project. Results of these trials are tabulated below:

Process	What we did	Results	Rejected/ selected	Reason for rejection/ selection
RGS90 Stigsnaes hydrolysis	Not tested. During the course of this WRAP project RGS90 closed its large scale demonstration plant at Stigsnaes due to technical and commercial difficulties so it was not possible to test the process with BFR-containing WEEE polymers	Sodium hydroxide debromination for BFRs is not yet proven. However RGS90 believes it should work based on their previous work in this area.	Selected	The RGS90 process includes a downstream pyrolyser and is closely linked to a large scale 'carbogrit' plant. These could 'mop up' any degradation products which are not fully destroyed by the hydrolysis step. RGS90 has tested a large scale plant which could potentially co-process PVC and WEEE polymer so process data is available.
Potassium hydroxide debromination	Debromination of BFR polymer in Creasolv Solvent with KOH/Octanol tested at lab scale by Fraunhofer IVV	Incomplete reaction of BFR component, even in melt phase. High dioxin formation.	Rejected	Excessive dioxin formation and incomplete BFR removal makes process commercially unattractive without further development
Creasolv	2 runs at 5Kg scale by Fraunhofer IVV of a modified version of the Creasolv process agreed between Axion and Fraunhofer with scale-up in mind. Trials conducted on real WEEE polymer collected in the UK (HIPS-FR from TV sets)	First run produced good quality recyclate. Second run less successful due to attempt to recycle some of the process fluids without adequate clean-up	Selected	Good BFR extraction demonstrated. Dioxins also removed. Final polymer cleaning step used in trial would be difficult to scale up. Alternative route identified but not tested in Phase 2.
Ionic liquid	Synthesis and testing by Brunel of 13 different potential ionic liquid solvents. Several runs at lab scale with different process routes to establish optimum extraction method.	One ionic liquid compound performed particularly well. BFR extraction efficiency close to target specification. Difficult to recover all solvents	Selected	Good BFR extraction demonstrated. Dioxins also reduced.

Process	What we did	Results	Rejected/ selected	Reason for rejection/ selection
High pressure hot water debromination	Series of lab scale trials of ABS at increasing temperature with both high pressure hot water (up to 250C) and hot methanol (up to 220C).	Only limited BFR extraction achieved with both hot water and hot methanol. High dioxin formation observed.	Rejected	High dioxin formation, poor BFR extraction and polymer degradation would make it difficult to sell final product. Process likely to be expensive
Filter BFR removal	3 days of lab scale filtration trials with HIPS dissolved in toluene using Mavag pressure filter. Trials conducted at Ionic Solutions Ltd, Bradford. Mesh sizes down to 12 micron and range of filter aids tried	Only limited BFR removal observed due to very fine BFR and antimony trioxide particles in polymer samples (0.2-5 micron)	Selected	Polymer solution was s easy to handle at moderate temperatures (30-50C). Further development of filter aid and filter mesh combinations could yield a commercially viable process.
Centrevap	Small scale lab test	Process results confidential pending possible patent filing. More testing required.	Selected	If technical issues can be resolved this could be a high throughput and flexible process solution for a wide range of polymer types. Although the energy load is higher than Creasolv (all of the solvent has to be evaporated) the process technology is relatively simple and has been proven on virgin polymers. Offers potential for a flexible process that would be suitable for several different polymer types.
Supercritical carbon dioxide antisolvent precipitation	Extended series of lab scale precipitation trials with supercritical CO2 at a range of pressures conducted by Nottingham University on solutions of BFR polymer in a wide range of conventional solvents.	Precipitation achieved with toluene, ethyl acetate and methyl ethyl ketone at pressures of 20bar and above. None produced a clean, dry polymer. At the pressures used a substantial amount of residual solvent remained in the polymer. This would require further processing.	Rejected	Discussions with supercritical CO2 process equipment manufactured indicated that substantial further process development would be required in order to generate a commercially viable process design.

Process	What we did	Results	Rejected/ selected	Reason for rejection/ selection
Antisolvent	Lab scale precipitation trials with a range of conventional solvents conducted by Nottingham University, based on lessons learned from CO2 precipitation work.	Toluene with methanol provided an effective combination, producing a floc-like precipitate that air dried to 5% solvent content within 2 hours. Ratio of methanol to toluene required is approximately 4:1.	Selected	Unfortunately toluene/methanol and all of the other conventional solvent combinations tried formed constant-boiling azeotropes at commercially viable pressures. This necessitates the use of sophisticated membrane separation processes to recover the primary and precipitation solvents. This increases process cost and complexity. Despite this drawback it was decided to include this process in the commercial evaluation because its energy consumption is potentially low.
Incineration with energy recovery	No trials conducted during this project (many other trials have been conducted previously in Scandinavia and Germany – see earlier sections) but detailed process design discussions were conducted with the technical manager of one of the UK's leading large scale dry process municipal waste incinerators	Co-combustion at about 1% by weight with municipal solid waste will not disrupt incinerator operation unduly, although it will increase operating cost for the air pollution control system. Some regulatory or emission consent changes may be required, depending on interpretation of the latest waste acceptance criteria.	Selected	Incineration with energy recovery in MSW incinerators is likely to be the only immediately available alternative to landfill for most BFR-containing polymers until other recycling processes are developed in the UK.

Fraunhofer IVV analysed the most relevant samples from the laboratory trials for polybrominated dioxins and furans and compared them to limits set in the German Dioxin Ordinance⁷². This is a piece of local legislation which only applies in Germany. It restricts the amount of specified compounds that may be present in new items placed on the market in Germany to below 1ppb total for certain classes of compound and 5ppb total for a broader range of compounds.

The results were calculated in terms of two different units. The table below presents the analysis results in nanograms per gram of sample:

Dioxin tests	Ng/g sample					
	Golden Sample of ABS-FR (contains stabiliser but no Sb2O3)	Golden sample of ABS-FR after heating with hot water for 1 hr at 250C by Critical Processes	Input to Creasolv extraction trial No 1 on HIPS TV plastic	Product from Creasolv extraction trial No 1 on HIPS TV plastic	Best' run from Fraunhofer KOH Debromination trials	Statutory Threshold set by German ChemVV
concentrations in ng/g sample						
2,3,7,8-TeBDF	78	2975	3	0	64	
2,3,7,8-TeBDD	<0,01	0	<0,01	<0,01	19	
1,2,3,7,8-PeBDF	11	260	2	3	13	
2,3,4,7,8-PeBDF	100	1231	9	1	2	
1,2,3,7,8-PeBDD	0	12	0	0	4	
1,2,3,6,7,8-HxBDD + 1,2,3,4,7,8-HxBDD	1	11	<0,4	<0,4	1	
1,2,3,7,8,9-HxBDD	<0,4	7	<0,7	<0,7	1	
Sum 4 [ppb]	179	4219	12	1	89	1
Sum 5 [ppb]	190	4497	15	5	103	5

⁷² Chemikalienverbotsverordnung, Bundesgesetzblatt (1996) 818

The table below presents the same dioxin test results in terms of toxicity equivalent (TEQ):

Dioxin tests	Ng I-TEQ/g sample				
	Golden Sample of ABS-FR (contains stabiliser but no Sb2O3)	Golden sample of ABS-FR after heating with hot water for 1 hr at 250C by Critical Processes	Input to Creasolv extraction trial No 1 on HIPS TV plastic	Product from Creasolv extraction trial No 1 on HIPS TV plastic	Best' run from Fraunhofer KOH Debromination trials
concentrations in ng/g sample					
2,3,7,8-TeBDF	7.8	297.5	0.3	0.0	6.4
2,3,7,8-TeBDD	<0,01	8.8	<0,01	<0,01	147.9
1,2,3,7,8-PeBDF	0.5	13.0	0.1	0.1	0.7
2,3,4,7,8-PeBDF	50.1	615.5	4.7	0.6	1.0
1,2,3,7,8-PeBDD	0.1	6.1	0	0	1.9
1,2,3,6,7,8-HxBDD + 1,2,3,4,7,8-HxBDD	0.1	1.1	<0.04	<0.04	0.1
1,2,3,7,8,9-HxBDD	<0.04	0.7	<0.07	<0.07	0.1
I-TEQ (8PBDD/F)	58.7	943	5.2	0.8	158

14. Process design assumptions

Standard design assumptions were used to compare all of the process options that were evaluated in the course of the project in order to ensure that the comparisons were fair and realistic. These assumptions are set out below.

14.1. Commercial parameters

We have assumed that Annex 2 of the WEEE Directive is implemented in the UK and therefore that BFR polymers must be treated separately.

We also assume that mechanical recycling of WEEE polymers in the UK will be a cost-effective alternative to landfill. We therefore assume that mechanical recycling processors will develop who will produce separated streams or BFR-free polymer for re-use and that they will make a profit on the sale of this material. There are several polymer recycling companies in the UK and mainland Europe that are developing their business in this direction.

If the WEEE Directive is enforced then these companies will not be able to sell their BFR-containing polymer for direct re-use. It will therefore have to be disposed.

The cheapest disposal route in the UK is landfill- at a cost of about £45/te for bulk disposal. We have therefore assumed in our base-case evaluations of the Creasolv and Incineration with energy recovery disposal options that they will be able to attract a similar gate fee (£45/te) for BFR-containing WEEE polymers delivered to their sites.

However the Centrevap process option will not remove BFRs effectively enough to achieve the targets set for this project so operators of this process option will have to compete with exporters of WEEE polymers to China. These buyers are currently paying around £100/te for sorted WEEE plastics so this is the input price assumed for the evaluation of the Centrevap process option.

Detailed assumptions are:

- UK economic conditions
- Plant to be constructed on an existing serviced chemical site
- Feedstock: Relatively clean, sorted, size-reduced BFR-containing styrenic WEEE polymers (HIPS, ABS or ABS/PC) produced as a waste stream from several WEEE polymer mechanical recycling plants across the UK. It was assumed that the mechanical recycling plants would use sorting techniques of the type tested during this project to recover BFR-free WEEE polymers for immediate re-sale at a profit.
- Feedstock contains 10% brominated flame retardant and 10% inert additives (contamination, fillers, etc). Note that the intermediate commercial evaluations conducted for all the process options in Phase 2 assumed 2% inert content. This was raised to 10% for the final evaluations following a request from Plastics Europe.
- It is assumed that the amount of Penta BDE in the feed is negligible. Penta BDE is not generally used with the thermoplastic polymers typically recovered from WEEE.
- The BFR-containing polymers which the mechanical recycling plants would separate for treatment or disposal in accordance with Annex 2 of the WEEE Directive would attract a disposal gate fee similar to current UK landfill cost of £45/te when delivered to the BFR treatment processes. Note that an input cost of £100/te was assumed for the Centrevap option as explained above.
- Where high quality, compounded BFR-free polymers are produced from a BFR extraction process they are expected to sell for around 60% of November 2005 virgin polymer prices. This equates to a selling price assumption of £600/te for ABS and ABS/PC and £510/te for HIPS (average £560/te). Note that the Phase 2 evaluations presented in section 15.1 and in Appendix 3 used a lower polymer price assumption of 45% of June 2005 virgin polymer prices. This equated to a selling price assumption of £450/te for ABS and ABS/PC and £425/te for HIPS. The price assumption was raised in Phase 3 based on market feedback that high grade WEEE polymer recyclates will attract better prices than originally assumed because manufacturers are keen to include high quality recycled content in their products.
- Plant assets financed 40% with equity, 60% by leases and debt. Lease period 5 years, interest rate 7%. Debt period 3 years, interest rate 12%.
- Working capital financed 100% by equity.
- VAT rate 17.5%. Corporation Tax rate 30%.

The bulk polymer separation trials conducted during Phase 2 of this project indicated that roughly 10% of UK WEEE polymers are styrenic and contain BFRs (weighted average across all categories of WEEE).

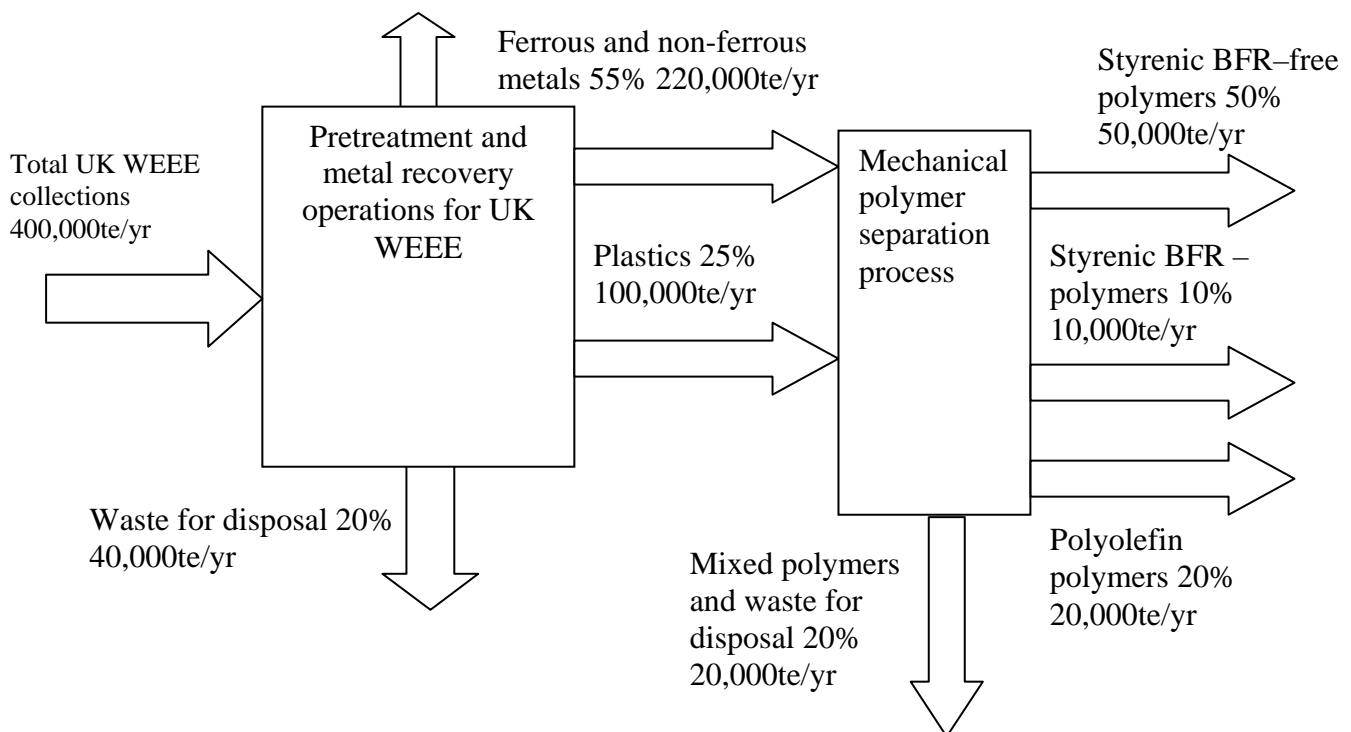
The UK WEEE collection target for 2006 is about 400,000te/year (6Kg/person per year).

Pre-treatment and separation of bulk WEEE produces approximately 55% metals, 25% mixed plastics and 20% waste and other materials in the form glass, wood, dirt, concrete and other materials.

The mixed plastic fraction separates into approximately 50% BFR-free styrenic polymers, 10% BFR-containing styrenic polymers, 20% polyolefin polymers (all BFR-free) and about 20% waste and other polymers including PVC, thermosets and specialist thermoplastics such as POM and nylon.

The target BFR separation plant throughput of 10,000 te/yr for this project therefore equates to the BFR-containing styrenic polymer fraction from about 100,000te/year of WEEE polymer or about 400,000te/year of undismantled whole WEEE.

The overall mass balance is shown below:



14.2. Operating parameters

- Plant throughput: 10,000te/year.
- Plant designed for 24 hour /day, 7 day per week operation
- Plant overall equipment efficiency (OEE) 80%⁷³.
- Steam cost £8/te (delivered on a cost/te basis by the site owners)
- Cooling water 1.4p/te (delivered on a cost/te basis by the site owners)
- Power cost £70/MWh
- Fuel cost (for mobile plant) 75p/litre
- Hazardous waste landfill disposal cost £80/te
- Water effluent disposal cost calculated from expected effluent composition according to the standard 'Mogden Formula' which is used by all water authorities in the UK to calculate trade effluent treatment charges. The disposal prices used were those charged in 2004 by United Utilities PLC, a major UK utility company.
- Process operator job cost £25,000/year – number of operators/shift varying according to process complexity
- Other salaries (management, admin, laboratory, etc) in the range £23,000 to £50,000/year. Total of £153,000, the same for all process options apart from incineration, which was costed based on discussions with incinerator operators.

⁷³ OEE is the product of capacity utilisation, quality rate and operating time. To achieve 80% OEE a plant could operate at 93% of rated capacity, produce on-spec material for 93% of the time and run for 93% of the available operating hours each year ($93\% \times 93\% \times 93\% = 80\%$). Alternatively it could run at 100% of rated capacity, produce 100% on-spec product and run for 80% of the available operating hours and achieve the same OEE ($100\% \times 100\% \times 80\% = 80\%$)

15. Short-listed process options

As a result of the lab trials the following process options were considered for process design followed by commercial and environmental evaluation:

- Creasolv
- Ionic liquid extraction
- Centrevap
- Antisolv
- RGS90 Stigsnaes
- Incineration with energy recovery

Outline process designs and business models were prepared for each option.

The detailed analysis results for the Ionic liquid extraction, Antisolv and RGS90 Stigsnaes options are presented in Appendix 3. These options were not pursued further in Phase 3 of the project because the initial commercial and environmental evaluations during Phase 2 indicated that they would be unlikely to be commercially viable in the UK context.

15.1. Comparison of process options

The commercial and environmental evaluations of the 6 most promising process options are summarised below.

The table shows the results estimated in Phase 2 for the Ionic Liquid, Antisolv and RGS90 process options while the figures shown for the Creasolv, Centrevap and Incineration with energy recovery options are the revised results estimated during Phase 3 of the project.

Process	Yield of usable polymer from feed	Capital cost	Solvent cost	Utility & waste treatment cost	Gate fee charged	Net product revenue	Final polymer selling price	Operating profit/ (loss) at full output	Project IRR
		£m	£/te feed	£/te feed	£/te feed	£/te feed	£/te finished polymer	£/te feed	
Creasolv	77%	11.8	12.5	67	45	479	560	226	negative
Ionic Liquid	76%	5.4	210	171	45	473	560	58	negative
Centrevap	81%	6.1	6	62	-100	357	560	191	16%
Antisolv	77%	9.3	87	108	45	479	560	106	negative
RGS90	nil	-	-	-	95	-	-	-	-
Incineration with energy recovery	nil	-	-	-	210	-	-	-	-

The gate fee shown for the Centrevap process option is -£100/te because this process will not remove brominated flame retardants. It will therefore only be useful for producing high grade recyclate from WEEE polymers which are already BFR-free. The process operator will have to pay a positive price of around £100/te for this feed material.

Note that the capital cost estimates for the Ionic Liquid and Antisolv process options were not re-estimated in Phase 3. Based on the lessons learned during more detailed design for Creasolv and Centrevap in Phase 3 it is likely that the true capital costs will be roughly double the costs shown in this table.

Project internal rates of return (IRR) were not estimated for the RGS90 feedstock recycling process or the option of incineration with energy recovery because these are both existing commercial processes where the process operators were not prepared to divulge their internal operating costs. In these two cases we worked with the process operators to estimate what their gate fee would have to be for BFR-containing WEEE polymers if they were to achieve the same rate of return that they would obtain when processing their normal feed material.

In the case of the RGS90 option the gate fee was lower than for its normal feed material (PVC) due to the higher hydrocarbon content of WEEE polymers.

In the case of incineration with energy recovery the gate fee was considerably higher than for the normal feed of municipal solid waste (MSW). The base gate fee assumed for MSW entering an incinerator was £45/te – to compete with landfill. The reasons why the gate fee required to treat BFR-containing WEEE polymers in the UK is higher than for MSW are explained in section 19.3.

15.2. Analysis

The commercial and technical analysis that was conducted at the end of Phase 2 highlighted Creasolv and Centrevap as the two most promising process options.

Creasolv demonstrated good levels of BFR extraction in practical trials during phase two of the project. It had potential to achieve the proposed RoHS limit of 0.1% for Deca BDE content and the 'Penta Directive' requirement of 0.1% for Octa BDE with further process development.

The business model for Creasolv based on these initial results demonstrated potential for attractive commercial returns at a gate fee of £45/te for the feed material.

At present this gate fee is not achievable in the UK for size-reduced WEEE polymers. Exporters to China are currently paying £50-150/te for WEEE polymers containing BFRs. However if the WEEE Directive is fully implemented in the UK and separate treatment of BFR-containing polymers is mandated in accordance with Annex 2 of the directive then the export route may be closed off and this material should attract a gate fee in competition with landfill.

The Centrevap process will not remove BFRs which are partly or fully soluble in solvents such as toluene, ethyl acetate, DMF, THF and dichloromethane. These include many of the target flame retardants for this project, including penta, octa and deca BDE. However the process has potential to remove many other insoluble additives and impurities efficiently and at relatively low cost.

Details of the process designs and commercial analyses of the Ionic Liquid, Antisolv and RGS90 process options are attached at Appendix 3. These processes are not presented in detail in this main report because the business modelling and environmental assessment work during Phase 2 indicated that they would not be competitive with the Creasolv, Centrevap or Incineration with energy recovery disposal options.

Details of the development work during Phases 2 and 3 of the Creasolv and Centrevap processes are attached at Appendix 4.

Results of the large scale trials and the final process designs for the Creasolv and Centrevap processes are presented in Sections 16 and 17 below.

Section 18 presents an analysis of the option of disposing BFR-containing WEEE polymers in UK waste incinerators with energy recovery.

Section 21 compares the environmental performance of the process options and Section 22 compares the commercial performance of the optimised Creasolv and Centrevap process designs with the alternatives of incineration with energy recovery and landfill.

16. Creasolv process trials

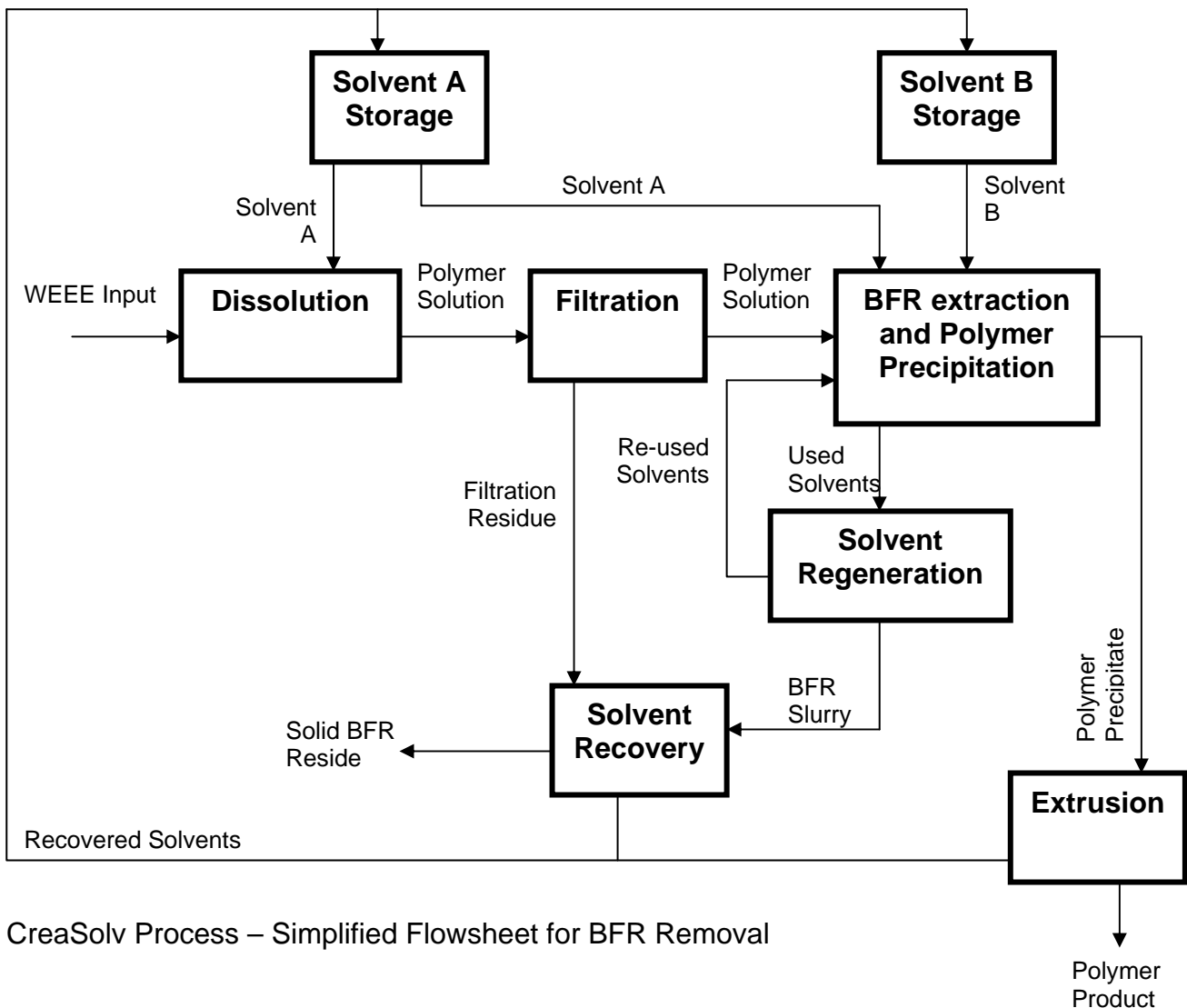
16.1. Creasolv process background

Dr Andreas Maeurer and his team at Fraunhofer IVV in Freising have spent several years developing this solvent separation process for WEEE polymers. The basic process concept is patented and there is a related company which plans to market the proprietary 'Creasolv' solvent mixture as a consumable.

A pilot facility is available at Freising for the dissolution, filtration, BFR-extraction and polymer-precipitation parts of the process while other aspects (solvent cycling, polymer drying and compounding) have been tested at other facilities in Europe.

In the course of this project the Creasolv process extraction sequence has been enhanced further with input from Axion and other partners in the project. As a result WRAP and Fraunhofer Group have agreed to share the IP that they have jointly developed and to make available the full patent and knowhow package for license in the UK and elsewhere.

16.2. Flowsheet



Creasolv Process – Simplified Flowsheet for BFR Removal

16.3. Process description

The Creasolv Process is a batch process which uses a high boiling point solvent to dissolve the feed plastic. A series of precipitation steps follow using a combination of proprietary Creasolv solvents. These reduce the bromine content in the polymer to less than 0.1%.

The BFRs are extracted into the solvents and the solvents are recovered by a proprietary process.

The main steps in the process are dissolution, filtration, a series of extractions and extrusion of the final product.

Input feed material

The input feed material to the plant consists of shredded plastic waste of approximate size between 30-50 mm. The plastic waste should be pre-sorted so that it is primarily BFR-containing HIPS and ABS.

Dissolution

Regenerated Creasolv solvent from previous batches is stored under ambient conditions in carbon steel storage tanks ready for use in the dissolution process.

A jacketed-dissolution vessel is filled with Creasolv solvent and heated via the heating jacket. The polymer is added.

At elevated temperature, the polymer and BFRs are both soluble in the hot Creasolv.

Filtration

Any undissolved polymers and other insoluble impurities are removed by filtration. A pump draws from the dissolution vessels to feed the filters. The filters are self-cleaning and will discharge the collected solids intermittently for treatment in the solvent recovery unit. The filtrate contains the dissolved polymer and all other soluble additives, while the filter residue contains the undissolved polymer, insoluble additives and inerts such as paper, fluff and metals.

BFR extraction and polymer precipitation

The filtered solution from the dissolution vessel is pumped into a solvent extraction unit. A second proprietary Creasolv solvent is added. This causes the polymer and the BFRs to separate.

The bulk of the excess solvent is removed from the debrominated polymer in a series of special extraction units. The recovered solvent mixture is pumped to store tanks and then passed to a special solvent regeneration unit.

Solvent regeneration

A novel solvent regeneration process has been developed as a result of the collaboration between WRAP and Fraunhofer IVV. This process separates the BFRs from the two Creasolv extract solvents and separates the solvents from each other ready for re-use. The detail of this part of the process is confidential to Fraunhofer IVV and WRAP.

BFRs are recovered by the solvent regeneration unit as a concentrated bromine-rich slurry. This slurry is passed to the final solvent recovery unit along with the filter residues from the first stage of the process.

Extrusion

The polymer gel particles from the extraction/ precipitation step are passed to a vacuum vented twin screw or ring extruder for removal of the remaining solvent down to below 1%. 1% is the limit required to allow subsequent processing of the polymer by injection moulders. The polymer product is cooled in a water bath and pelletized.

Additives and masterbatch can be added at this stage to modify the final polymer properties if required.

The solvents removed by venting during extrusion are returned to the solvent regeneration unit for recovery

Final solvent recovery unit

The Solvent Recovery Unit receives slurries from the filters and the solvent regeneration unit. It processes these slurries separately batch-wise and recovers almost all the solvents by heating under vacuum, resulting in a dry, free-flowing bromine-rich inert residue which is safe for disposal to landfill or may be treated further to recover bromine and antimony.

The mixed solvents that are recovered by this unit are returned to the solvent regeneration process.

A representative of the bromine and antimony industries has indicated that they would be prepared to take back the bromine and antimony residues at zero cost for use as feedstock for new products if they were separated to an adequate level of purity.

If this could be arranged it would improve the process economics by removing the need for hazardous waste disposal of the solvent recovery residues and would also improve the environmental impact performance.

Fraunhofer IVV claims to have developed a method to separate the bromine and antimony components of the residue from the solvent recovery unit. The two fractions could then be recovered relatively straightforwardly by the bromine and antimony industries.

Axion has not yet been able to test the separated fractions produced by Fraunhofer IVV so the process evaluations presented in this report assume that bromine and antimony cannot be recovered for useful applications.

ENERGY USED

- Hot utility requirement (Low Pressure Steam- 5 bar): 4.7 te of steam/te feed
- Cold utility requirement (Cold Water): 60.5 te/te feed
- Power (Average Draw): 208 kWh/te feed

EFFLUENTS PRODUCED

Water Effluent

None

Vapour Effluent

The extruder producing the final polymer and the final solvent recovery unit will both generate small quantities of solvent emissions to atmosphere via the vacuum system. The great majority of these emissions can be controlled by a cold trap fitted on the input side of the vac pump, particularly as the Creasolv solvents have high boiling points. Any residual emissions from the vacuum pump can be eliminated by means of a biological filter if required.

Solids

BFR leaves the solvent regeneration process as a slurry in Creasolv solvent. The solvent is recovered and recycled from the slurry by the solvent recovery unit and discharged for landfill disposal as a dry free-flowing powder.

Solid residues are also produced from the primary filter as a slurry in Creasolv solvent. This residue is also treated in the solvent recovery unit. The filter residue solids are discharged from the solvent recovery unit as a dry cake for landfill disposal.

16.4. Technical scale trials conducted

The table below summarises the technical scale trials that were conducted by Axion and Fraunhofer IVV during Phase 3 in order to optimise and validate the process conditions for the Creasolv process.

Trial	Aim of Trial	Trials conducted	Results
Creasolv Process Trial	<p>To test the feasibility of the Creasolv BFR extraction and solvent regeneration processes and identify potential scale-up issues.</p> <p>To confirm the process at semi-commercial scale and iron-out any further scale up problems.</p>	<p>A series of six lab scale and six technical scale (10 kg) BFR extraction trials were carried out at the pilot facilities of Fraunhofer IVV in Freising, Germany during Autumn 2005.</p> <p>Process operating conditions and the process sequence were changed significantly in the course of the trials as problems were identified and systematically eliminated</p> <p>Two large scale pilot plant trials of about 150 kg polymer each (total process volume including solvents of about 1.5 m³ per batch) were conducted in late January and February 2006.</p>	<p>The optimised Creasolv process is now a robust and operable design. It has been shown to reduce the concentration of a wide range of brominated flame retardants in real mixed ABS and PS WEEE polymers close to the target set for this project (0.1%).</p> <p>Regenerated solvents were used in all of the technical scale trials. It was demonstrated that the process will work successfully with regenerated solvents.</p> <p>Volumes of solvents used, precipitation times, operating conditions, etc. were decided and confirmed resulting in a more repeatable process.</p> <p>Recycled solvents were used for the second large scale trial and also proven to be successful as the BFR content of the final product (0.12%) was close to the target set for the project (0.1%).</p> <p>Overall, the large scale trials have proven that it is a scalable process. With further optimization it should be possible to achieve reliably a final product bromine content below the target of 0.1%.</p>

Trial	Aim of Trial	Trials conducted	Results
Solvent Recovery System	To test if the solvent recovery system is able to recover solvent from the filter and BFR residues from the Creasolv process, and produce a dry residue, suitable for landfill.	A technical scale trial was conducted at Formeco SRL in Italy using filter residue and the solvent regeneration slurry from the 1 st large scale trial.	<p>The solvent recovery unit that was tested in these trials is a well-established, robust and relatively inexpensive batch system. This process requires addition of a high surface area powder to absorb residual polymer and produce a powdered final product.</p> <p>Both trials produced a dry residue suitable for landfill.</p> <p>The trials of solvent recovery for the Creasolv process used a proprietary food grade drying agent and gave good results.</p> <p>However, this material is expensive so in a production plant, it will be better to substitute a waste or lower cost material.</p> <p>We tried using waste powders in trials for the Centrevap process. These were not successful initially (see below) but we believe that with further optimization, a cost effective solution can be found.</p>
Extruder	To extrude the solvent-containing polymer gel from the Creasolv process to obtain dry polymer pellets.	<p>A novel low temperature extruder configuration that is capable of removing most of the residual solvent in the polymer gel without excessive heating was designed.</p> <p>A trial was conducted at PERA using a small Rondol twin screw extruder with products from the 5th and 6th technical scale trials.</p> <p>The standard Rondol twin-screw configuration was modified as a result of the initial tests. Further trials were conducted with the revised configuration.</p> <p>The same concept was tested in Germany on a larger ring extruder from Extricom using product from the two large scale Creasolv trials.</p>	<p>The twin screw extruder extraction system was tested successfully at PERA in a series of trials. The initial tests reduced solvent content to below 10%.</p> <p>The initial Extricom trials showed that the Ring extruder with multiple vacuum vents is capable of reducing solvent content in the bulk Creasolv products down to less than 5%.</p> <p>Further modifications to the ring extruder configuration were made and a second set of ring extruder trials at Extricom in July 2006 resulted in even better solvent recovery. Solvent content was reduced to below 0.5%. This should make the material processable in standard injection moulding machines.</p>

16.5. Large scale trial results

Creasolv Trial

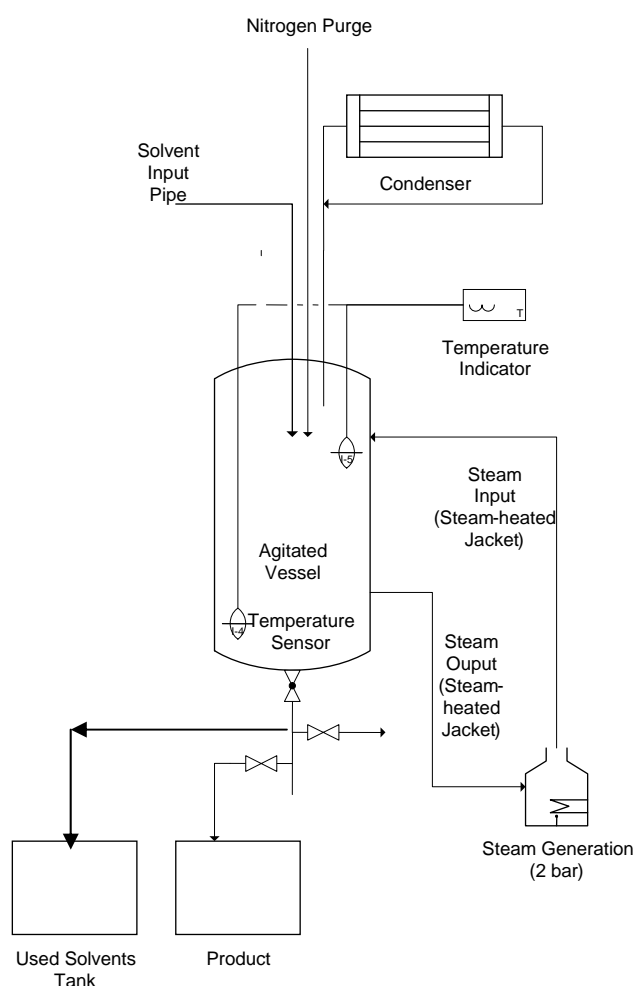
The two large scale Creasolv trials were carried out in the pilot plant facilities at Fraunhofer IVV, Freising, Germany. The aims of the large scale trials were:

- To show that the Creasolv process can be scaled up to 150 kg batch sizes.
- To prove the repeatability of the bromine extraction rates of the small scale trials in the large scale trials.
- To prove the consistency of the procedures in the process.

The two large scale trials are named Wrap Trial 1 (WT1) and Wrap Trial 2 (WT2) for easy identification.

Equipment configuration

The diagram below shows the equipment layout in the pilot plant.



Feed material

The input black waste polymers were derived from a TV-set dismantling line in Germany. They were shredded to particles of 20mm and subjected to a sink & float separation to enrich BFR containing polymers.

The picture below shows the input shredded polymer chips.



Trial summary

The dissolution and filtration of the polymer solution was carried out in 3 batches prior to the trial in the pilot plant. The picture below shows the technical scale plant, where the dissolution and filtration was carried out.



The photograph below shows the reactor at Fraunhofer IVV where the large scale trials were conducted:



The details of the intermediate precipitation and solvent regeneration steps are confidential.

The product from the final step of WT1 prior to final solvent removal is shown below. The size distribution of the particles varies significantly.



The particle size distribution was improved significantly in the final large scale trial by Fraunhofer IVV (WT3) as a result of a further confidential process change.

Results

The table below shows the amount of bromine that was left in the polymer compared to the initial amount of bromine in the polymer and the percentage removal of bromine. All results are corrected for solvent content to convert to dry polymer basis.

The dry mass values have been calculated from the X-Ray Fluorescence Spectroscopy analytical results provided by Fraunhofer IVV for the bromine and antimony concentrations that have been removed and the solvent content measured for the polymer at each process step.

	Bromine content WT1	Antimony content WT1	Bromine content WT2	Antimony content WT2
WEEE Input	8.81%	4.44%	6.99%	2.83%
Product	0.04%	2.20%	0.12%	2.29%
% Reduction	99.5%	50.5%	98.3%	19.08%

In both trials, there is a more than 98% removal of bromine from the polymer and although only the product from WT1 meets the specification of less than 0.1%, the product from WT2 is only off-specification by about 0.02%.

There was a reduction in antimony content in both trials, with a greater reduction of 50% in WT1, as compared to only 20% in WT2. This is likely to be because there was a higher starting concentration of antimony in WT1 as compared to WT2.

Types of BFR Removed

The product from trial WT1 was analysed in more detail to investigate the effectiveness of the Creasolv process in removing the various types of BFRs, namely Octa BDE, DecaBDE, TBBPA and TBPE. Samples from the products were tested by Fraunhofer IVV using gas chromatography.

The table below shows the concentrations of the various types of BFRs measured in the feed polymer and the product from trial WT1:

Flame retardant type	OctaBDE	DecaBDe	TBBPA	TBPE
Average concentration in polymer feed	3.36%	0.77%	2.43%	0.49%
Average concentration in Creasolv product	0.0092%	0.0089%	0.0037%	0.0008%
% Removal	99.7%	98.8%	99.8%	99.8%

The table below shows the concentrations of the various types of BFRs measured in the filtered polymer solution and product from trial WT2:

Flame retardant type	OctaBDE	DecaBDe	TBBPA	TBPE
Average concentration in polymer feed	3.27%	1.36%	6.09%	0.47%
Average concentration in Creasolv product	0.0199%	0.0182%	0.143%	0.0018%
% Removal	99.4%	98.7%	97.6%	99.6%

All the values above have been corrected for estimated dry polymer content.

Conclusions for the Creasolv trial

The large scale trials WT1 and WT2 have proven that the process can indeed be scaled up to a much larger scale. The analytical results have supported this by showing that the bromine contents in the final products are close to or within the target of 0.1%, and thus demonstrate very good and repeatable extraction rates at close to production scale.

Following the WRAP-funded trials Fraunhofer IVV conducted a further large scale trial on their own.

Further optimization of the process in terms of agitation, etc will allow for improved bromine extraction rates and enable the target bromine concentration to be met reliably.

After the second large scale trial WT2, Fraunhofer IVV proceeded to conduct a third large scale Creasolv trial. This trial achieved similar results to trials WT1 and WT2. Further improvements to simplify the process sequence were made which resulted in slightly lower capital and operating costs.

Solvent recovery trials

The solvent recovery unit uses a simple batch evaporation process to recover the remaining solvent from the filter and solvent regeneration unit residues. In this case, the solvents to be recovered are the Creasolv solvents and the contaminants are the extracted BFRs, antimony trioxide, inerts from the initial filtration and any undissolved polymers. The solvent is vapourised by hot oil in the heating jacket surrounding the vessel. The vapours are then conveyed to a condenser to be cooled by cooling water. The condensed solvent is collected in a tank for its reuse.

The solvent recovery vessel is equipped with a rotating blade which keeps the contents to be treated constantly in movement allowing maximum extraction of the solvent, concentration of the residues and avoids the residues sticking to the boiler's walls and bottom.

The picture below on the left shows the solvent recovery unit, while the picture on the right shows the interior of the solvent recovery vessel.



Source: Solutex- Solvent Recycling Units, Industrial Series Brochure

Two laboratory solvent recovery trials were carried out on 8 March 2006:

1. to establish that the solvent recovery unit was able to recover the solvent from the filter residue and produce a dry residue, suitable for landfill.
2. to establish that the solvent recovery unit was able to recover the solvent from the solvent regeneration slurry and produce a dry residue, suitable for landfill.

The main difference in the two trials was the feed material. The drying agent used in both trials remained the same- Tix-dry (a high surface area silica powder used in the food and pharmaceutical industries). This material had been proven to work successfully in previous trials. Tix-dry is however rather expensive at around £2-3 per kg.

Feed materials

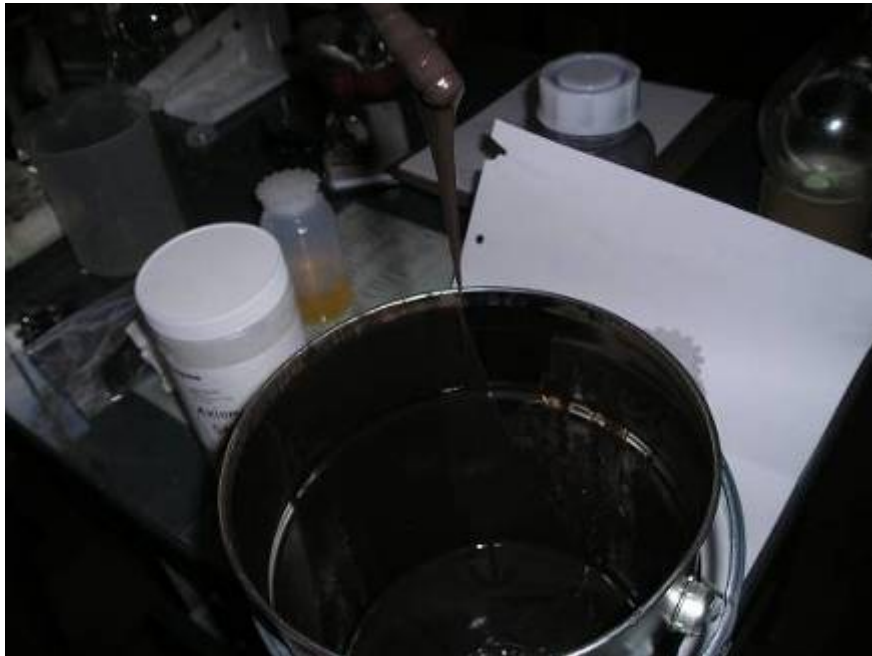
The first trial used the filter residue from the 1st large scale Creasolv trial (WT1). This contained styrenic WEEE polymers dissolved in Creasolv Solvents, together with any undissolved polymers (such as ABS), insoluble additives and inerts such as paper, fluff and metals. The filter residue infeed had a solvent concentration of 44%.

The picture below shows the filter residue feed before the solvent recovery process:



The second trial used the solvent regeneration slurry also from the 1st large scale Creasolv trial (WT1). This contained WEEE polymer dissolved in Creasolv Solvents and a high concentration of BFRs. The solvent regeneration slurry had an infeed solvent concentration of 53%.

The picture below shows the solvent regeneration residue before the solvent recovery process.



Equipment configuration

The 2-litre test evaporator consists of a jacketed vessel with PLC-controlled hot oil heater and an agitator that scrapes the base and sides. Up to 750mmHg vacuum (12-15mbar absolute pressure) can be applied by means of a vacuum pump. The evaporator has a glass top so that the material can be observed during evaporation and there is a water cooled condenser to capture the solvent. The evaporator can be tipped to discharge the product after evaporation. Apart from the glass top, this is a copy of the configuration of their full scale machines.

The picture below on the right shows the test apparatus, while the picture on the left shows the scraper inside the vessel.



Trial results

Trial summary for trial 1:

280g of the filter residue and 24g (7.8%) of Tix-dry drying agent was added into the vessel. The distillation took place under a 12 mbar vacuum and a hot-oil temperature of 200C. The distillation lasted for 2.58 hours, including 1 hour to remove the final residual solvent.

36g of solvent was collected as distillate. 190g of solids was obtained. The solvent concentration of the solids residue from the solvent recovery unit was 9%. This was obtained by a weight-loss experiment. The solids residue was dry and had particles as large as 30 mm. The picture below shows the solids residue and the solvent recovered (distillate) from the solvent recovery unit.



Trial summary for trial 2:

260g of the filter residue and 18g (6.5%) of Tix-dry drying agent was added into the vessel. The distillation took place under a 12 mbar vacuum and a hot-oil temperature of 200C. The distillation lasted for 2.25 hours, including 1 hour to remove the final residual solvent.

86g of solvent was collected as distillate. 132g of solids was obtained. The solvent concentration of the solids residue from the solvent recovery unit was 18%. This was obtained by a weight-loss experiment. The solids residue was dry and had particles as large as 30 mm. The picture below shows the solids residue and the solvent recovered (distillate) from the solvent recovery unit.



Conclusions for the solvent recovery trial

The solid residues from both solvent recovery trials had rather large particles as can be seen in the pictures above, instead of the crumbly powder obtained for the Centrevap trials. This is probably because of the high temperatures used in the solvent recovery process, which caused the polymer in the solution to melt and form a sticky mess, thus making it unable to reach a crumbly stage.

It can also be observed that the recovered solvents are slightly yellowish in colour. This is attributed to the high temperature at which the solvent recovery was performed, and thus might have resulted in the degradation of the polymer. Thus, the by-products of the degradation might have ended up in the recovered solvents.

The higher boiling point of the Creasolv solvents means that a production scale solvent recovery unit will need to be designed for operation at a higher vacuum (lower absolute pressure) than was used in these trials in order to lower the process temperature required.

The Solvent Recovery Unit is a standard piece of equipment used to recover solvents for re-use. It has been proven in the two trials that using an appropriate drying agent, it is able to recover the solvents and produce a dry residue from the filter residue and distillation slurry for the Creasolv process, and from the centrifuge residue for the Centrevap process.

An area which requires further investigation would be to identify a lower cost drying agent than Tix-dry, preferably a waste material. Suggestions for such a drying agent include saw dust, spent activated carbon or cat litter.

With the appropriate operating conditions and suitably effective drying agent, a final dry crumbly residue will be obtained, and the final solvent content in the residue can be significantly reduced.

Separation of bromine and antimony in the residues for feedstock recycling

Both BFRs and antimony trioxide are found in the residues from the solvent recovery system. Fraunhofer IVV has developed a low cost recovery technique which leaves a bromine-rich fraction containing only 20ppm of antimony trioxide (plus drying powder and a small amount of residual polymer) and a second antimony-rich fraction with much reduced bromine content and which contains further drying powder, some residual polymer and the other impurities that were present in the input polymer.

Mixed bromine and antimony residues cannot be recovered so these separated residue fractions will be attractive to the bromine and antimony industries for material recovery and should avoid the need for landfill of the process residues.

However, for prudence, the financial projections presented in this report and also the environmental impact assessments assume that the bromine and antimony residues must be landfilled.

Extrusion Trial- Extricom Ring Extruder

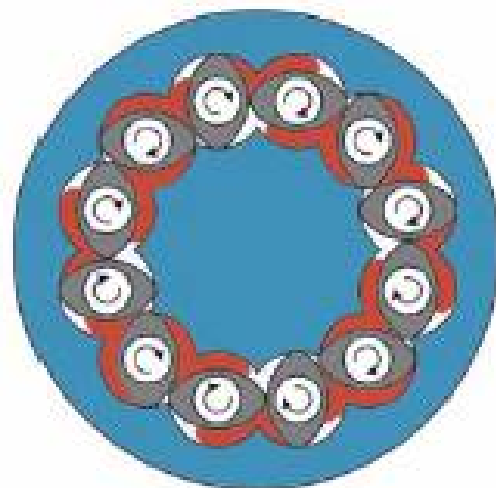
The Ring extruder⁷⁴ has twelve small screws arranged in a circle, each screw meshing with two neighbours. This gives high output from a relatively short extruder compared to a conventional twin screw. Two or three sets of three or four vacuum vents can be arranged along and around the Ring extruder, giving considerable scope for vacuum venting to remove volatiles.

The picture below shows an Extricom ring extruder.



The 12 screw shafts in the ring extruder are orientated in a ring and each screw revolves around its own axis. The outer barrel and the stationary inner core enclose the screws with a tight gap. Transport of materials takes place in around the stationary inner core and around each screw.

The picture below on the left shows the 12 screws arranged in the barrel, while the picture on the right shows the rotation direction of the screw and the material spaces.



The extrusion trials were conducted at Extricom (Laufen, Germany) on March 14th and July 18th 2006.

⁷⁴ www.extricom.de/download/ringextruder.pdf

Feed material

In the first set of trials at Extricom's test facility in Laufen the materials fed to the extruder were as follows:-

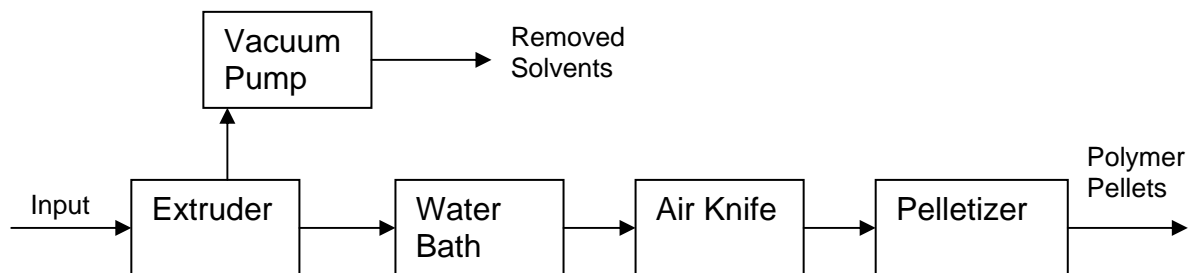
- 90 Kg of polymer particles from the 1st large scale Creasolv trial (WT1), with about 40% solvent concentration.
- 120 Kg of polymer particles from the 2nd large scale Creasolv trial (WT2).

Equipment configuration

The following equipment was used during the trial:-

- Extricom RE3 Ring extruder
- Vacuum Pump
- Water bath
- Air knife
- Pelletizer

The extrusion trials had the following layout.

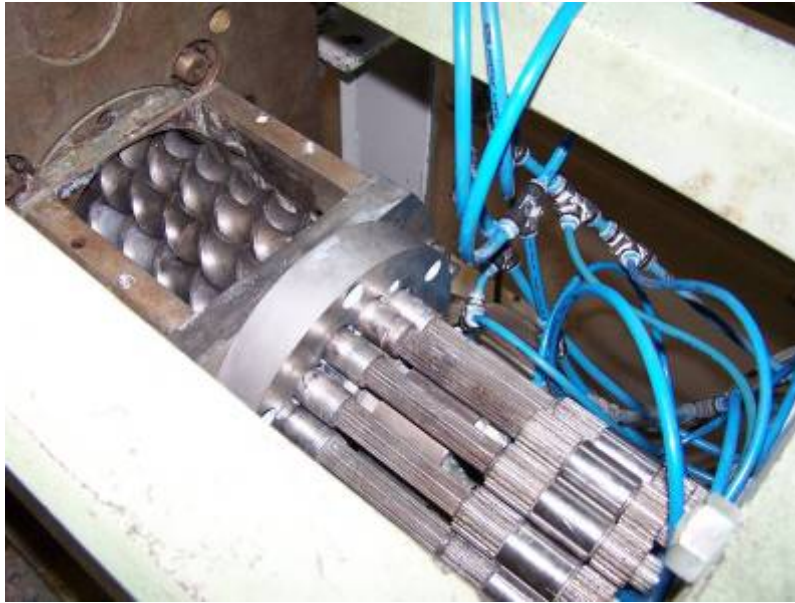


The input is fed into the extruder and is heated up. As it passes the vacuum ports, the high temperature, together with the vacuum evaporates any solvent in the pellets. The melted polymer then exits the extruder through a die-plate in strands. The strands are cooled in a water bath. Thereafter, the strands pass through an air-knife which blows off any water on the strands, before being cut into pellets in the pelletizer.

The picture on the right below shows the complete equipment set-up.



The picture below shows the interior of the ring extruder barrel.



Results of first set of extrusion trials at Extricom

A weight-loss test was conducted at Fraunhofer IVV on the ring-extruded pellets from the WT1 trial product. The samples were finely ground and then left in an oven for several hours. The test indicated that the ring extruder achieved an 87.5% reduction in solvent content from 40% to below 5%.

The second set of trials were also conducted at Extricom's test facility at Laufen:

The sample material available was combined into 4 homogeneous samples:

Purge - 75Kg Extruded, but not pelletised, material from the 17th March trial (mixed output of trials WT1 and WT2)
Granulate - 100Kg Pelletised material from 17th March trial (originally mixed product from bulk trials WT1 and WT2)
WT1/2 - 100Kg Precipitated polymer from bulk trials WT1 and WT2 (mixed product from both trials)
WT3 - 100Kg Precipitated polymer from bulk trial WT3

A series of trials were conducted over two days on the four feed samples in order to optimise the extruder conditions and to establish how many passes were required on the Extricom trial unit in order to achieve the target solvent concentration

The key findings of the second set of trials were:

- The specification of <1% was achieved after 3 passes through the trial extruder using a sample from WT3 with a starting solvent concentration of 22%
- The minimum solvent concentration achieved was <0.5%
- The maximum solvent extraction achieved was 25% in a single pass.
- The rate of solvent extraction falls rapidly with solvent concentration
- The rate of solvent extraction was nearly identical for throughputs between 25 and 100 kg/h

Conclusions for the extrusion trials

These trials have demonstrated that the ring extruder with multiple vacuum vents is capable of extraction of a large amount of the solvent from Creasolv materials and can reduce solvent content to below 1%

Further modifications to the extruder and vacuum system configuration should improve solvent recovery further and allow reduction to well below 1% solvent content in a single pass.

Analysis of the results of the ring extruder trials indicated that it should also be possible to achieve the same solvent reduction in a large twin screw unit.

One other option which was not tested in this project is the possibility of using a devolatiliser combined with an extruder to remove the residual solvent. This technique is commonly used for removal of water from recycled PET. The best known equipment for this application is the 'Vacurema' unit from Erema in Austria⁷⁵.

Erema was consulted during the project to see if they would be able to assist with trials but they declined because their test facility was not available or rated for explosion-proof operations. However Erema have recently expressed interest in developing solvent-based recycling applications for their equipment. It would be interesting to test the Vacurema unit for final solvent removal in future. It has undergone a lot of development for water removal so this experience is likely to be beneficial for solvent extraction.

⁷⁵ www.erima.at

16.6. Mass balance

A full scale mass balance has been prepared for the Creasolv process at a throughput of 10,000te/yr WEEE polymer. This mass balance is based on the experimental results measured in the technical and large scale trials. The detailed results are confidential but the mass balance may be summarised as follows:

Stream No.	INPUT (te/yr)			OUTPUT (te/yr)	
	WEEE polymer Input	Make-Up Solvents	Drying Agent	Polymer product	Residue to Landfill
Polymer	7,920			7,656	264
BFR	1,000			4	996
Antimony	80			3	77
Inerts	1,000			0	1,000
Solvents		143		38	105
Drying Agent		0	486	0	486
Total	10,000	143	486	7,701	2,928

Total Input: 10,629 te/yr

Total Output: 10,629 te/yr

Part of the solvent that is consumed will be lost in the residue that is disposed to landfill and part will be present at less than 1% in the final polymer product. At this level it is not expected that the solvent will have any detrimental effect on product quality or moulding performance for the injection moulding and extrusion applications targeted by this process. The residual solvent in the product is non-toxic and relatively involatile.

Note that as stated in Section 14 above, the 10,000te/yr feed to the process represents the separated BFR-containing polymers from around 100,000te/yr of WEEE plastic or 400,000te/yr of collected WEEE items because about 25% of WEEE is polymer and about 10% of WEEE polymers contain BFRs.

16.7. Business Model

Creasolv process business model

£'000	Year 1	Year 2	Year 3	Year 4	Year 5
Profit and Loss					
Sales Value	0	1,721	3,689	4,918	4,918
Operating costs	-770	-2,534	-2,534	-2,534	-2,534
EBITDA	-770	-812	1,155	2,385	2,385
Interest	-192	-381	-325	-196	-101
Depreciation	-297	-1,187	-1,187	-1,187	-1,187
Pre-tax profit	-1,259	-2,380	-1,925	1,002	1,097
Taxation (estimate)	0	0	0	-301	-329
Net profit	-1,259	-2,380	-357	701	768
Operating Cash Flow					
Revenues (inc VAT)	0	2,023	4,334	5,779	5,779
Construction costs (inc VAT)	-6,973	-6,973	0	0	0
Operating costs (inc VAT)	-905	-2,977	-2,977	-2,977	-2,977
Debt Service	-498	-1,911	-2,013	-1,949	-1,132
VAT (paid)/recovered	1,132	1,219	-116	-396	-417
Corporation tax (approx)	0	0	0	0	-301
Dividends paid	0	0	0	0	-421
Surplus	-7,244	-8,619	-772	457	531
Balance sheet					
Fixed assets	5,638	10,385	9,198	8,011	6,824
Current assets	3,691	1,005	234	691	1,223
Current liabilities	3,213	5,282	3,680	2,670	1,707
Net assets	6,115	6,108	5,752	6,032	6,340
Equity	7,374	9,747	9,747	9,747	9,747
P&L account	-1,259	-3,639	-3,996	-3,715	-3,408
	6,115	6,108	5,752	6,032	6,340

Capital cost of the plant is estimated to be £11.8 million on a serviced UK site. It is estimated that a further £5 million of funding will be required for working capital.

The process is projected to be just profitable assuming a gate fee for the feed material of £45/te and revenue for the product of 60% of virgin polymer (average £560/te). However at this polymer price the overall project IRR is projected to be just negative. This is the scenario presented above.

With a product price of 80% of virgin polymer the business is projected to be an attractive and profitable investment with an overall project IRR of 19%.

16.8. Discussion

The Creasolv process uses an elegant combination of proprietary solvents which removes brominated flame retardants effectively from HIPS and ABS.

As a result of design and scale-up work with Axion and other members of the WRAP project team it has been modified so that it achieves an excellent reduction in BFR content. Technical and large scale trials reliably achieved or nearly achieved the target final BFR concentration set for this project (less than 0.1% total). The process removed all BFR types found in the chosen WEEE polymer samples including TBBPA and OctaBDE.

A solvent regeneration and recovery system has been designed and tested which should cut solvent losses from the process to commercially and environmentally acceptable levels.

The assumption in the financial projections presented in this report is that the final recycled product will sell at around 60% of virgin polymer price (average £560/te). This is higher than the average price used in the models presented in the second interim report for this project (47% of virgin).

It was decided to increase the assumed selling price because market intelligence gathered in the course of the project by Axion has demonstrated that there is growing unmet demand from manufacturers of electrical equipment for high grade recycled polymers. Demand is growing because manufacturers want to diversify their sources of polymer supply, reduce costs and also include recycled content for marketing reasons. Several manufacturers have indicated informally that they would be prepared to pay up to 80% of virgin price (£750/te) for high grade recycle.

The business model indicates that, using Axion's assumptions, the process should be commercially viable in the UK at 10,000te/year throughput with a gate fee for the segregated and size-reduced input material of £45/te.

At present in the UK this type of BFR-containing material is being exported to the Far East for mechanical recycling and is attracting positive prices up to £100/te, depending on quality.

If the regulatory environment changes and either the Chinese or European authorities refuse to allow direct re-use of BFR-containing polymers then the Creasolv process would become competitive as the alternative disposal routes would be incineration with energy recovery or landfill. Both of these disposal routes would attract minimum gate fees of at least £45/te in the UK.

If there is positive demand for halogen-free recycle from equipment manufacturers and the price for high quality recycled polymer rises to around 80% of virgin polymer price then the Creasolv process would be an attractive investment although it would still need to attract a gate fee of £45/te for the input material.

Tests by Fraunhofer IVV indicate that it will be possible to separate the residues from the process into a bromine containing fraction and an antimony containing fraction by means of a relatively inexpensive process change. This should make the residues attractive for recycling to feedstock by the bromine and antimony industries. This would reduce operating costs by eliminating landfill costs for the residues and also further improve the environmental impact of the Creasolv process option.

Some technical concerns remain:

The process uses relative simple and well-tried technology but the process sequence is quite complex with several variables to control. Before investment in a full scale plant further trials will be required to prove that the process can be controlled effectively and deliver consistent output material composition.

The final solvent recovery step using a twin screw or ring extruder is novel and has been tested in three trials. In these trials solvent content of the polymer has been reduced to below 0.5%, but only with 3 passes through the trial extruder. Indications from the first three trial sessions are that it should be possible to optimise the extruder configuration so that 0.5% final solvent concentration can be achieved in a single pass but this is still to be proven in practice. Further process development will be required to demonstrate this.

17. Centrevap process trials

17.1. Centrevap process background

The Centrevap process design was developed in the course of this project as a result of discussions between Axion and other project participants and observation of the results of other process trials conducted for the project. Similar process ideas have been patented previously in the US and Germany but differ in detail to the concept proposed here⁷⁶⁷⁷⁷⁸

17.2. Basis for the process design

It was observed that there is a difference in solubility between WEEE polymers and the additives they contain and that this could be exploited to remove the insoluble additives.

Several different solvents can be used to dissolve the styrenic polymers found in WEEE. A summary of the solubilities of the polymers and BFRs most often found in WEEE is presented in the second interim report for this project.

Unfortunately Penta BDE is completely soluble in all of these solvents and the other BFRs likely to be found in styrenic WEEE polymers are partly soluble.

Trials in the course of Phase 3 of this project have also demonstrated that the BFRs commonly found in WEEE polymers are partial soluble in the solvent used for this trial at the temperatures and concentrations that are required for practical process operation. This means that the Centrevap process is not a viable option for removal of BFRs from WEEE polymers down to the level targeted by this project

However the process should still have commercial potential as a method for separating any impurities and additives such as antimony trioxide, fillers and some pigments and stabilisers which are not soluble in the types of solvent which will dissolve styrenic polymers. These solvents include toluene, xylene, styrene, THF and dichloromethane for styrenic polymers and methyl ethyl ketone or tetra hydro furan for PVC.

All trials conducted for this project to date have used toluene as the solvent and HIPS as the target polymer.

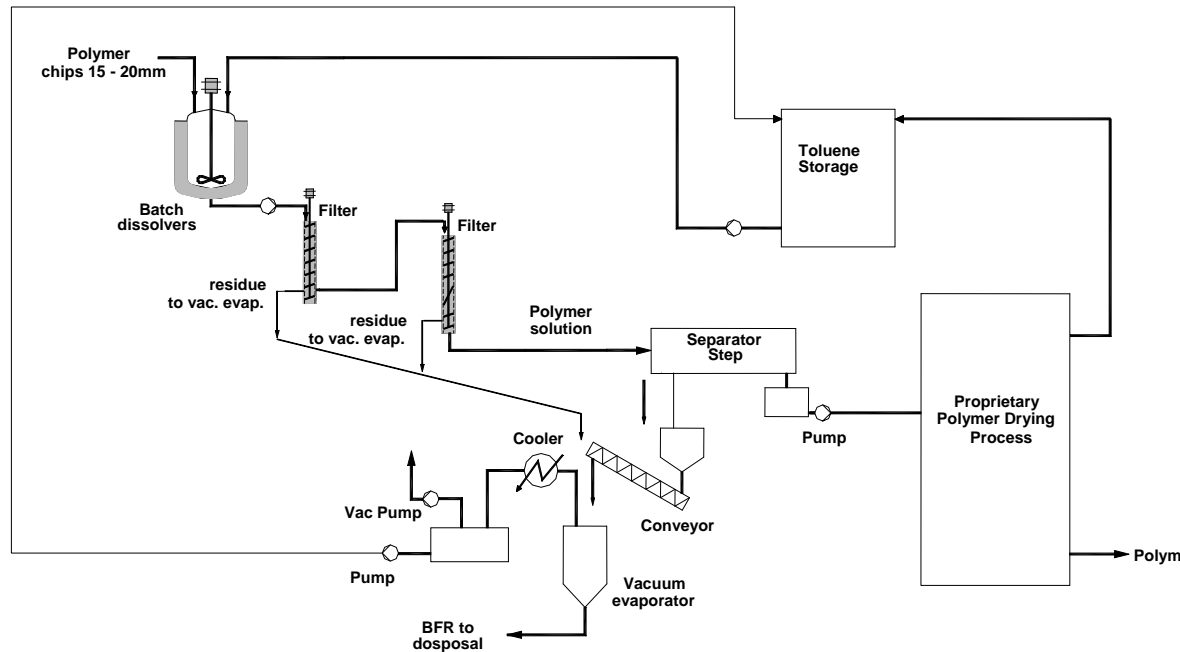
⁷⁶ US Patent 5,824,709, Oct 1998, 'Method for recycling waste plastic material containing styrene polymer', Motoshi Suka

⁷⁷ German patent DE 4319180, August 1993, 'Method for recycling products made of polystyrene', BASF

⁷⁸ German patent DE 4119303, June 1991. 'Process to break down bulky composite plastic waste, particularly those containing chlorinated hydrocarbons', Rolf Germerdonk

17.3. Flowsheet

The Centrevap process flowsheet is as shown below.



17.4. Process description

In the version of the process modelled for this project toluene is used to dissolve the polymer. A bulk supply of the selected solvent is stored under ambient conditions in a carbon steel storage tank.

The tank also receives recovered solvent from the process. It is assumed that the solvent will be delivered in bulk tankers and sufficient capacity will be provided to off load 22,000 litres of solvent whilst still maintaining production.

Ground, segregated plastic waste is dissolved in toluene alternately in two batch agitated dissolving vessels in order to provide a continuous feed to the rest of the plant. Toluene is pumped into the dissolution vessel and heated to a temperature of 50°C. Thereafter, the plastic waste is added and the dissolution process is carried out at 65°C.

The suspension formed in the dissolution tanks is pumped through a rotary brush filter to a decanter centrifuge, followed by a disk-stack centrifuge.

The filter removes large particles greater than 1 mm in size in order to protect the centrifuges.

The centrifuges remove undissolved solids of decreasing particle size. The decanter removes most particles in the range 1mm to 50 micron and the disk-stack centrifuge removes remaining particles down to 0.3 micron.

The particles removed by the filters and centrifuges will include all un-dissolved plastics, metals and fillers from the dissolved polymer plus any un-dissolved brominated flame retardants and antimony trioxide.

The centrifuge and filter residues are collected as a sticky but pumpable slurry. They are discharged to an agitated holding tank from which they are pumped batchwise to the solvent recovery unit.

The solvent recovery unit is a steam-heated scraped surface heat transfer unit. It operates under vacuum and recovers the toluene from the slurry, leaving the BFR and fillers as a dry residue.

A high surface area powder such as spent activated carbon is added with the solvent recovery feed in order to 'soak up' residual polymer which would and a free-flowing solid residue is dropped into drums for off site disposal.

The liquid centrate leaving the disk stack centrifuge is discharged to a surge tank.

The centrate is then pumped to an evaporator system where the solvent is pumped to high pressure and heated then evaporated in a flash drum, followed by a wiped film evaporator where more solvent is removed.

In the wiped film evaporator the polymer is concentrated solvent and becomes a melt. The vaporised toluene is condensed and returned to the toluene storage tank for reuse.

The melt is discharged from the base of the evaporator and pumped by a high pressure gear pump direct as a melt into a vented extruder which recovers and recycles more solvent and produces a pelletised polymer product with less than 1% solvent content.

Total residence time through the whole process from after the primary filter to polymer pellet is of the order of 10-15 minutes. This minimises the potential for polymer degradation.

ENERGY USED

- Hot utility requirement (Low Pressure Steam- 5 bar): 0.947 te of steam/te feed
- Cold utility requirement (Cold Water): 23 te/te feed
- Power (Average Draw): 579 kWh/te feed

EFFLUENTS PRODUCED

Water Effluent

None

Vapour Effluent

The evaporator will be fitted with a condenser, but some solvent will slip to atmosphere past the cold trap on the vacuum pump. A final clean up of this stream using activated carbon or a biological filter may be necessary to meet emission limits when detailed design is carried out.

BFR is discharged from the process in slurry in toluene. The toluene is recovered and recycled from the slurry yet there may be a very small amount of VOC emission when dropping the dried BFR and fillers into drums for disposal.

Solids

Solid wastes comprising insoluble additives plus the high surface area powder used to assist the solvent recovery process are produced at the solvent recovery unit step. The residue will be discharged as a free-flowing dry solid and sent for disposal to landfill.

17.5. Technical scale trials conducted

Several technical scale trials and large scale trials have been carried out over the period of the project to fully explore the various process possibilities and test all the equipment involved in the plant design.

Both pressure leaf precoat filtration and centrifugation were tested as possible methods for removing the very fine insoluble additives from the polymer solution.

Precoat filtration potentially offered the advantage of being relatively low cost and well-tried technology. Numerous tests were conducted at technical scale in order to find a filter mesh/precoat combination which gave an acceptable filtration rate. No combination was found which gave a commercially viable filtration rate so this process route was abandoned in favour of centrifugation.

Equipment tests were carried out on the centrifuge, thin-film evaporator (filmtruder), solvent recovery unit and extruder.

The table below shows the trials that have been conducted over the course of the project which led to the final design of the process.

Trial	Aim of Trial	Trials conducted	Results
Filtration	To identify if filtration is a suitable means of separating the insoluble BFR and antimony particles from the toluene-polymer solution.	Laboratory scale trials took place in August and September 2005. The trials were conducted at the laboratory of Ionic Solutions Ltd in Bradford. 43 different filter aid / support mesh combinations were tried with assistance from 5 different filter aid suppliers.	Filtration was rejected as a possible option. This is because the BFR and antimony particles were so fine that they required deposition of precoat filter media to aid the filtration. The filtration blocked repeatedly, and was difficult to control.

Trial	Aim of Trial	Trials conducted	Results
Centrifuge	To identify if using a centrifuge is a suitable means of separating the insoluble BFR and antimony particles from the toluene-polymer solution.	<p>A 300Kg trial using a disk stack clarifier centrifuge to separate decaBDE and antimony trioxide from virgin HIPS polymer took place over 2 days in early September at the trial facility of Westfalia Separator in Oelde, Germany.</p> <p>A second 300Kg trial was conducted at Oelde in December using real WEEE polymer from the same sample used for the Creasolv trials. The second trial used a filter followed by a continuous decanter centrifuge prior to the disk stack clarifier to remove the larger particles and increase the effectiveness of the clarifier. This was carried out at Westfalia on December 6th.</p> <p>A third 300Kg trial was conducted at Oelde in February using HIPS and PS from WEEE collected in the UK to prove this process route. The third trial was similar in set-up to the second trial, and used a filter followed by a continuous decanter centrifuge prior to the disk stack clarifier to remove the larger particles and increase the effectiveness of the clarifier. This was carried out at Westfalia on February 16.</p>	<p>Centrifuging is a potential option for a solvent recycling plant. Analytical results of the samples taken from the centrifuge trial showed that a substantial amount of the antimony was separated but insufficient BFR was separated to achieve the target removal rates. This was due to the partial solubility of the target BFRs in toluene at the elevated temperatures required for effective centrifugation.</p> <p>The first trial successfully demonstrated that very small insoluble particles can be removed using a disk stack centrifuge. However some of the larger particles dropped out of suspension too early and would have eventually blocked the centrifuge.</p> <p>The second trial (using real WEEE polymer) demonstrated that the combination of filter, decanter centrifuge and disk stack clarifier provides a robust and reliable separation solution for insoluble particles. This trial was partially successful because there was a higher proportion of ABS in the feed sample than expected. ABS is only partially soluble in toluene so a substantial amount of polymer was separated by the filter and decanter centrifuge. The trial did demonstrate however that use of a decanter ahead of the disk stack clarifier provides a stable and operable process by avoiding build-up of larger particles in the disk stack unit.</p> <p>The third trial (using HIPS and PS from UK WEEE) further confirmed that the filter, decanter and centrifuge combination was a feasible separation option. As the WEEE in this trial was hand-sorted and identified, the dissolution worked very well with only a small amount of filter residue.</p> <p>Although results of the bromine and antimony removal varied in all 3 trials due to the changing conditions, they were consistent in showing a high antimony removal but substantially lower bromine removal.</p>

Trial	Aim of Trial	Trials conducted	Results
Thin-Film Evaporator	To identify if a thin-film evaporator is able to evaporate sufficient solvent from the centrate to obtain a polymer melt with better than 5-10% solvent concentration.	<p>Laboratory scale trials were conducted during September and December 2005 at the laboratory facility of BUSS-SMS at Pratteln, Switzerland. A laboratory rotovaporator and a kneader were used. Samples from both centrifuge trials were tested</p> <p>A 2000 kg large scale trial was carried out during late March. Products from the 3 Westfalia trials and a made-up solution using HIPS and PS from WEEE collected in the UK were used as the feed material. This was carried out at BUSS-SMS on 13-16 March 2006.</p>	<p>The lab scale trials showed that thin-film evaporation under vacuum is able to reduce the solvent concentration to the desired 10% solvent concentration and the material foaming behaviour indicated suitability for scale-up to industrial scale.</p> <p>The results of the large scale trial showed that with the appropriate operating conditions-(temperature and pressure) and a suitable filmtruder configuration, a polymer melt with less than 1% solvent concentration can be obtained and fed directly to a water bath and pelletizer.</p>
Solvent Recovery System	To identify if the chosen solvent recovery system is able to recover the solvent from the centrifuge residue and obtain a dry BFR and antimony residue, suitable for landfill.	<p>A technical scale trial using the toluene/HIPS residue from the first centrifuge test was conducted during November in Italy.</p> <p>A second technical scale trial using the toluene/HIPS residue from the third centrifuge test was conducted at in Italy with the aim of using an E-cat (spent FCC catalyst) as an alternative low cost waste material for the drying agent. This trial was conducted at Formeco SRL on 8-9 March 2006.</p>	<p>Recovery of toluene from the residue was straightforward using a batch scraped surface solvent recovery unit. A free-flowing powder was produced. It was necessary to add 5% of a high surface area drying agent to 'soak up' the polymer and keep the residue mobile.</p> <p>The drying agent used in this first technical scale trial was a food grade material and highly expensive.</p> <p>The drying agent used in the second technical scale trial was spent FCC catalyst (E-cat). This proved to be unsuccessful as the E-cat was too fine with a very low bulk density, thus it was easily carried over by the solvent vapours into the distillate.</p> <p>Discussions with activated carbon manufacturers have also eliminated spent activated carbon as an alternative drying agent. This is because, spent activated carbon contains up to 100 times its weight in moisture content and would be ineffective as a drying agent. Furthermore, solvents absorbed by the activated carbon during its use might be released during solvent recovery and contaminate the distillate.</p> <p>Other possible low cost drying agent alternatives include saw dust and 'cat-liter'.</p>

Trial	Aim of Trial	Trials conducted	Results
Extruder	To extrude the polymer melt entering at a 5-10% solvent concentration to obtain dry polymer pellets.	The products from the thin-film evaporator trial at BUSS-SMS were used for the extrusion trials at PERA. The trial was carried out on 20 March 2006.	<p>In preparation for this extrusion, trial artificial samples of HIPS infused with toluene was used to set up the extruder in advance at PERA.</p> <p>The extrusion was performed on a twin-screw extruder with vacuum to remove as much solvent as possible. Due to the low solvent content in the infeed, the extruder was only able to reduce the solvent content in the pellets from less than 1% to less than 0.5%.</p>

17.6. Trial results

This section details results from trials conducted in the last phase of the project. This includes the third centrifuge trial at Westfalia, the large scale thin-film evaporator trial at BUSS-SMS, the second technical scale solvent recovery trial at Formeco SRL and the extrusion trial at PERA as these used the optimised process conditions.

Further details of the earlier Centrevap trials are contained in Appendix 5

Third centrifuge trial

Initial laboratory scale trials showed that when a 20% Polymer-Toluene Solution was spun in a laboratory centrifuge at 3-5 Gs, some solid material was separated and dropped out immediately but about 80% remained in suspension. Further discussions with centrifuge companies concluded that a higher G-force was required to separate all the solids.

Centrifugation is an accelerated method of sedimentation. Rapid sedimentation is attained by introducing rotation to the liquid / solid media, generating an acceleration that can be over 12000 times more powerful than gravity. This method eliminates the need for filter media.

A centrifuge works by spinning a vessel containing the material to be separated at high speed. This pushes the 'heavy phase', usually the solids, to the outside of the vessel.

The feed material travels in through the feed pipe and through the bowl where it immediately hits the rotating centrifuge bowl. As a result of the differing densities of the polymer (toluene) solution and the solids, the feed material separates into two materials: Concentrated residue (BFR and Antimony Trioxide) and the Centrate (Polymer solution).

Following the first two large scale centrifuge trials conducted at Westfalia, in Oelde, Germany to observe the effects of a larger G-force in the separation of the 20% Polymer-Toluene Solution, a third large scale centrifuge trial was also conducted at Westfalia to confirm the effectiveness of using a centrifuge in the separation process. The main reason for this third trial was due to the excessive filter residue produced in the second trial. This was because of a larger than expected amount of ABS in the infeed material which resulted in a low product yield in the second trial.

Feed material

As the infeed material was crucial in determining the amount of filter residue obtain after the sieving stage and thus indirectly affecting the yield of the experiment, it was decided that the infeed would be provided by Axion. This infeed was obtained by hand-sorting UK television sets which contained BFRs and were made of HIPS and PS. These television sets were then shredded to obtain chips about 15-20 mm.

Due to the way in which the feed material for the trial was obtained, the bromine and antimony concentration of the polymer chips was less than for the second trial.

Equipment configuration

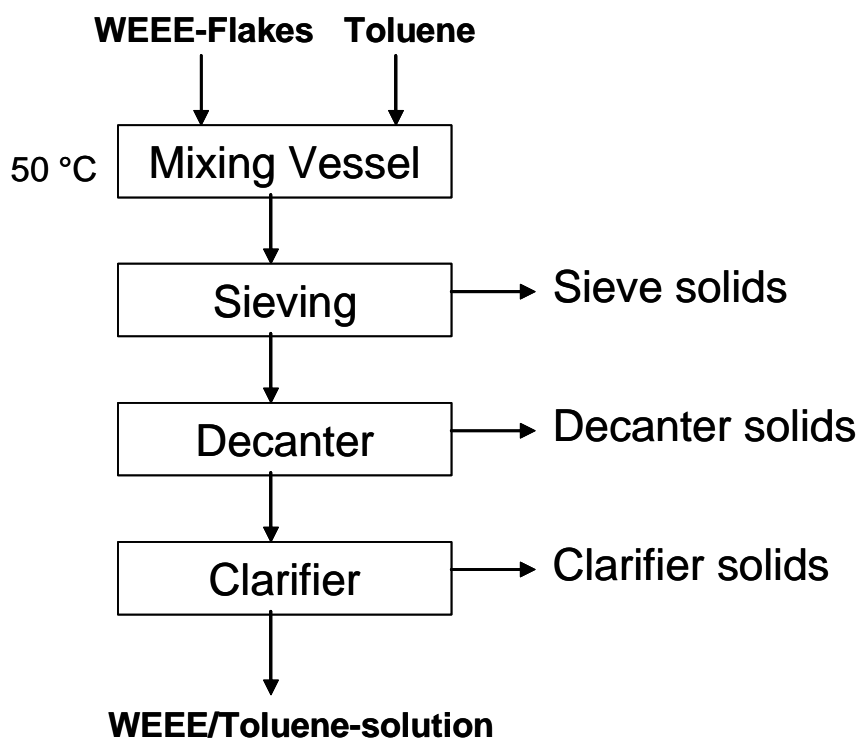
The feed material was dissolved in toluene in the same steam-jacketed stirred vessel that was used for the second centrifuge trial. The dissolution step was conducted the day before the main trial in order to save time. The polymer solution was left in a heated and agitated vessel for about 6 hours to ensure that all the polymer had completely dissolved. There was no visible undissolved polymer prior to the start of the filtration.

The following equipment was set up in the pilot plant area:

- A simple basket filter with 2mm slotted mesh
- a CA225 decanter centrifuge
- the same SC 6 disk stack centrifuge that was used for the first trial

The separators were set up so that each could be used one after the other in batch mode with the liquid phase being returned each time to the stirred vessel ready to feed the next separation.

The process sequence was as shown below:

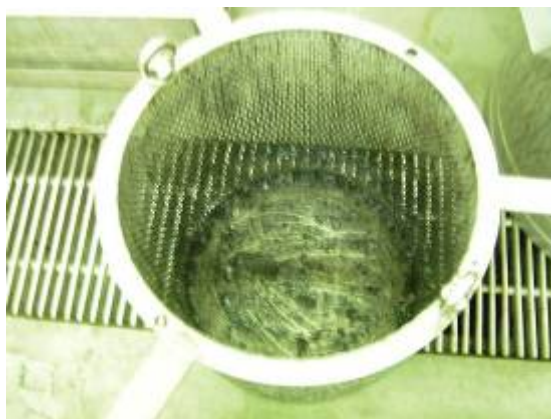


Trial summary

75 Kg of WEEE polymer was mixed with 250 Kg of toluene with the vessel maintained at 50C to create a 23% mixture. This concentration was similar to the polymer solution concentration in the second trial. The used the following operating conditions for the decanter and the centrifuge:-

- Decanter: 500 litres per hour at 55C
- Disk-stack: 200 litres per hour at 65C

The filtration was relatively clean, with only a very small amount of filter residue, and most of the polymer solution passing through the strainer basket to the filtrate.



A total of 1.5 Kg of material was collected in the strainer basket. It appeared to be mostly thin wires, small nuts and bolts. 321 Kg of suspension was collected for feed to the decanter centrifuge.

The decanter centrifuge also separated a large quantity of undissolved solids, yielding 220 Kg of centrate and producing a semi-solid residue of 72.5 Kg. This amount of decanter residue is larger than expected due to an inappropriately sized regulator ring (too small), thus resulting in leakage of the polymer solution into the residue. Under actual operating conditions, the amount of residue obtain would be significantly lesser.

The decanter centrifuge is shown below.



The interiors of the decanter centrifuge are shown below, and can be seen to be relatively clean.



The disk stack clarifier worked very well and there was no build-up on the disk-stack bowl, which was similar to the second trial. The pictures below show the interiors of the disk-stack.



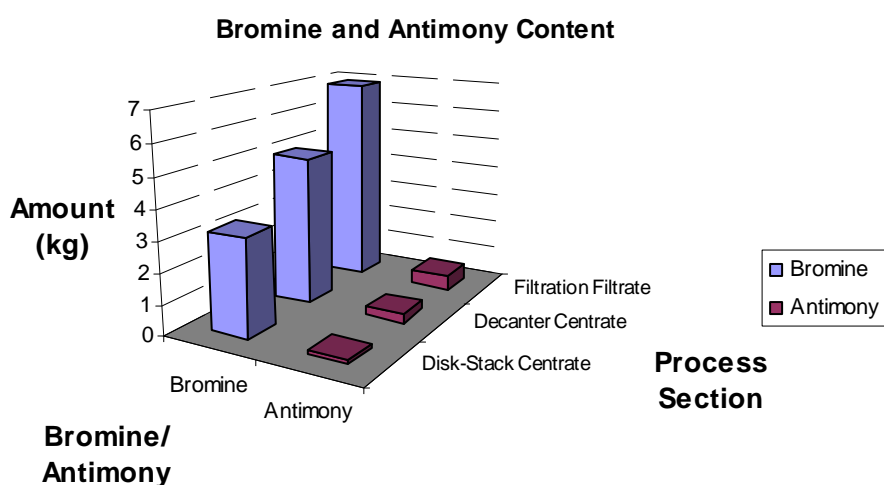
The disk stack trial yielded 208 Kg of centrate plus 4.5 Kg of solid residue.

The centrate was shipped to Switzerland for use in the large scale Buss-SMS evaporation trial.

Results

The bromine and antimony content of the feed, centrate and residue samples was analysed at Fraunhofer IVW by X-Ray Fluorescence:

	Dry basis	
	Bromine	Antimony
Filtration Filtrate	9.35%	0.66%
Decanter Centrate	9.78%	0.61%
Disk-Stack Centrate	6.73%	0.27%
% Reduction	28.0%	58.9%



These results show an approximately 60% reduction in antimony content to 0.27% on dry polymer (solvent-free) basis, and an approximately 30% reduction in the bromine content to 6.73% on dry polymer basis in the disk stack centrate product.

Note that the actual antimony bromine concentration measured in the disk stack centrate was 0.06% and 1.55% respectively. However the polymer concentration in the centrate was 22% so the dry basis concentration of antimony in the final product after removal of the solvent was 0.27%

Most of the BFRs present in the feed sample are fully or partly soluble in toluene, which explains why they were not removed by the centrifuge.

Conclusions for third centrifuge trial

It can be observed that the results of the second and third trials seem varied in terms of both antimony and bromine reduction. We believe this is because the input concentrations of both elements in the two trials varied significantly, with 0.75% antimony concentration (wet basis) in the filtrate solution on the second trial, but only 0.15% in the third trial. This reasoning is further confirmed by the relatively similar antimony concentrations (wet basis) in the disk-stack centrate (product) which are 0.03% and 0.06% for the second and third trials respectively.

The difference in the bromine removal rates in the second and third trials can be explained by the differing solubility of BFRs in toluene. Thus, it is dependent on the type of BFRs in the infeed polymers, and since the infeeds for the two trials came from two different sources (two different countries), the types of BFRs in them are probably different.

The third trial confirmed that the combination of a decanter centrifuge with a disk stack centrifuge would be able to provide a robust and flexible process design with a very short process residence time. This design would be able to reduce the antimony concentration to a very low level, and also possibly reduce a portion of the bromine concentration. It would also

remove any other insoluble impurities where there is a density difference between the impurity particle and the carrier solvent.

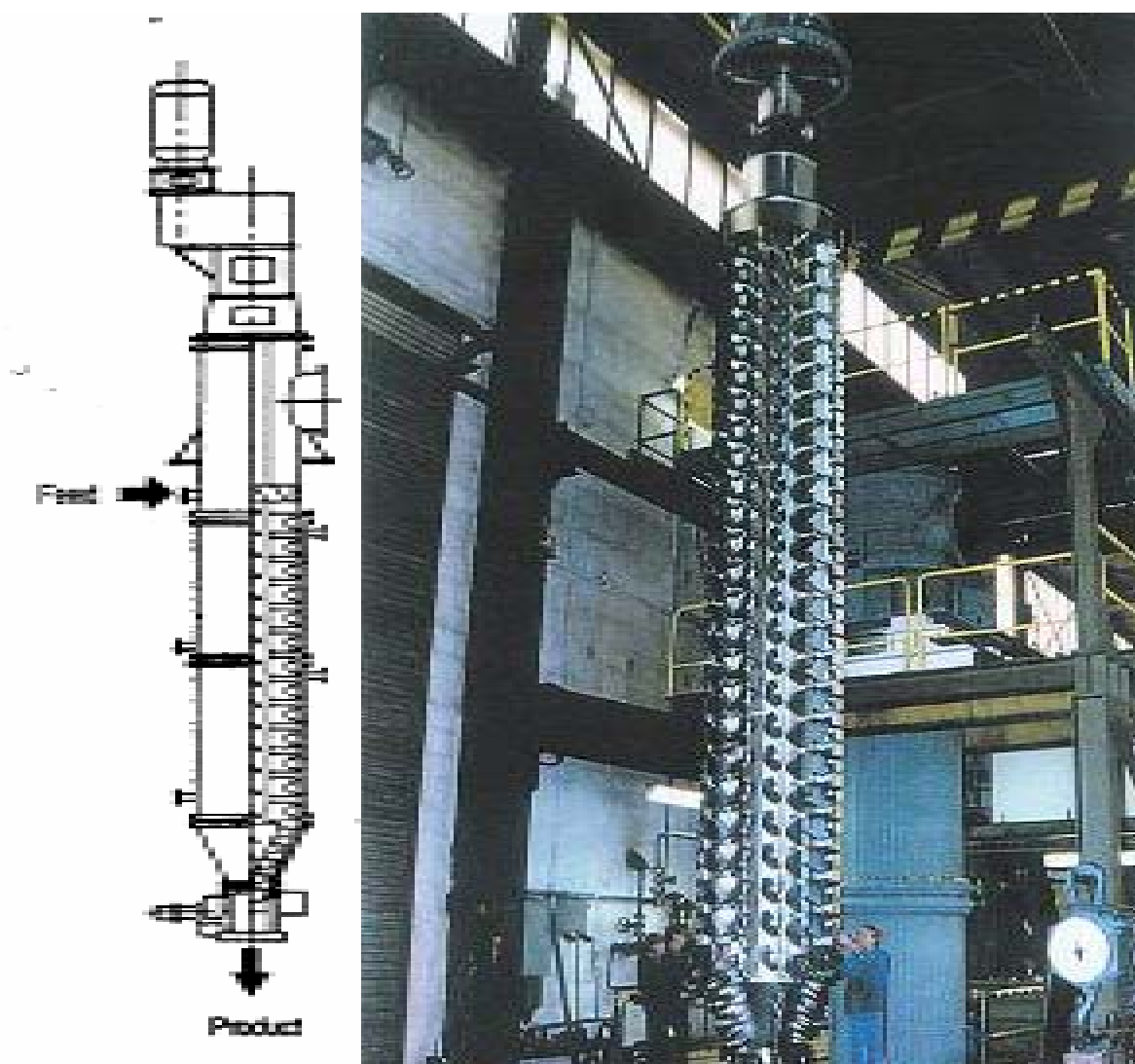
Thin-film evaporator trial

Initial laboratory scale trials in a laboratory rotovaporator and kneader showed that it is possible to reduce the solvent concentration of the disk-stack centrifuge centrate from about 80% down to the desired 10%. These laboratory scale trials were conducted during September and December 2005 at the laboratory facility of BUSS-SMS at Pratteln, Switzerland.

The Thin Film Evaporator comprises of a vertical heated drum, a revolving rotor system and distribution device. The incoming filter residue (feed) is first distributed evenly along the inside of the heated body (drum) by a distribution device. The revolving rotor system which comprises of several blades then spreads the product into thin films over the heated wall of the drum. The thickness of the layer is defined by the clearance between the blade and the heated wall.

In front of the blades, a highly turbulent film is formed. This is where surface renewal takes place and excellent conditions for high rates of mass and heat transfer are achieved. Due to the positive product transport characteristic of the rotor system, the product flows continuously from the inlet, along the processing zone, to the outlet. The extracted volatiles are exhausted by a vacuum system and liquefied in a separate condensing system.

The pictures below show a diagram of a Buss-SMS 'Filmtruder' thin-film evaporator together with a photograph of the rotor from a large unit⁷⁹.



⁷⁹ Source Buss-SMS www.sms-vt.com

A large scale trial of 2000 kg infeed polymer solution was carried out at the pilot plant facility of BUSS-SMS at Pratteln, Switzerland, from the 13-16 March 2006. The aim of this trial was to prove the ability of the thin-film evaporator to concentrate the polymer solution from the disk-stack centrifuge centrate, and obtain a polymer melt with a solvent concentration of less than 5%.

Feed Material

The feed material for the trial is detailed in the table below. In order to meet the trial requirements of about 1500 Kg of polymer solution, a 'made-up solution' of polymer chips and toluene was made a week prior to the trial. 160 Kg of HIPS and PS polymer chips shredded from UK television sets and hand sorted for polymer type was dissolved in 640 Kg of Toluene. This polymer solution was passed through a 100-micron filter to remove any undissolved polymer, nuts, bolts, metal wires, etc. The rest of the infeed material was from the three Westfalia centrifugation trials.

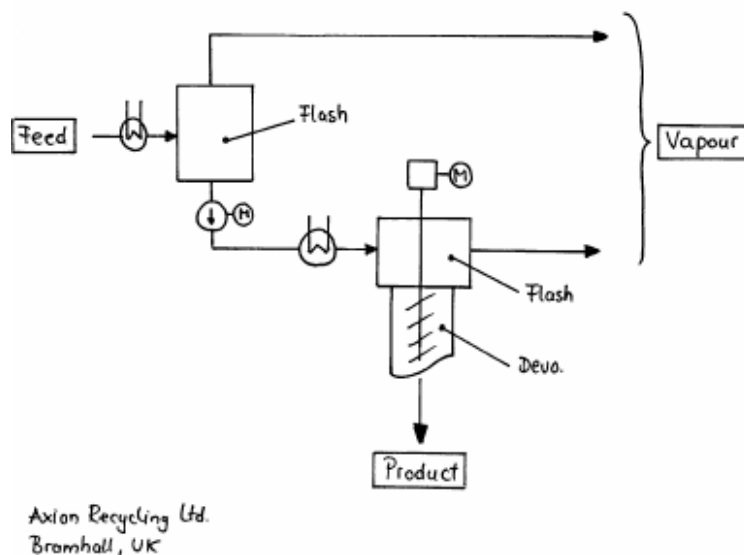
Source	Weight (Kg)	Polymer Concentration (%)
Made-Up Solution	800	19.8
Westfalia Trial 1 (a)	122	9.6
Westfalia Trial 1 (b)	122	15.6
Westfalia Trial 2	190	17.4
Westfalia Trial 3	210	22.0
TOTAL	1444	-

Equipment configuration

The following equipment was set up in the pilot plant area:

- Dissolution, agitated vessel
- Heat exchangers
- Flash box
- Thin-film evaporator
- Condensers
- Water bath
- Pelletizer

The diagram below shows the general set-up of the equipment.



Trial Summary

The feed material from one of the above sources was first heated to about 180C via a heat exchanger. When the pressure in the line reached 10 bar, the flash valve opened and released the super-heated polymer solution into the flash box which flashed about 60% the solvent away. The concentrated polymer solution with about 30% solvent concentration is slightly

cooled, before it enters the thin-film evaporator where it is heated to temperatures up to 250C. More than 99% of the remaining solvent was evaporated in the thin-film evaporator, resulting in a highly concentrated polymer melt with less than 1% solvent concentration.

The polymer melt is extruded vertically through a three hole die plate above a water bath which the melt strands pass through before being pelletized in the pelletizer.

The throughput of the trial fluctuated due to regulation of the flash valve, but averaged about 180 Kg/h.

Both the flash box and the filmtruder operated under vacuum of about 200 mbar. The solvents (toluene) recovered from the flash box and the filmtruder is condensed in separate condensers.

The short residence time of the filmtruder helped in preventing the degradation of the polymer due to the high temperatures in the filmtruder. Additionally, stabilizers were also added to ensure that there was no degradation of the polymer due to the high temperatures.

The polymer concentrate from Westfalia trial 1(a) was passed through the evaporator without any stabilizer to allow for comparison of the effects of the stabilizer on the physical properties of the polymer product. The concentrate from Westfalia trial 1(b) was not used at all as the quantity was deemed insufficient.

Some of the finished polymer pellets were sent for extrusion trials at PERA.

Results

Mass balance calculations have shown that about 62% of the recovered solvent was removed by the flash box, while the filmtruder removed the remaining 38% of the recovered solvent for the various infed materials.

A simple weight-loss experiment at PERA prior to the extrusion trials showed that the solvent content in the pellets (polymer melt from filmtruder) was as low as 0.07%. This is a 99.7% reduction in solvent concentration from an input polymer solution with a solvent concentration of about 80%.

Conclusions for the thin-film evaporator trial

Although the flash box and the thin-film evaporator has a high capital cost, it achieves such a good solvent removal rate that it eliminates the need for a vented extruder to remove further solvent, and only requires a pelletizer to make polymer pellets for sale.

Solvent recovery trial

The technology used in the solvent recovery section of this process is similar to that used in the solvent recovery section of the Creasolv Process. Thus, a description of the equipment used in the trial and an explanation of the workings of the equipment and technology is available in the Solvent recovery trial section of the Creasolv Process Trials summary.

Two solvent recovery trials were carried out in November 2005 and March 2006.

The first solvent recovery trial was to establish that the solvent recovery unit was able to recover the solvent (toluene) and also produce a dry residue, suitable for landfill.

The second trial was to experiment with another drying agent which is a 'low-cost waste by-product' of another industry as an alternative to the recommended drying agent. The recommended drying agent was a food-grade additive and this is costly. The main difference in the two trials was the drying agent used.

Feed material

The first trial used the disk-stack centrifuge residue from Westfalia trial 1. This contained a polymer solution made using HIPS golden sample dissolved in toluene, concentrated in antimony and slightly in bromine.

The second used the disk-stack centrifuge residue from Westfalia trial 3. This contained a polymer solution made using HIPS and PS from UK television sets dissolved in toluene, and also concentrated in antimony and bromine. The significantly

lower bromine and antimony concentration in this residue as compared to the first residue is because a large amount of the bromine and antimony was already removed by the decanter, prior to the disk-stack.

The table below shows the breakdown of the feed for both trials.

Solvent Recovery Trial	Polymer	Toluene	Antimony	Bromine
Trial 1 Infeed	13%	62%	17%	8%
Trial 2 Infeed	20%	74%	4%	2%

The first solvent recovery trial used Tix-dry as a drying agent, while the second solvent recovery trial used spent fluid catalytic cracking catalyst (FCC) catalyst as a drying agent. Spent FCC catalyst is a waste material that is generated in large quantities by the petroleum refining industry. The amount of drying agent added was about 7%-10% of the total input mass into the vessel.

Trial results

Trial summary 1:

930g of the centrifuge residue and 75g (7.5%) of Tix-dry drying agent was added into the vessel. The distillation took place under a 16 mbar vacuum and a hot-oil temperature of 120C. The distillation lasted for 3 hours, including 1 hour to remove the final residual solvent.

625g of solvent was collected as distillate, including 15g of water which might have entered the unit when the cover was removed during the distillation. 336g of solids was obtained and the estimate solvent residual content in the solid residue was 0.5%. The solids residue was dry and crumbly but pourable.

Trial summary 2:

830g of the centrifuge residue and 40g (4.5%) of spent FCC catalyst drying agent was initially added into the vessel. This was followed by another 100g (15% in total) of FCC catalyst drying agent which was added during the distillation to aid the drying process. The distillation took place under a 20 mbar vacuum and a hot-oil temperature of 180C. The distillation lasted for only 1.25 hours, before it was stopped and concluded that the E-cat was an unsuitable alternative.

400g of solvent was collected as distillate.

464g of solids was obtained and because the experiment was unsuccessful, the residual solvent content of the solid residues was not obtained.

The solids residue remained as a big lump, coated with FCC catalyst as shown below.



The picture below shows the distillate and the carried over FCC catalyst.



Conclusions for the solvent recovery trial

The small scale trial at Formeco demonstrated impressive results for such a simple and practical machine. It is definitely a viable option to recover the solvents and produce a dry residue, suitable to be sent for landfill. This has been adequately demonstrated in the first trial.

Tix-dry is expensive so the choice of a suitable waste material as the 'drying agent' will be vital to ensure acceptable process economics. As the second trial has shown, the spent FCC catalyst is unsuitable, and thus further trials need to be done to find a more suitable drying agent. Other possibilities would also include spent activated carbon, saw dust or cat-litter.

Extrusion Trial

Following trials on the thin-film evaporator at Buss-SMS to remove toluene from solutions of HIPS, this extrusion trial was arranged to determine whether any additional removal of solvent was possible. The output pellets from the thin-film evaporator was re-extruded on a conventional twin screw extruder and a vacuum pump used to remove any solvent vapour formed during extrusion.

The extrusion trials were conducted at PERA (Melton Mowbay) on March 20th 2006.

Feed material

The infeed material to the extruder was the pellets obtained from the pelletizer at BUSS-SMS. Thus, the contents of the infeed material would be mainly polymer, very small amounts of solvent (toluene), bromine and antimony.

A weight-loss experiment performed at the start of the trial showed that the infeed had a solvent concentration of 0.07%.

Equipment

The following equipment was used during the trial:-

- Rondol twin screw extruder
- Vacuum Pump
- Water bath
- Air knife
- Pelletizer

The picture on the right below shows the complete equipment set up.



Trial Summary

The infeed pellets were fed into the extruder and heated to a temperature of up to 180°C. As they passed the vacuum port (-0.69 bar), any excess solvent would be evaporated. There were no fumes observed at the extruder die, but a very faint toluene odour was observed at the outlet of the vacuum pump and in the extruded pellets.

Results

A similar weight-loss experiment, whereby the extruded materials were stored in a vented oven at 80°C for two hours showed that after the extrusion, the solvent content of the polymer was about 0.034%. This showed a solvent content reduction of about 50% from the initial 0.07%.

Conclusions for the extrusion trial

As the input to the extruder from the thin-film evaporator has such a low solvent content, the amount of solvent that the extrusion process actually removes will be very small, as compared to the large capital cost required to acquire an extruder.

Furthermore, the output from the thin-film evaporator being at 0.07% has already met the target solvent concentration of less than 1%, so an additional extruder would not significantly improve the product performance.

17.7. Mass balance

A full scale mass balance has been prepared for the Centrevap process at a throughput of 10,000te/yr WEEE polymer. This mass balance is based on the experimental results measured in the technical scale trials.

The detailed results of this mass balance are confidential to WRAP but the mass balance may be summarised as follows:

Stream No.	INPUT (te/yr)			OUTPUT (te/yr)	
	WEEE Input	Make-Up Solvents	Drying Agent	Polymer	Residue to Landfill
Polymer	7,920	0	0	7,336	584
BFR	1,000	0	0	780	220
Antimony	80	0	0	8	72
Inerts	1,000	0	0	0	1,000
Toluene	0	104	0	6	99
Drying Agent	0	0	483	0	483
Total	10,000	104	483	8,129	2,458

Total Input: 10,587 te/yr

Total Output: 10,587 te/yr

The total quantity of solvent that circulates within the process will be much less than for the Creasolv process at around 20-30 tonnes. This is because the process cycle time is much faster.

Part of the solvent that is consumed will be lost in the residue that is disposed to landfill and part will be present at less than 1% content in the final polymer product. At this level it is not expected that the solvent will have any detrimental effect on product quality or moulding performance. The residual solvent in the polymer is not expected to leach out under normal conditions of use.

Solvent losses will be greater and product yield will be reduced where the feed material contains large amounts of fillers, paper or 'fluff', which can absorb solvent and will also increase the volumes of residue that must be disposed to landfill.

The input polymers targeted by the Centrevap process will be different to those targeted by the Creasolv process because it does a different job.

The Centrevap process will remove insoluble impurities in a polymer down to very small particle size and is therefore potentially of interest for producing very clean recyclates.

It may also be capable of removing some pigments and insoluble additives such as lead stabilisers. It will not remove carbon black pigment because the density difference between carbon particles and polymer solution is too small and carbon particles used as pigments are extremely small.

Like the Creasolv process, the Centrevap process must be fed with a single, separated polymer type so the feed will always have been subjected to a sorting or mechanical separation process. However the flexibility of the Centrevap process option means that the same plant could in principle be used to recycle several different polymer types just by changing the solvent to suit each polymer.

The wider range of feed polymers that could be improved by the Centrevap process means that it has potential to treat a greater feed volume than the Creasolv process. Up to around 50% of the WEEE polymers that are collectable in the UK (approx 50,000 te/yr) could be treated by the process and there are larger volumes of other polymer types such as rigid or flexible PVC which could in principle be treated with the correct solvent combinations.

There are alternatives to the Centrevap process. Several companies in Europe are operating or developing mechanical recycling processes to separate BFR-containing polymers from BFR-free materials and to upgrade the BFR-free fraction to a high specification. These processes are already becoming commercially viable in Europe and can be built at lower capital cost than currently projected for the Centrevap process.

The Centrevap process has potential to complement these mechanical separation processes when the requirement is to treat polymers containing difficult fillers or pigments or to produce really high grade recyclates.

17.8. Business model

Centrevap process business model

£'000	Year 1	Year 2	Year 3	Year 4	Year 5
Profit and Loss					
Sales Value	0	1,249	2,676	3,568	3,568
Operating costs	-670	-1,651	-1,651	-1,651	-1,651
EBITDA	-670	-402	1,025	1,917	1,917
Interest	-114	-222	-182	-102	-51
Depreciation	-150	-600	-600	-600	-600
Pre-tax profit	-934	-1,224	-887	1,215	1,266
Taxation (estimate)	0	0	-73	-365	-380
Net profit	-934	-1,224	170	851	886
Operating Cash Flow					
Revenues (inc VAT)	0	1,468	3,145	4,193	4,193
Construction costs (inc VAT)	-3,525	-3,525	0	0	0
Operating costs (inc VAT)	-788	-1,940	-1,940	-1,940	-1,940
Debt Service	-269	-995	-1,034	-987	-572
VAT (paid)/recovered	610	634	-117	-320	-336
Corporation tax (approx)	0	0	0	-73	-365
Dividends paid	0	0	0	-102	-510
Surplus	-3,972	-4,359	54	771	470
Balance sheet					
Fixed assets	2,850	5,250	4,650	4,050	3,450
Current assets	1,528	169	223	994	1,464
Current liabilities	1,613	2,678	2,063	1,894	1,410
Net assets	2,766	2,742	2,810	3,150	3,505
Equity	3,700	4,900	4,900	4,900	4,900
P&L account	-934	-2,158	-2,090	-1,750	-1,395
	2,766	2,742	2,810	3,150	3,505

Capital cost of the plant is estimated to be £6.0 million on a serviced UK site. It is estimated that a further £2.5 million of funding will be required for working capital.

The process is projected to be profitable assuming a cost for the feed material of £100/te and revenue for the product of 60% of virgin polymer.

17.9. Discussion

As for the Creasolv process the projected recycled polymer price has been increased by £124/te to £560/te (60% of the virgin polymer price) because consultations with manufacturers have demonstrated increasing interest in high grade recycled content.

In the case of the Centrevap process it is assumed that the process operators will have to pay £100/te for the infeed material in competition with exports to China because this process will not remove BFRs and it is therefore only suitable for upgrading substantially BFR-free polymer. Note that this is different to the Creasolv process where a gate fee of £45/te in competition with landfill is assumed.

At a recycled polymer price of 60% of virgin and a cost of £100/te for the input material (to compete with export to China) it makes a satisfactory return for investors. These are the results shown above.

At a higher recycle price of 80% of virgin polymer it makes very attractive returns and the project internal rate of return rises from 16% to 40%.

However there is a fundamental difference in the performance of the two process options. The Creasolv process will remove BFRs down to the target level of 0.1% while the Centrevap process will not.

Concerns regarding the Centrevap process remain. They include:

- It will not be effective for removing brominated flame retardants.
- As for Creasolv the economics of the Centrevap process depend heavily on being able to recover virtually all of the solvent used in the process. The recovery rate predicted by the process mass balance is better than 98%. Test work conducted for this project indicates that this level of recovery should be achievable with good quality process design around the solvent recovery and vacuum systems.
- The process design and business model have been developed with HIPS as the target polymer and toluene as the chosen solvent. To dissolve ABS or ABS/PC more expensive solvents such as dichloromethane, dimethyl formamide or tetrahydrofuran will be required. Provided the level of solvent losses can be tightly controlled as envisaged in the current mass balance the extra cost of these solvents should not affect commercial viability.
- The volatile solvents used by Centrevap are more flammable than the Creasolv solvents and will create VOC emissions more readily

However there are some important factors in favour of this process option if the process objective is to produce high grade polymer, free of insoluble contaminants:

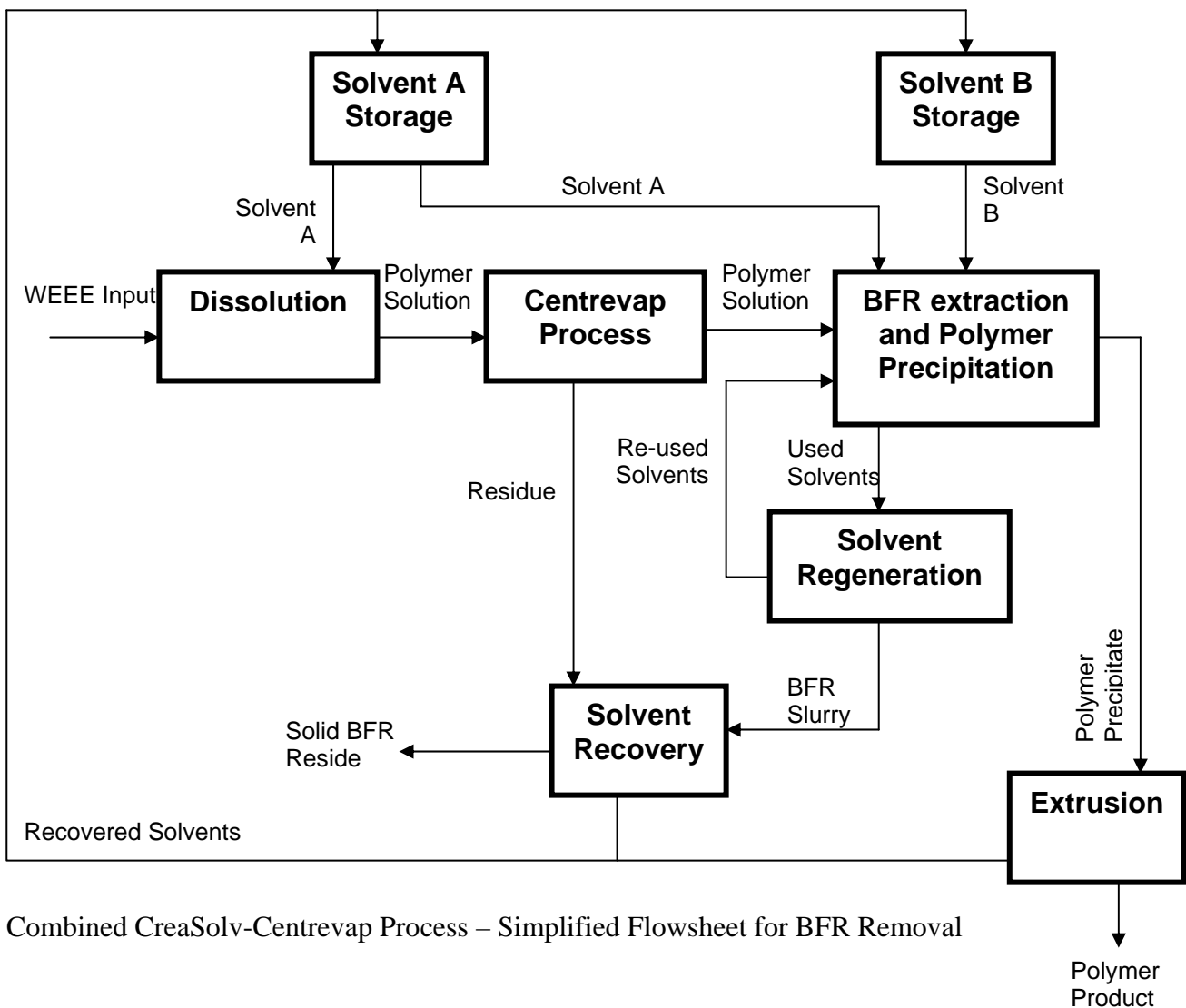
- The process sequence is simple and should be relatively easy to control on a truly continuous basis
- The evaporation technique used is well established at bulk scale for virgin polymers
- The low boiling solvents proposed are easier to remove than the higher boiling solvents used by Creasolv
- Residence time for material passing through the system will be short, requiring low process inventories and helping to limit polymer degradation
- The process will be capable of processing any soluble polymer to remove all insoluble additives, not just BFRs. Initial tests have been made at lab scale with unplasticised PVC and these appear to be promising.
- Energy consumption and operating cost for the Centrevap process are now lower than for Creasolv because of changes made to the Creasolv process in order to achieve maximum BFR reduction
- Although the Centrevap process capital cost has increased since the first process design was completed as a result of the introduction of a second centrifuge step, the estimated capital cost and working capital requirement is now lower than for Creasolv because the Creasolv plant cost has also increased substantially.
- The maximum insoluble particle size left in the product from the Centrevap process will be submicron. The maximum particle size left by the Creasolv process will be limited to the 50-100micron range by the primary filter used at the start of the process.

18. Combined Creasolv/Centre vap process design option

18.1. Creasolv-Centre vap process background

The Creasolv-Centre vap process is a spin-off idea based on all the trials that have been carried out over the course of the project. This process combines the benefits of the individual Creasolv and Centre vap processes. It has not been tested in this project but the tests of the two process options individually indicate that it should result in a very clean product that meets the bromine concentration limit of less than 0.1% while also reducing antimony and other insoluble additives below 0.1%.

18.2. Flowsheet



Combined CreaSolv-Centre vap Process – Simplified Flowsheet for BFR Removal

18.3. Process description

The Creasolv-Centre vap Process is a batch process which uses a high boiling point solvent to dissolve the feed plastic.

Combination with the Centre vap process at this stage results in the removal of all impurities, such as antimony, fillers and additives that are more than 0.3 microns.

A series of precipitation steps follow using a combination of proprietary Creasolv solvents. These reduce the bromine content in the polymer to less than 0.1%.

The BFRs are extracted into the solvents and the solvents are recovered by distillation.

The main steps in the process are dissolution, impurity removal, a series of extractions and extrusion of the final product.

Input feed material

The input feed material to the plant consists of shredded plastic waste of approximate size between 30-50 mm. The plastic waste should be pre-sorted so that it is primarily HIPS and ABS.

Dissolution

Regenerated Creasolv solvent from previous batches is stored under ambient conditions in a carbon steel storage tank ready for use in the dissolution process.

A jacketed-dissolution vessels is filled with Creasolv solvent and heated via the heating jacket. The polymer is added. At elevated temperature, the polymer and BFRs are both soluble in the hot Creasolv.

Impurity removal

Any undissolved polymers and other insoluble impurities are removed by filtration and centrifuges, similar to that in the Centre vap process. A pump draws from the dissolution vessels to feed the filters. The centrifuge centrate contains the dissolved polymer, soluble additives, and any impurities less than 0.3 microns in size. The residue contains the undissolved polymer, insoluble additives and inerts such as paper, fluff and metals.

BFR extraction and polymer precipitation

The filtered solution from the dissolution vessel is pumped into a solvent extraction unit. A second proprietary Creasolv solvent is added. This causes the polymer and the BFRs to separate.

The bulk of the excess solvent is removed from the debrominated polymer in a series of special extraction units. The recovered solvent mixture is pumped to store tanks and then passed to a special solvent regeneration unit.

Solvent regeneration

A novel solvent regeneration process has been developed as a result of the collaboration between WRAP and Fraunhofer IVV. This process separates the BFRs from the two Creasolv extract solvents and separates the solvents from each other ready for re-use

BFRs are recovered by the solvent regeneration unit as a concentrated bromine-rich slurry. This slurry is passed to the final solvent recovery unit along with the filter residues from the first stage of the process.

Extrusion

The polymer gel particles from the extraction/ precipitation step are passed to a vacuum vented twin screw extruder for removal of the remaining solvent down to about 1%. The polymer product is cooled in a water bath and pelletized.

Additives and masterbatch can be added at this stage to modify the final polymer properties if required.

The solvents removed during extraction are returned to the solvent regeneration unit for recovery

Final solvent Recovery Unit

The Solvent Recovery Unit receives slurries from the filters and the solvent regeneration unit. It processes these slurries separately batch-wise and recovers almost all the solvents by heating under vacuum, resulting in a dry, free-flowing bromine-rich inert residue which is safe for disposal to landfill.

The bromine industry may be interested in taking the bromine-rich fraction from the solvent regeneration unit as a source of bromine feedstock in which case it may also be diverted from landfill.

The mixed solvents that are recovered by this unit are also returned to the solvent regeneration process.

ENERGY USED

- Hot utility requirement (Low Pressure Steam- 5 bar): 4.7 te of steam/te feed
- Cold utility requirement (Cold Water): 60.5 te/te feed
- Power (Average Draw): 214 kWh/te feed

EFFLUENTS PRODUCED

Water Effluent

None

Vapour Effluent

The extruder producing the final polymer and the final solvent recovery unit will both generate small quantities of solvent emissions to atmosphere via the vacuum system. The great majority of these emissions can be controlled by a cold trap fitted on the input side of the vac pump, particularly as the Creasolv solvents have high boiling points. Any residual emissions from the vacuum pump can be eliminated by means of a biological filter if required.

Solids

BFR is discharged from the process in slurry in Creasolv solvent. The solvent is recovered and recycled from the slurry by the solvent recovery unit as a dry free-flowing powder.

Solid wastes are also produced from the primary filter residue at the solvent recovery unit. The solids will be discharged as a dry cake and transported from site for landfill disposal.

18.4. Mass balance

A full scale mass balance has been prepared for the Creasolv-Centrevap process at a throughput of 10,000te/yr WEEE polymer. This mass balance is based on the experimental results measured in the technical scale trials. The detailed results of this mass balance are confidential but the mass balance may be summarised as follows:

Stream No.	INPUT (te/yr)			OUTPUT (te/yr)	
	WEEE Input	Make-Up Solvents	Drying Agent	Polymer	Residue to Landfill
Polymer	7,920	0	0	7,534	386
BFR	1,000	0	0	3	997
Antimony	80	0	0	0	80
Inerts	1,000	0	0	0	1,000
Solvents	0	155	0	38	117
Drying Agent	0	0	582	0	582
Total	10,000	155	582	7,575	3,162

Total Input: 10,737 te/yr

Total Output: 10,737 te/yr

Part of the solvent that is consumed will be lost in the residue that is disposed to landfill and part will be present at less than 1% in the final polymer product. At this level it is not expected that the solvent will have any detrimental effect on product quality or moulding performance. The residual solvent in the product is non-toxic.

18.5. Discussion

As can be seen from the large scale trials, the Centrevap process is unable to attain the target bromine concentration of less than 0.1%. However, it is able to reduce the antimony concentration significantly, down to at least 0.14%. This is because the centrifuges mainly perform a physical separation. As the BFRs are partially soluble in toluene at high temperatures, the centrifuges are unable to remove a significant amount to meet the target concentration. On the other hand, the antimony being completely insoluble achieves higher reduction rates as the centrifuges are able to remove anything above 0.3 microns.

The Creasolv process is a chemical separation process, and is able to achieve the target bromine concentration through the preferential solution of BFRs in its solvents. It is unable to reduce the antimony concentration as the antimony is mainly removed via redistribution in the used solvents. The bottleneck in the Creasolv process in this aspect is that the purity of the polymer product is dependent on the size of the filters in the process. In this design, the filter mesh is sized at 100 microns. Thus, any impurities in the polymer such as additives and fillers that are smaller than 100 microns have a high chance of re-emerging in the final product.

By combining the two processes, a polymer product with extremely low impurities (0.3 microns) and a low bromine concentration of less than 0.1% can be obtained.

Cost estimation for this option indicates that the capital cost will be higher at £14m, compared to £11.8 million for the standard Creasolv process. This is mainly due to addition of the two high cost centrifuges to the process flowsheet.

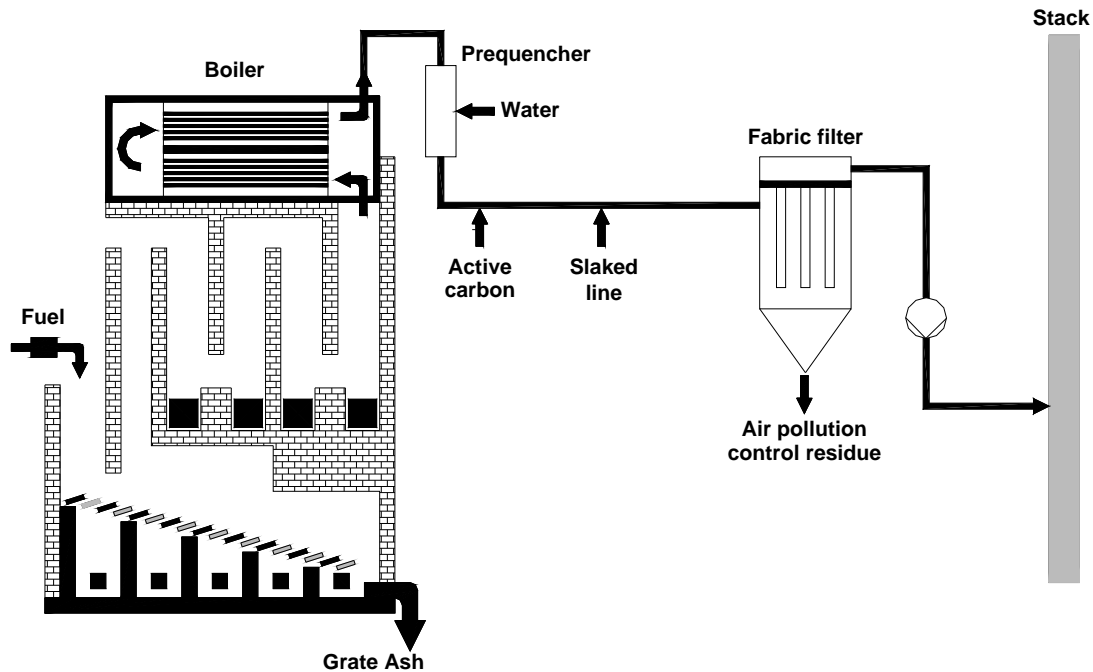
As a result the financial returns for the combined Creasolv-Centrevap process will be significantly lower than for the conventional Creasolv process option. The process will not be commercially viable at a price of 60% of virgin polymer but it will make money at 80% of virgin polymer price.

The higher price level will be more easily achievable if the polymer solution is centrifuged prior to bromine extraction. Centrifuging will ensure no insoluble impurities above 2-3 micron size, compared to 50-100 micron for the standard Creasolv process. This will improve extrusion performance, appearance and impact strength of the final polymer material.

19. Incineration

An option for disposing polymers containing brominated flame retardants is to co-combust them with municipal solid waste (MSW) in municipal waste incinerators. This is the disposal route currently recommended by the polymer industry trade association, Plastics Europe⁸⁰.

19.1. Flowsheet



19.2. Process description

As for the other process options considered in this project it is assumed that a mechanical recycling process will yield a waste stream of BFR containing polymers. This will be sent for incineration.

The total BFR-containing polymer separated in this way across the UK is unlikely to exceed 30,000te/yr. This assumption is based on a total long term collectable WEEE polymer volume in the UK of about 300,000te/year.

On this basis, the maximum amount of BFR-containing polymer that would need to be processed at a single incineration site is unlikely to exceed 3,000te/yr. Assuming an average plant processes 300,000te/yr of MSW, 1% of WEEE polymer will be incinerated with MSW in each incinerator.

The BFR containing polymer is fed with MSW to an incinerator operating at temperatures $>800^{\circ}\text{C}$. Large inerts present in the waste collect at the bottom of the furnace as grate ash which is sent to land fill whilst fine inerts in the polymers such as fillers are either combusted or are captured in the incinerator's air pollution control system as air pollution control residue.

An energy recovery boiler situated on the flue gas line recovers energy from the combustion process in the form of electrical power. The power generation efficiency of the combustion and energy recovery stage is typically 28%. 1kg of BFR polymer produces 11.2MJ of power.

Previous work in Germany to test co-combustion of WEEE polymers containing BFRs with MSW was conducted on the TAMARA demonstration incineration plant at Karlsruhe⁸¹. This plant has a wet scrubber system

⁸⁰ www.plasticseurope.org

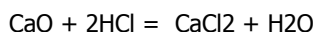
Most UK waste incinerators do not use wet scrubbers to catch pollutants. All of the latest and largest plants use dry air pollution control systems.

About 50% of UK plants use slaked lime (calcium hydroxide) emulsion injection followed by activated carbon injection followed by bag filters.

The water in the slaked lime emulsion evaporates as it contacts the raw incinerator flue gas, cooling the gas to the temperature that the bag filters can withstand. The water in the emulsion also provides a reaction medium for contact between the slaked lime and the flue gas acids.

The other 50% of UK plants use dry quicklime and activated carbon injection followed by water injection to cool the flue gases before the bag filters.

The chemical reactions involved are essentially the same in both cases:



Activated carbon is injected in relatively small quantities and its function is to capture cadmium, mercury and other volatile heavy metals plus any dioxins and other residual organic species in the flue gas.

After passing through the boiler the HCl and HBr content of the raw flue gas is neutralised by the injection of a slaked lime-water slurry. Activated carbon is also injected with the slurry to absorb heavy metals, dioxins and furans. The water in the slurry acts as a coolant reducing the temperature of the gas by approximately 100oC to 150oC to prevent damage to the bag filter in the next stage of the process.

Finally the flue gas passes through a filter bag which recovers solid particulates from the gas before its release to atmosphere.

The filtrate recovered contains fine inerts, calcium halides and carbon and is known as 'Air pollution control residue' (APC). The APC residue is then treated and disposed of as hazardous waste. It is classed as hazardous waste due to its irritant properties resulting from its large lime concentration.

Energy Generation

3.1 MWhr of electrical power/te of BFR incinerated

Effluents Produced

Water

None, Water evaporates and leaves the process with the flue gas.

Vapour

The vapour contains the burned polymers, inerts and the bromine free BFRs.

Solids

Grate ash collects in the bottom of the furnace after the combustion stage. This grate ash contains inerts which are subsequently sent to landfill.

APC residue is captured in the bag filter. The residue is made up of lime, calcium halides, carbon and fine inerts. The residue is classed as an irritant therefore must be disposed of as hazardous waste.

Emission quantities (based on polymer feed rate of 1429Kg/hr):

Kg/hr	Grate ash	Air pollution control residue
Inerts	11	4
Activated carbon		75
Calcium bromide formed by reaction between lime and BFR combustion products plus unreacted excess lime added to ensure complete scrubbing		264
Total	11	343

⁸¹ 'Recycling of Bromine from plastics containing brominated flame retardants in state-of-the-art combustion facilities', Vehlow J, Hunsinger H, Bergfelt B, Jay K, Mark F, Tange L, Drohmann D, Fisch H, APME Technical paper

19.3. Business model

There is no additional capital cost associated with this process as it will take place at an existing incinerator site. The cost of providing the incineration plant is taken into account in the gate fee charged by the incinerator operator to its suppliers of feed material.

The calorific value of WEEE polymers (40MJ/kg) is approximately four times the value of that for MSW (10MJ/kg).

Incinerator economics are based primarily around charging a gate fee for incoming material. This is supplemented by the value of power generated from steam generated in the incinerator waste heat boiler.

The power generation systems of UK MSW incinerators are sized for a calorific value of 10MJ/kg.

Burning high calorific value material such as WEEE polymer generates about four times more heat per tonne than burning MSW. Provided the incinerator is running at full capacity WEEE polymers will therefore displace four times the mass of MSW being incinerated.

To maintain the revenue of the incineration plant the gate fee that the incinerator must charge in order to cover its capital and operating costs must be four times higher for WEEE polymer than for MSW (~£180/te compared to ~£45/te for MSW).

Further extra incineration costs are incurred when burning BFR-containing polymers as a result of;

- a larger quantity of lime being required: 112Kg/te for BFR polymer compared to 6.5Kg/te for MSW (adds cost of about £12/te BFR polymer)
- disposing the Air Pollution Control (APC) residue to hazardous waste landfill: 200Kg/te for BFR polymer compared to 17Kg/te for MSW(adds cost of about £17/te BFR polymer)

For this model it is assumed that no additional activated carbon would need to be added to capture additional brominated dioxin equivalents that would be generated as a result of combustion of BFR polymers. If additional carbon would need to be added this would increase the cost for carbon and also the APC residue disposal cost.

Summary of costs:

	£/te BFR feed
Gate fee charged by MSW incinerator for BFR polymer in order to maintain incinerator revenue	180
Additional lime cost compared to MSW	12
Additional hazardous waste landfill cost compared to MSW	17
Total additional cost	209

This analysis indicates that incineration of BFR polymer with energy recovery as a 1% addition to the feed to existing large scale MSW incinerators in the UK would have a net cost around £209/te. This is £164/te more than the £45/te gate fee assumed for the other process options considered in this project.

Note that £45/te was chosen as the reference gate fee as this is the current UK landfill cost. Landfill is therefore a much less expensive disposal option for BFR-containing polymers than incineration with energy recovery in the UK context.

19.4. Discussion

All UK MSW incinerators are required by the Waste Incineration Directive (WID) to achieve a minimum flue gas temperature of 850C.

The WID requires that some wastes are incinerated at higher temperatures with a minimum flue gas temperature of 1100C.

The specifications for materials which require higher temperature incineration are set out in the European Waste Catalogue section of DEFRA's guidance note on the WID⁸². This guidance indicates that WEEE polymers containing BFRs would almost certainly be required by the WID to be processed at 1100C even though plastics are cleared for combustion at 850C. This is because the European waste catalogue specifies that wastes containing dangerous substances as specified in the European Directive on classification, packaging and labelling of dangerous substances 67/548/EEC⁸³ must be incinerated at the higher temperature.

Most mixtures of WEEE polymers will contain some octa or penta BDE, which are classified as dangerous substances and would therefore qualify for the higher incineration temperature. However any incinerator operator that considers burning WEEE polymers containing BFRs may be able to negotiate with the regulators that the BFR-containing polymers are not dangerous because the BFRs are locked in the polymer matrix

If the 1100C temperature is required then this would mean that bulk Municipal Solid Waste (MSW) incinerators could not be used to co-combust BFR-containing polymers in the UK. Instead, more expensive dedicated incinerators for dangerous wastes would be required.

UK incinerators are usually only licensed by their local authority to burn MSW collected in their local area as import of waste for incineration is a political 'hot potato'. This would need to be taken into account when considering the commercial viability of an incineration strategy for WEEE polymers containing BFRs.

The incineration of Bromine-containing compounds can increase the corrosion rate of an incinerator. The corrosion of boiler parts has been related to a combination of relatively high halogen levels, high temperatures in the flue gas and deposits on heat transfer surfaces. Corrosion mechanisms include deposit build up, evaporation of metal chlorides, and melting of salt deposits⁸⁴.

APC residue is treated as hazardous waste because it is an irritant due to the large excess of lime that it contains.

Normal APC residue contains about 15% chlorides. The soluble halide content of air pollution control residue leaches in landfills and will not meet the landfill directive hazardous waste acceptance criteria which came into force on July 16th 2005.

The leaching criteria for non-hazardous landfills are not as onerous as for hazardous landfills so the strategy likely to be adopted in future by incinerators is to neutralize the excess lime with an acid such as HCl or H₂SO₄ so that the irritant nature is lost and the material can be disposed to non-hazardous landfill. This will increase neutralization cost and the total waste volume but will reduce disposal cost/te because non-hazardous landfill is less expensive.

At present UK incinerators would have to charge extra gate fees to accept high calorific value material in order to maintain their current revenue levels. However experience in the Netherlands and elsewhere in Northern Europe where recycling levels are significantly higher than in the UK indicates that as municipal waste recycling improves, the calorific value of the MSW stream reduces below 10MJ/Kg. When this happens incinerators are happier to accept high CV material with no additional gate fee in order to maintain their heat balance. We are still some way from this position in the UK.

⁸² <http://www.defra.gov.uk/environment/ppc/wasteincin/pdf/wid-guidance-edition3.pdf>

⁸³ http://ec.europa.eu/environment/dansub/main67_548/index_en.htm

⁸⁴ Rademakers. P, et al, Review of corrosion in waste incinerators, and possible effects of bromine, 2002
<http://www.ebfrp.org/statements/TNO-AKZO-corrosion-study2002-Final.pdf>

20. Material property testing

The material test work concentrated mainly on the samples from the large scale Creasolv process trials as the Creasolv process was the only option considered which removed BFRs to the levels targeted by this project. However some testing was also done on samples from the large scale Centrevap process trials.

20.1. Material Properties

Results of the material property testing that was done by London Metropolitan University Polymer Centre for the samples produced in the initial collection, processing trials during Phase 2 and for the Creasolv and Centrevap samples from the large scale processing trials conducted during Phase 3 of the project are attached as Appendix 2.

The most significant results for the Creasolv process were:

Sample	MFI	Notch Impact Strength	Unnotched Impact Strength	Tensile Strength	HDT
Creasolv Starting HIPS	10.0 g/10 min	9.7 kJ/m ²	47 kJ/m ²		
Phase 2 Lab scale Creasolv product		2.9 kJ/m ²	7.9 kJ/m ²		75°C
Polymer Centre result – AX 06 050 Ring Extruder 3 rd Pass	3.86 g/10min	5.7 kJ/m ²	26.4kJ/m ²	31 MPa	80°C
Polymer Centre result - AX 06 009 Ring Extruder 4 th Pass	2.73 g/10 min	4.9 kJ/m ²	26.2 kJ/m ²	33 MPa	82°C
Axion in-house result - AX 06 050 Ring Extruder 3 rd Pass	3.6 g/10 min	9.2 kJ/m ²	36.5 kJ/m ²	28 MPa	
Axion in-house result - AX 06 009 Ring Extruder 4 th Pass	3.6 g/10min	8.0 kJ/m ²	36.7 kJ/m ²	30 MPa	
Typical HIPS	3 -15 g/10 min	5 – 12 kJ/m ²		13-42MPa	75-95°C

The results from the Polymer Centre showed the processing had significantly reduced the impact strength. HIPS.

Parallel measurements at Axion Recycling in Salford however showed higher impact strength for both the Run 3 and Run 4 material, although still less than the input material. It should be noted however that certification of Axion's lab as part of their ISO 9001 programme is ongoing and that the figures from the Polymer Centre have been used throughout for the discussion of the results.

The results show that recycling by the Creasolv process has reduced both impact strength and MFI substantially.

20.2. Discussion of MFI Reduction

Whilst MFI as a low shear test is not a definitive guide to the flow on polymer under high shear conditions within a mould the reduction from 10 to 3 g/min is an indication of a substantial rise in viscosity. Closed loop recycling to the original TV backs may therefore be difficult since problems in one or more of the following areas may occur:

- Incomplete Mould filling
- Excessive clamping forces
- Excessive processing temperatures

However the composition of the two materials is substantially different since approximately half of the antimony trioxide and essentially all of the brominated flame retardants have been removed.

A number of mechanically and thermally intense processing stages also separate the starting and finishing materials.

It was therefore considered important to localise the cause of the reduction in MFI to see if this could be alleviated thus enabling true closed loop use of the end product.

Since the processing can be easily divided between the reactor and extruder phases a list of potentially MFI influencing factors was drawn up for each step.

Reactor

- Removal of flame retardants
- Removal of antimony trioxide
- Addition of nucleating agent
- Loss of butadiene rubber

Extrusion

- Thermally induced chain scission
- Shear induced chain scission
- Radical induced cross-linking

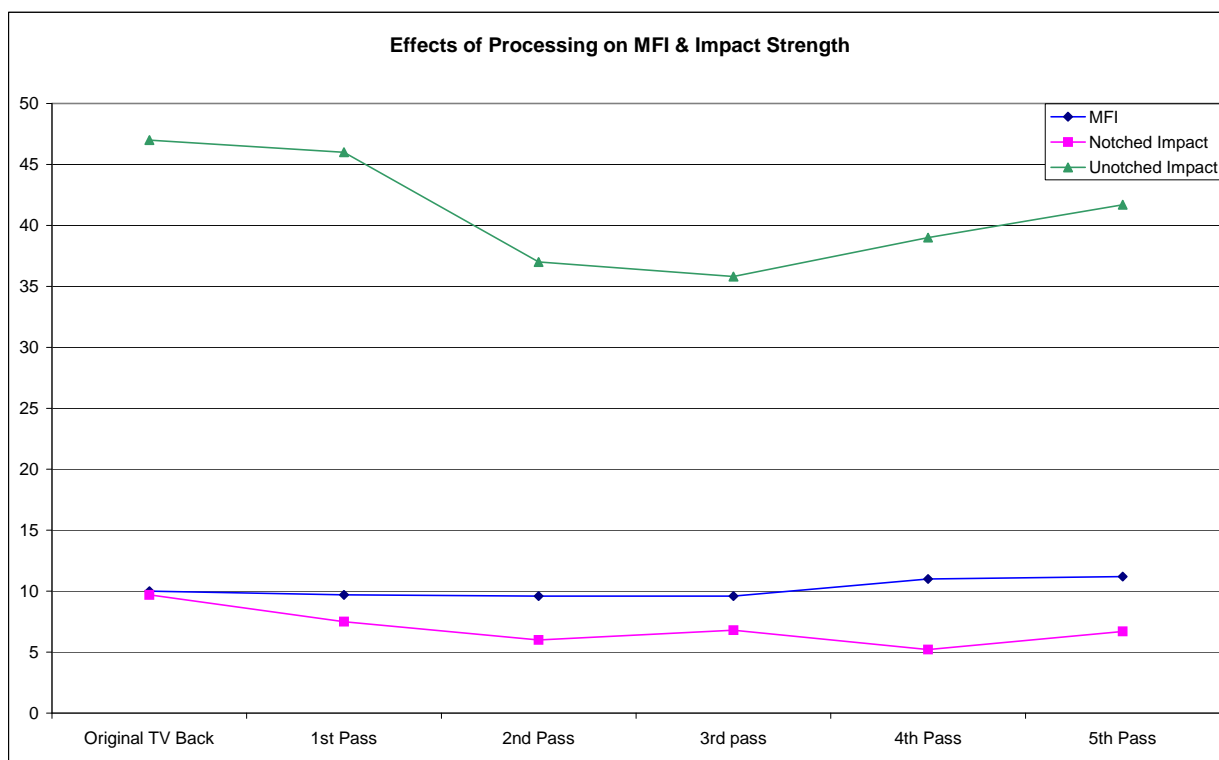
Dealing firstly with the extrusion stage were this to contribute to the reduction in MFI then it would be necessary for the effects of cross-linking to exceed those of chain scission. This would normally not be the case since generally such processing leads to an increase in MFI with a corresponding loss in molecular weight due to chain scission.

Two good indicators of chain scission in this case would be a reduction in molecular weight and an increase in monomeric styrene and whilst we did not have the ability to perform monomeric styrene determinations, SEC (Size Exclusion Chromatography) plots for the molecular weight distribution in Runs 1 to 3 have been made by the IVV. A suitable method for the assessment of rubber cross-linking was not available to the team.

Reference to the literature and manufacturers guidance on the processing of HIPS showed that the temperature and process stability is good and that production of monomeric styrene was very strongly dependent on temperature and residence time. Ignoring the effects of high levels of shear deformation little chain scission would be expected at temperatures below 260°C and the solvent removal was conducted at temperatures around 210°C with relatively little high intensity mixing.

In order to quantify the likely influence of the extrusion step on its own a sample of the starting material was subjected to multiple passes on a lab twin screw. Process conditions were chosen to be more rigorous than in the Ring Extruder, but still within the expected processing tolerance of the material.

It was considered important to use the starting material since this allows for the exclusion of the effect of solvent, both in the reactor phase and also in the subsequent solvent extraction process. A number of potential experiments to quantify the in-extruder effects of the solvent were assessed, but these would require extensive access to a lab scale twin screw with an optimised condenser system.



What can clearly be seen here is that the MFI was stable into the 5th extrusion pass and that the impact strength was also relatively stable after a noticeable reduction in the first extrusion pass.

The option of repeating this work with additional anti-oxidant was considered, however the lack of change in MFI was seen as a strong indication that the underlying polymer structure was relatively stable during processing. Looking at the impact strength figures given the defect sensitivity of the material any changes their size and distribution would be expected to influence this. Therefore when comparing samples that had been extruded on a twin screw with the one that had only been injection moulded the drop in impact strength on the very first extrusion run was seen as less significant than the fact that the impact strength results did not show a downwards trend during the subsequent runs.

Turning now to the in-reaction modifications of the starting material the primary object of the process is the removal of the brominated flame retardants and to a lesser extent the antimony trioxide synergist.

The Size Exclusion Chromatography plot for the WT3 sample showed that the extraction process had removed a portion of the lower molecular weight material in the polymer peak. This resulted in an increase in the average molecular weight from 160,000 to 190,000 g/mol. This increase would be expected to reduce the MFI although it appears to be too small to account for it alone. A similar increase in molecular weight was observed for WT1 and to a lesser extent WT2.

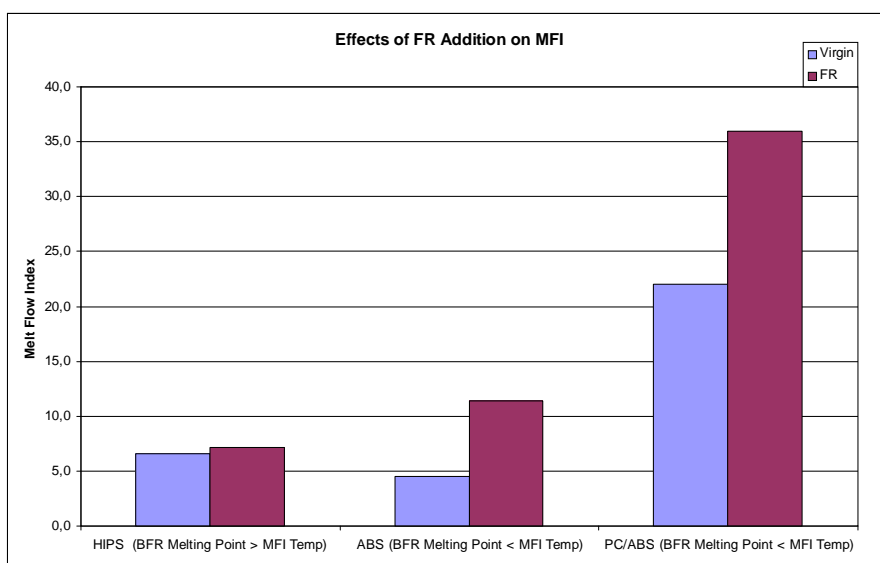
Interestingly the SEC plot was also monomodal, meaning that the SEC technique could not show differential changes in the polystyrene and rubber phases.

Since there was however considerable concern that the polymeric material being removed was butadiene-based an IR analysis was performed on the residual slurry after precipitation. This showed only the presence of polystyrene.

Both the brominated flame retardants and the antimony trioxide synergist are generally considered to be fillers, so their removal would be expected to result in an increase in MFI, however some of the flame retardants have melting points below the processing temperatures expected and have very low melt viscosities. Whilst the trend in brominated flame retardants is very much towards materials such as DecaBDE with melting points well above 300°C many of the older ones, which are also of most environmental concern, melt well below 200°C.

Just how significant this can be is shown in the following results for some of the specimen samples prepared by the IVV in 2004 in which the HIPS samples contain a BFR that melts above the MFI temperature and the ABS and PC/ABS samples contain BFR types where the melting point is below the MFI temperature:

Polymer	Composition
HIPS	HIPS (Atofina 7240) – Control
HIPS FR	HIPS (Atofina 7240) – 10% Deca BDE + 4% Antimony
ABS	ABS (Bayer Novodur P2HT) – Control
ABS FR	ABS (Bayer Novodur P2HT) + 5% Octa BDE + 5% TBBA + 0.5% TBPE + 3% Deca BDE
PC/ABS	PC/ABS (Dow Pulse A35-105) – Control
PC/ABS FR	PC/ABS (Dow Pulse A35-105) +7% TBBPA +3% Antimony



Like these earlier specimen samples the starting material for the large scale Creasolv trials WT1 and WT2 also contained large quantities of BFRs with melting points below the MFI temperature:

Flame retardant type	OctaBDE	DecaBDE	TBBPA	TBPE
Average concentration in polymer feed:				
WT1	3.36%	0.77%	2.43%	0.49%
WT2	3.27%	1.36%	6.09%	0.47%
Melting Point	70-250°C	~300	~180°C	~225°C

In the light of this observation the removal of the low melting point BFRs was felt to be a significant contribution to the reduction in MFI noted between input and output material.

There is considerable scope to redress this loss of MFI through the use of additives, which could easily be incorporated into the melt during the solvent extraction on the extruder. It is also likely that the reduction in viscosity would make the solvent extraction easier in comparison to the relatively low MFI end material produced in these trials.

Flame retardants delivering this effect would be of particular interest and many of the phosphor based systems exhibit low melt viscosities in the required temperature range.

What must however be noted is that these steps represent additional complexity and cost. In addition a major concern must be the lack of predictive methodology for assessing the likely MFI of the output polymer from the input material.

20.3. Discussion of Loss of Impact Strength

Since HIPS is as its name suggests is used in applications where good impact strength is important any loss of impact strength during the recycling process is significant.

During the progress of this project large improvements were made in final impact strength of the Creasolv product in comparison to the lab scale samples that were produced in Phase 2 of the project.

As with the MFI results an attempt was made to assess the individual contributions of the reactor and extrusion stages:

Reactor

- Loss of butadiene rubber
- Loss of rubber domain structure
- Removal of additives
- Addition of nucleating agents

Extrusion

- Thermally induced chain scission
- Shear induced chain scission
- Radical induced cross-linking
- Loss of rubber domain structure

In considering the possible causes it is important to pay regard to the fact that HIPS is not only a multi-component system, but also a micro-structured one. That means that changes in physical form can be just as significant as changes in chemical composition.

The primary components of HIPS are polystyrene, polystyrene/butadiene graft copolymer and polybutadiene. Whilst polystyrene and polybutadiene are highly incompatible the complex mixture formed by co-reacting styrene and butadiene leads to a stable product with very finely dispersed rubber domains in the polystyrene/graft copolymer matrix.

It is the interruption of crack propagation by these rubber domains that leads to the superior impact properties when compared to simple polystyrene. However this means that changes to the number, size and elasticity of these domains will affect the impact properties.

Although the structures within HIPS are of a size that would be amenable to light microscopy the black colour of the sample meant that only SEM would be suitable for evaluating this and we would recommend that this form part of any further investigating and process optimisation.

Parallel to this, multiple pass processing of the original TV backs also offered a good opportunity to look at the behaviour of the starting polymer under extrusion conditions in isolation to the effects of additive removal and solvent treatment.

This work showed that whilst the original starting material had a notched impact strength of about 10 kJ/m², this fell back to about 6 - 7 kJ/m² after the initial extrusion run. When this material was then processed further with multiple extrusion runs the further passes through the extruder did not reduce notched impact strength greatly.

In the light of this observation the value of 5 kJ/m² for the finished Creasolv product could be expected given the prolonged extrusion necessary to remove the solvent in the pilot trials.

Based on its observations of the pilot solvent removal trials Axion believes that a well-designed solvent removal extruder should be able to remove solvent down to the target concentration in only one or two passes. This should lead to reduced degradation of the impact strength.

20.4. Effects of Residual Solvent

At levels substantially above 1% a very large increase in MFI and decrease in HDT was noted. Interestingly notched Izod impact strength appears to be insensitive to solvent content over quite a wide range.

However what also became apparent is that thermo-gravimetric analysis is not suitable for solvent contents near or below 1%, since, although on the basis of thermo-gravimetric testing the Centrevap samples were all thought to contain very low levels of solvent, they showed inappropriate MFIs and HDTs.

Fraunhofer IVV compared its thermo-gravimetric solvent content results directly to ones measured using gas chromatography (GC) and found a significant underreporting:

Sample	ppm Creasolv solvent measured by GC	%Total Solids measured by GC	%Total Solids measured thermo-gravimetrically
Creasolv large scale trial Ring Extruder Run 3	8810	99,1%	99,7%
Creasolv large scale trial Ring Extruder Run 4	5310	99,4%	99,9%

However it should also be noted that the specification for 1% or less of residual solvent held up well in terms of its limited influence on the major physical characteristics. What could not be assessed within the scope of the project was the effect of such levels of solvent on ageing properties.

20.5. Centrevap test results

Samples from the large scale Centrevap process trials showed signs of plate-out during the tensile testing which may have been due to contamination with an incompatible polymer, but would also be consistent with some of the effects of elevated solvent levels noted by the IVV.

As with the Creasolv process results the Centrevap product test results demonstrate that solvent content appears to have only limited effect on notched impact strength and solvent content.

Notched impact strength is almost identical between samples that have a factor three difference in MFI due to residual solvent:

Sample	MFI	Notch Impact Strength	Unnotched Impact Strength	HDT
Starting HIPS from TV casings	10 g/ 10min	9.7 kJ/m ²	47 kJ/m ²	-
AX 06 006 Centrevap Run3	46.7 g/10min	10.6 kJ/m ²	43.6 kJ/m ²	51°C
AX 06 006 Centrevap Run4	16.0 g/10min	10.8 kJ/m ²	48.9 kJ/m ²	69°C
AX 06 008 Centrevap Run4 + further solvent removal on Rondol twin screw extruder	16.4 g/10min	10.7 kJ/m ²	60.6 kJ/m ²	69°C
Typical commercial HIPS	3-15g/10min	5-12 kJ/m ²	-	75-95°C

Overall, test results for the final large scale Centrevap samples show much better maintenance of material properties than for the Creasolv process. However it is important to remember that the Centrevap process did not remove the key BFRs.

20.6. Summary of material testing results

- The final large scale Creasolv process sample has a notched impact strength of 5 kJ/m². This is better than unmodified PS, but relatively low for HIPS
- The Creasolv extraction process raised the average molecular weight by between 6 and 18% (probably due to removal of lower molecular weight polymer in the solvent extraction process)
- Removal of the low melting point BFRs was a significant contribution to the reduction in MFI.
- Impact strength was found to be relatively independent of solvent content
- Thermo-gravimetric determination of solvent content is problematic
- HDT is a good indicator of solvent content
- The Centrevap process option maintained the impact properties of the material well.

21. Environmental impact assessment

21.1. Methodology

Two separate environmental impact assessments were conducted for this project:

- ISO 14040 standard qualitative and quantitative environmental impact assessment using conventional impact assessment methodology by White Young Green Consulting, Leeds
- Quantitative 'QWERTY' eco-efficiency analysis by Huisman Recycling Research, University of Delft, Netherlands

The White Young Green analysis may be compared directly with other environmental impact assessments prepared recently for WRAP.

The Huisman QWERTY analysis is specifically designed to assess the eco-efficiency of WEEE recycling processes and has now been used several times in Europe to assess other treatment methods for WEEE including dismantling, mechanical recycling, incineration with energy recovery and treatment of whole WEEE items in non-ferrous metal smelters.

Using the QWERTY technique to assess the processes developed in the course of this project will permit accurate quantitative comparisons with other WEEE treatment methods.

The QWERTY analysis is not performed under classic life cycle analysis standards as specified in ISO14040 because:

- Unusual system boundaries are applied. Only the end of life phase is reviewed, not the full product life cycle
- It is a sectoral approach rather than a classic product-oriented approach. It addresses the behaviour of individual materials in a larger system, including distribution of different materials to various destinations based on Axion's modelling of technology that does not yet fully exist.
- Some of the base technical and commercial data used in the analysis is confidential. Reporting under ISO14040 would require full disclosure
- Weighting of multiple input categories is applied in order to estimate a single indicator for comparison of disposal options. This is not in line with the stringent reporting requirements of ISO14040.

Details of the methodologies and assumptions used for each analysis are attached at Appendices 5A-5F.

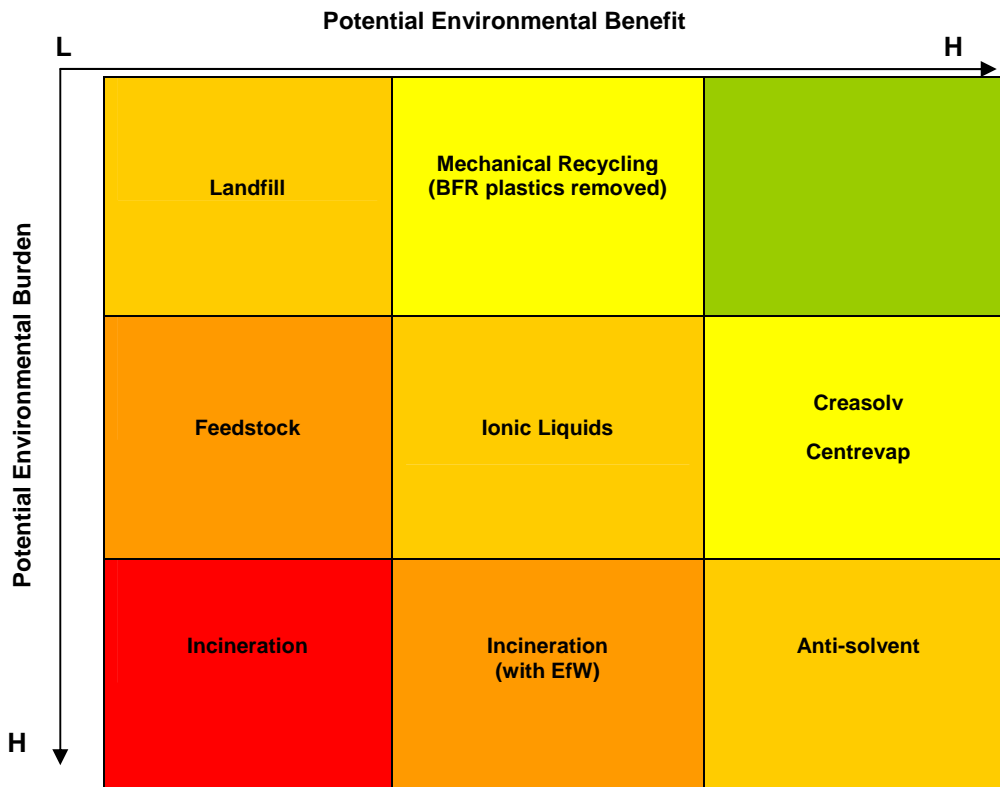
The full analyses were conducted for the short list of 6 possible processing or disposal options during phase 2 of the project. These results are detailed in Appendix 5.

The results were updated in Phase 3 only for the Creasolv and Centrevap process options. The updates were conducted because further process design and large scale testing work during Phase 3 had made significant changes to the process capital costs and mass balances. Appendices 5E and F present the Phase 3 update reports

The results and discussion in this section refer to the latest updated results.

21.2. Qualitative comparison

Initially White Young Green made a qualitative comparison of the potential environmental benefits and burdens of the disposal options considered in the course of this study. The full report is presented at Appendix 5A:



The qualitative assessment identified the Creasolv, mechanical recycling with BFR separation and Centrevap process options as combining the lowest environmental burden with the best environmental gain.

Note that landfill disposal is deemed to have very low environmental impact (because it consumes only the energy required to transport the material to the landfill site and because the plastic does not degrade appreciably in the landfill). However landfill also creates no environmental gain because no material is recovered to substitute production of virgin polymer.

The qualitative assessment included an evaluation of the potential environmental toxicology of the different process options. Detail of this assessment is included at Appendix 5.

21.3. Quantitative comparison

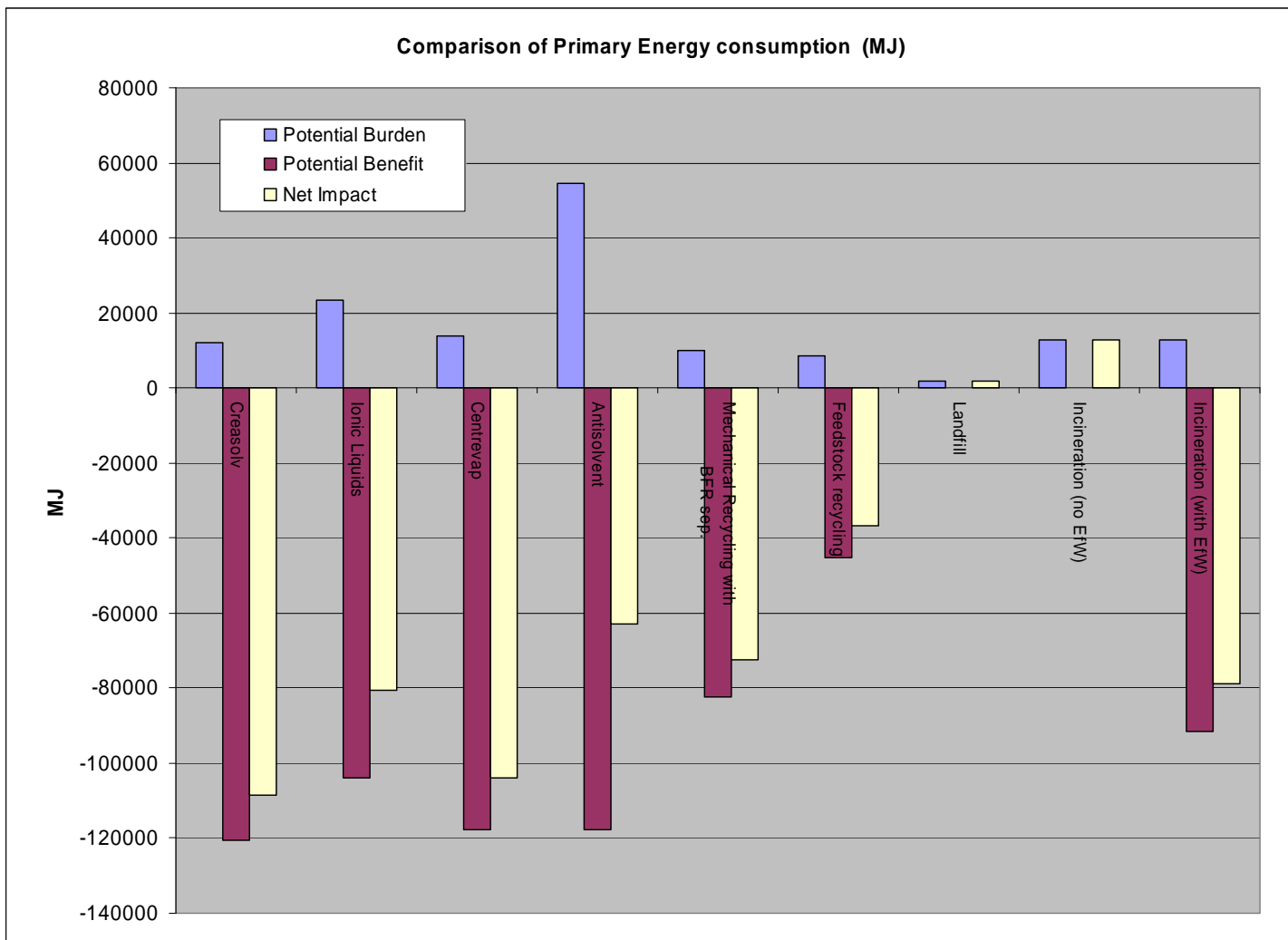
The quantitative analysis performed by White Young Green during Phase 2 of the project measured the environmental burdens and gains of the process options for three representative impact categories:

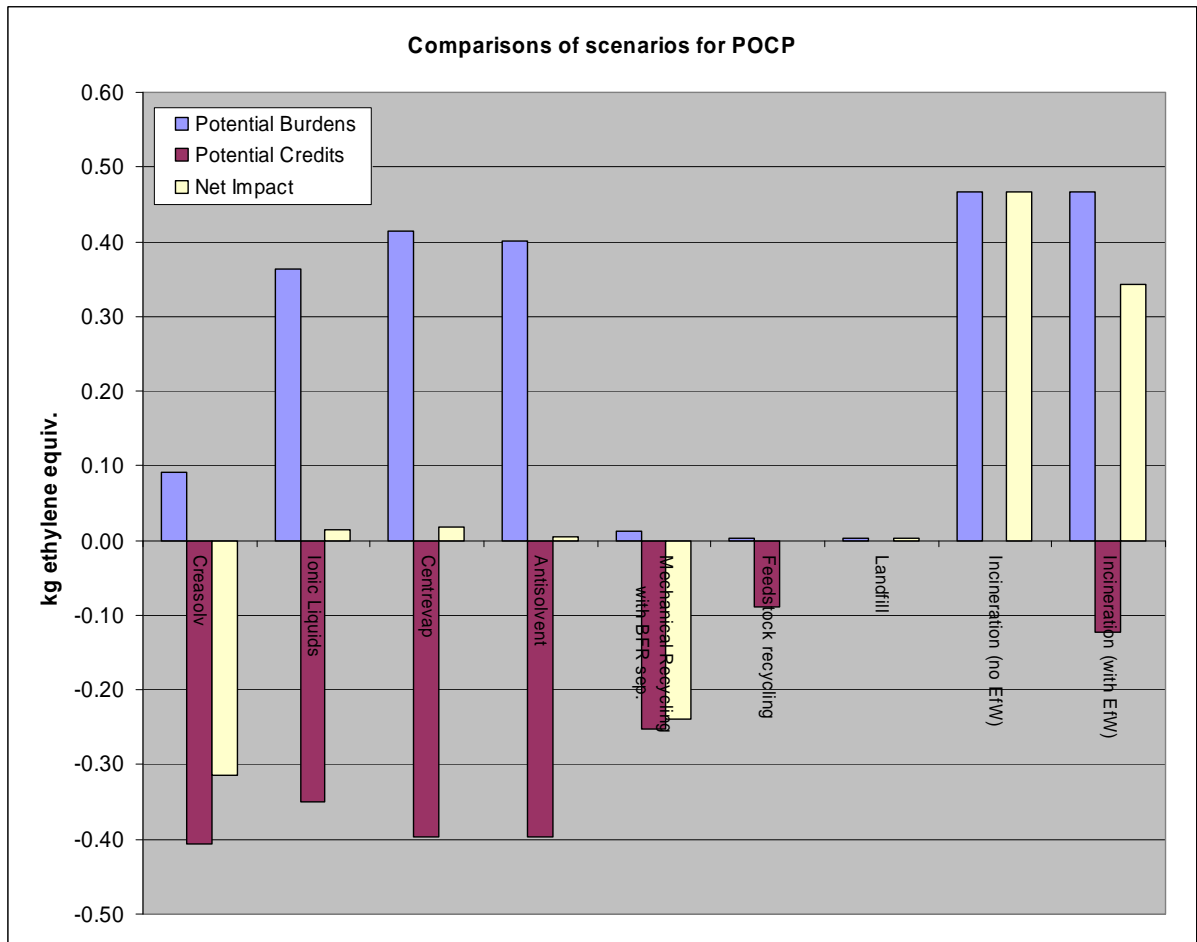
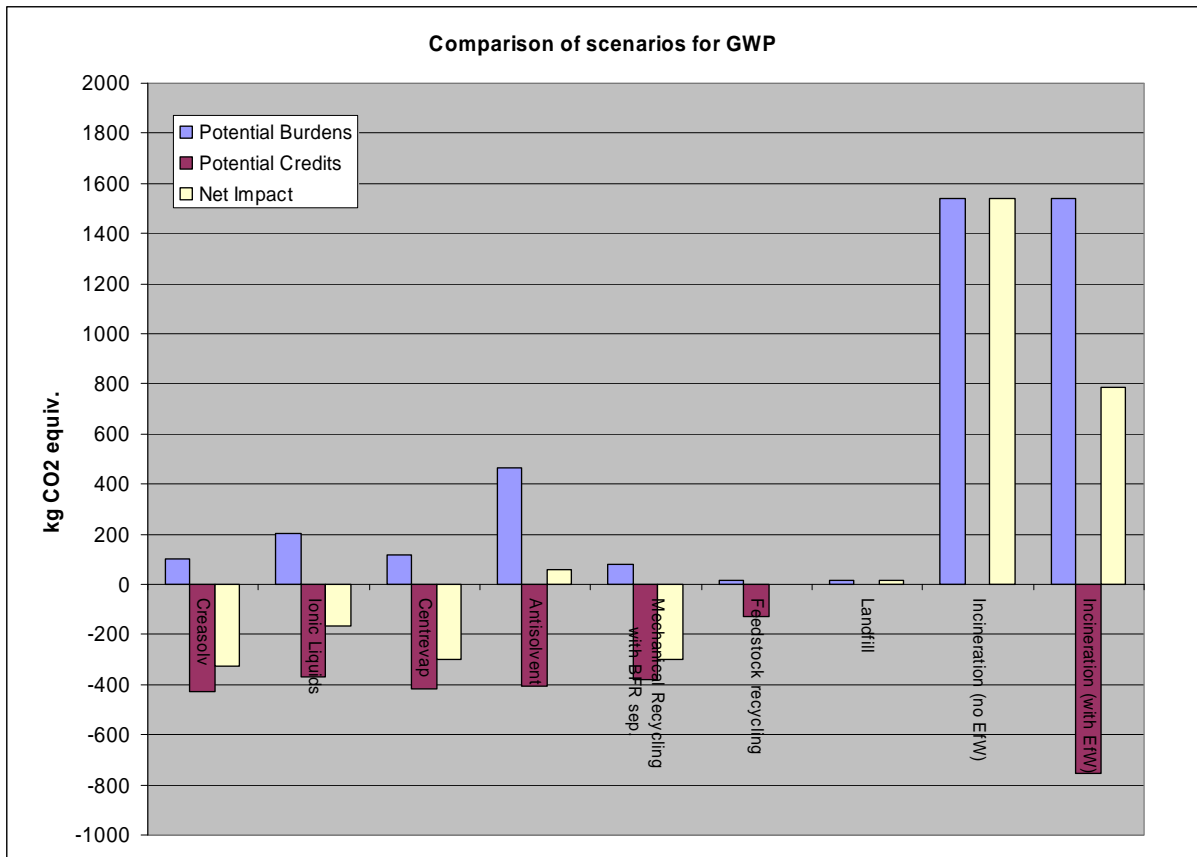
- Primary energy consumption (PE)
- Global Warming potential (GWP)
- Photochemical oxidation potential (POCP)

Detailed assumptions and analysis are presented in Appendix 5A, with the Phase 3 update report attached at Appendix 5F.

The updated analysis for the Creasolv and Centrevap processes alone, which was conducted during Phase 3, did not change the overall conclusions of the Phase 2 analysis so the results are presented in detail at Appendix 5F and are not repeated here.

The graphs below were prepared during Phase 2 of the project and compare the environmental impacts of all of the processes considered in detail during the project in each of the impact categories that were considered:





The quantitative comparison must be interpreted by comparing the relative impacts of each of the process options across each of the impact categories.

In terms of primary energy consumption and global warming potential Creasolv, Centrevap and mechanical recycling with BFR separation appear to provide the best net environmental gain because they avoid the substantial environmental impact of production of a significant quantity of high grade polymer.

In terms of primary energy consumption the environmental burden of these recovery processes (including transport of the materials from point of collection to point of treatment) is less than 20% of the burden of the virgin polymer production process, even when the yield of the recovery process is taken into account.

Centrevap is estimated to be less attractive than Creasolv and mechanical recycling in terms of photochemical oxidation potential because it has potential for greater emissions of volatile solvents.

Incineration with energy recovery does well in terms of primary energy consumption but looks less good in terms of global warming potential and photochemical oxidation potential.

See Appendices 5A and 5F for White Young Green's more comprehensive discussion of these results.

21.4. QWERTY analysis of options

The evaluation compares 4 'solvent routes' for removal of BFR's, namely: Creasolv, Centrevap, Antisolv and Ionic Liquid.

In addition Incineration (with and without energy recovery), the RGS90 process and controlled landfill are included in the evaluation.

Two basic treatment scenarios are evaluated:

- **Scenario 1** is the treatment of 1 kg of styrene based BFR plastics (ABS; ABS/PC and HIPS). It considers only recycling of BFR-containing polymers. The outcomes show which BFR treatment option is preferable for recovery of BFRs from 100% BFR-containing polymers.
- **Scenario 2** is the treatment of 1kg average mix of WEEE polymers with 10% of the above BFR plastics and 90% of non-BFR plastics of the same type. The outcomes show the added value of mechanical separation using conventional and widely-used processes for clean-up and separation of BFR-containing from BFR-free WEEE polymers followed by BFR removal from the 10% BFR-containing fraction in relation to the total material recycling of WEEE plastics.

The eco-efficiency analysis is based on the TU Delft QWERTY/EE approach. This contains a streamlined way of working plus comprehensive environmental and economic datasets on all stages of the end-of-life chain for various EU member states. Specific data on the BFR treatment processes was provided by Axion Recycling Ltd and included in the existing calculation framework.

The results of the initial analysis of all the process options considered in the project were presented in the 2nd interim report for this project. Details of the analysis method and its conclusions, including the initial eco-efficiency analysis for all process options are presented in Appendices 5C-5E.

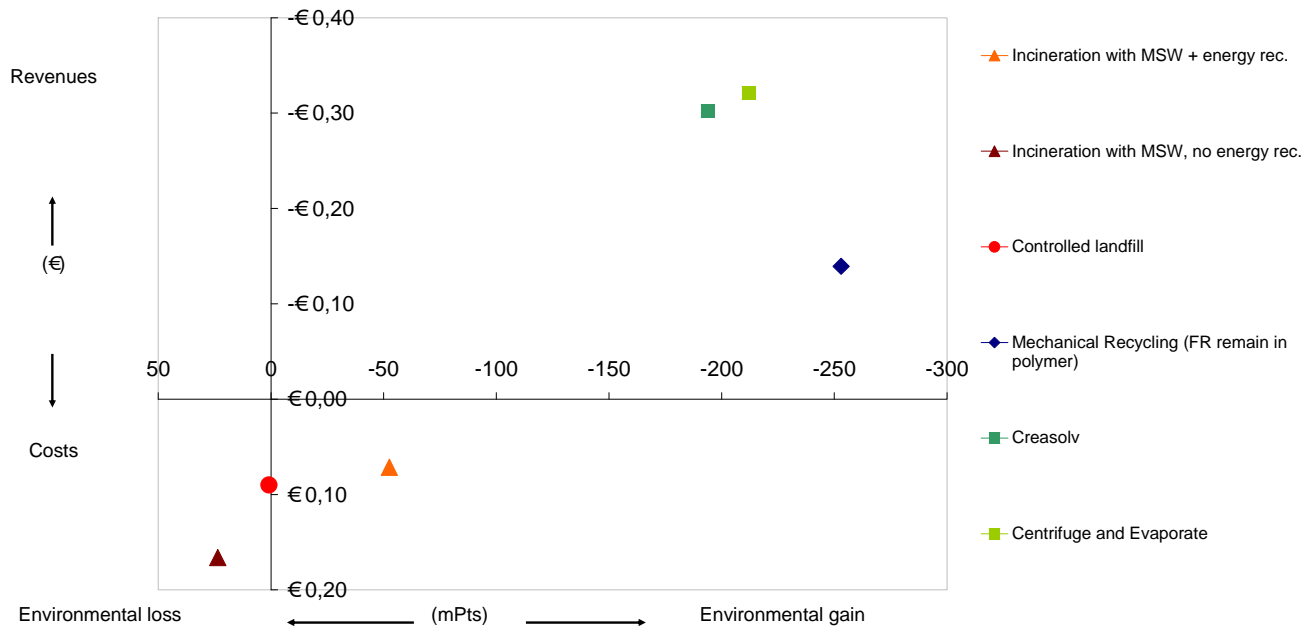
The initial analysis has been updated for this final report to take account of the design enhancements to the Creasolv and Centrevap process options that were made in the final part of the project and also to take account of changes to the economic assumptions that were recommended by the project steering group. A copy of Huisman's update report is attached at Appendix 5F.

Note that this analysis takes no account of the fact that the Centrevap process cannot remove BFRs. The Centrevap process is still included in the assessment because it may be a useful route for removal of other insoluble additives. In situations where Centrevap can remove additives usefully then the QWERTY analysis below is valid. The analysis below is not valid where the Centrevap process is employed to remove BFRs, because it cannot

The table below summarises the changes to the assumptions used for the final eco-efficiency analysis compared to the initial analysis presented in interim report 2:

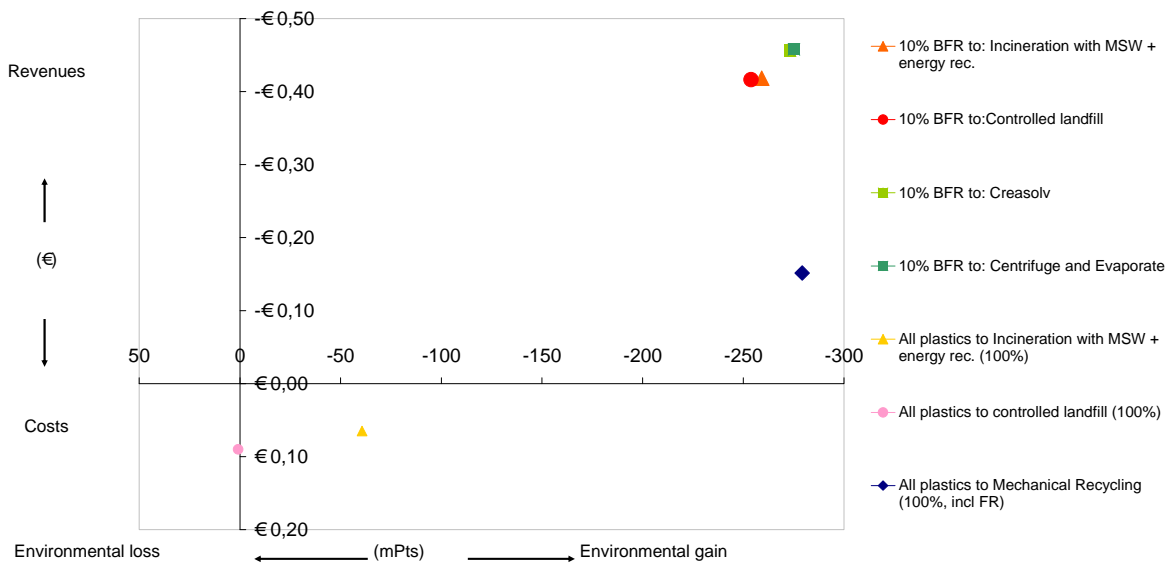
General parameters	Old	New
1. 1 £ =	€ 1,4610 (at 2006-06-07)	€ 1,4590 (at 2006-06-07)
2. Polymer selling price as a percentage of virgin	47%	60%
3. Power consumption	£ 0,06/ kWh	£ 0,07/ kWh
4. Gate fee (avoided incineration with MSW incl. energy recovery)	£ 35/ ton (€ 51,10/ ton)	£ 45/ ton (€ 65,70/ ton)
5. Drying agent	Not used	Neglected as waste materials will be used
6. Update revenues at incineration with energy recovery (higher oil-prices)	Level: \$ 50/ barrel	Level: \$ 70/ barrel
Creasolv		
7. Polymer recovery	99%	77%
8. Energy consumption	350 kWh/ ton	288 kWh/ ton
9. Steam consumption:	1050 kg/ ton	4953 kg/ ton
10. Solvent consumption:	14,4 kg/ hr Creasolv 6,0 kg/ hr G-PS-F	14,1 kg/ hr Creasolv 7,4 kg/ hr G-PS-F
Centrifuge - Evaporate		
7. Polymer recovery:	99%	81%
8. Energy consumption:	117 kWh/ ton	112 kWh/ ton
9. Steam consumption:	2217 kg/ ton	1779 kg/ ton
10. Solvent consumption:	11 kg/ hr Toluene	5,67 kg/hr Toluene

The graph below summarises the updated eco-efficiency comparison among the process routes considered for Scenario 1:



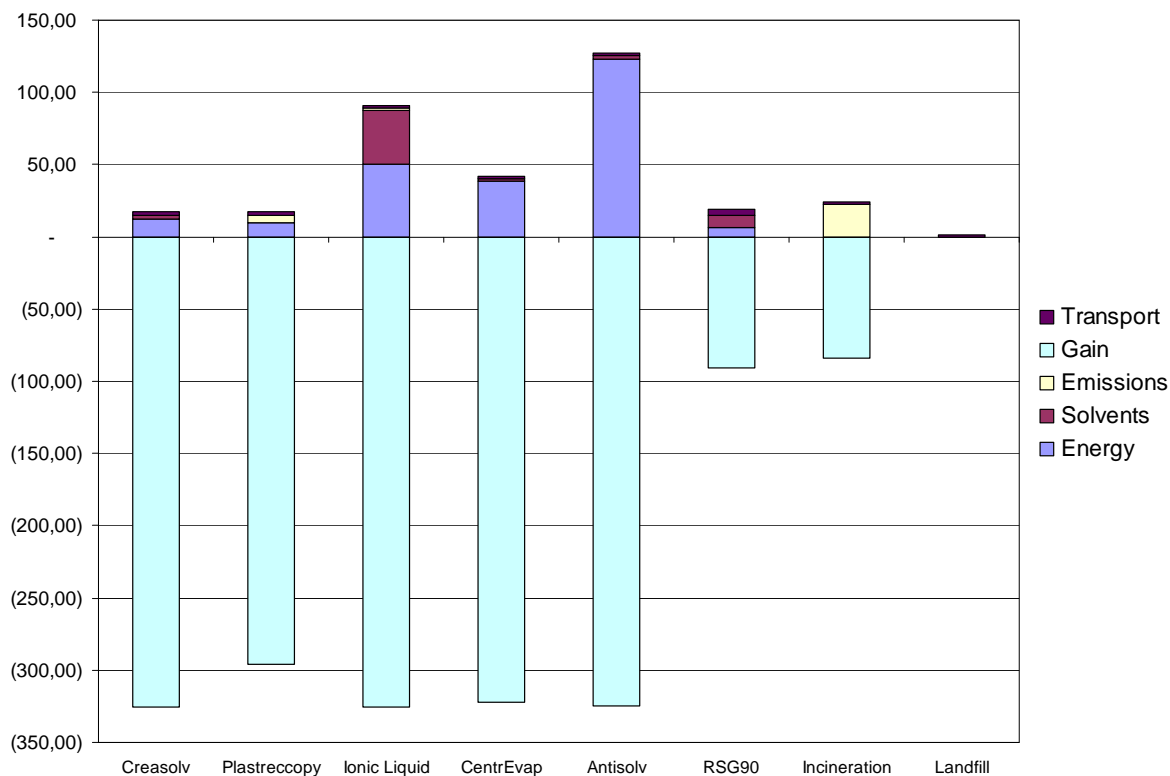
Comparison of environmental impacts and gains – Scenario 1 – BFR polymer treatment process applied to 100% separated BFR-rich WEEE polymer

The following graph presents the same updated analysis for Scenario 2 – which takes account of the full material flow including the mechanical recycling process which is required to separate BFR-containing from BFR-free polymer:



Comparison of environmental impacts and gains – Scenario 2 – Treatment of full WEEE polymer styrenic fraction with the 90% BFR-free fraction processed by mechanical recycling alone and the BFR polymer treatment process applied to 10% separated BFR-rich WEEE polymer

The graph below presents a weighted average of all the environmental impact and gain categories analysed by Huisman in the initial analysis for recycling scenario 2 using the eco-indicator 99 weighting system. This is a weighting system which has been agreed by a panel of European experts on life cycle analysis methods. A similar analysis for scenario 1 is included at Appendix 5E.



Comparison of environmental impacts and gains – Scenario 2 – mechanical separation of WEEE polymer followed by BFR polymer treatment process

The most important conclusion from the analysis of both scenarios 1 and 2 is the clear indication that mechanical separation of BFR-containing from BFR-free polymers followed by the Creasolv option is the most eco-efficient solution for treatment of WEEE polymers that contain BFRs.

The positive environmental and economic result is due to the relatively low consumption of energy and solvent, plus a high recovery of quality polymers. In addition, the scenario 2 results demonstrate the added value of proper treatment of the BFR part of WEEE plastic fractions: enabling proper environmental treatment of the BFR remaining from mechanical recycling of both environmentally as economically valuable non-BFR plastics.

Note that the Centrevap process appears to perform well under this analysis but this is only on the assumption that it can remove additives usefully. As the Centrevap process cannot remove the BFRs targeted by this project the environmental impact comparison for the Centrevap process is not relevant in the context of this project.

More detailed analysis of the options is included at Appendix 5C-F.

The QWERTY analysis conclusions are relatively stable with regard to different environmental impact categories. The outcomes under grouped Human Health, Ecosystem Quality and Resource Depletion classes point in the same direction.

21.5. Analysis

All three assessment techniques (qualitative, conventional quantitative and QWERTY) conclude that, of the treatment solutions considered, the Creasolv process appears to be the best environmental option.

Across almost all impact categories it has the best balance of environmental gain compared to environmental impact.

Although Centrevap appears to perform well it should be ignored in the context of this WRAP project because it will not remove the types of BFR targeted by this project.

Other points to conclude from the analysis:

- Landfilling BFR polymers has low environmental impact (at least in the short to medium term) but because no material is recovered it also has no environmental gain
- Incineration with energy recovery has a net environmental gain across almost all impact categories, although the gain is smaller than the gain from mechanical recycling or from the recovery processes tested in this project. It is certainly a more attractive option than landfill for polymers which are too dirty or commingled to be suitable for mechanical recycling

Disposal to non-ferrous metal smelting processes

Another disposal option which was considered in Phase 1 of this project is use of BFR polymer as a feedstock for non-ferrous metal smelting processes. Previous technical trials and environmental impact analyses have identified that these processes can provide an efficient treatment route for WEEE items that contain a high proportion of metals and polymers additives. Advantages of these processes include:

- Low emissions due to the Bromine content present due to sophisticated flue gas cleaning and good prevention of dioxin emissions.
- Recovery of the lead and antimony content, cadmium is removed effectively as well.
- A good environmental replacement by reducing coke consumption (coke is an environmentally burdening material).

Of special interest is the Umicore non-ferrous smelting process for materials containing both BFR's as well as precious and special metals⁸⁵. Typical examples are printed circuit boards, mobile phone handsets or similar small electronic devices. For such materials a single process can take care of the BFR's while simultaneously recovering valuable metals. Hence an extra separation step for BFR plastics can be avoided, saving costs and optimising metals (particularly precious metals) recovery rates.

Further analysis is required to assess whether the BFR plastics stream considered in this project is really suitable for the Umicore process both technically and economically as the metal content and value is relatively low.

In the initial screening analysis it was concluded that these types of processes are most suited to direct treatment of undismantled small WEEE items such as mobile phones and MP3 players. It is difficult to assess the crossover point where the cost of dismantling and polymer separation is outweighed by the material value of the polymer that is recovered.

An option is to use processes such as the one operated by Umicore to treat the BFR-metal-inert fraction obtained in the solvent routes. The Br and metal content is substantial in this case and it would otherwise be landfilled unless the bromine industry can accept it as a feedstock.

In this context a widened scope of the investigation including preceding steps in the recycling chain could be of interest.

For the longer term, it is advised to further improve the reliability of the environmental impact estimates by:

- repeating the calculations for actual mass and energy balances of full scale operations
- obtaining more accurate environmental impact inventories of the solvents consumed
- examining the potential dioxin formation and release compared to alternative disposal methods such as incineration and landfill and the effects of corresponding preventive measures
- including VOC emissions at solvent recovery when applicable.

⁸⁵ 'Optimising the recycling chain – the contribution of an integrated metals smelter and refinery', Hagelucken, C., Umicore Precious Metals Refining, International Conference on Mining and the Environment, Metals and Energy Recovery, Skelleftea, June 2005.

22. Sensitivity analysis

The sensitivity of the project returns to changes in input and output costs for the shortlisted processes is summarised below:

Input material gate fee or cost	£45/te gate fee			£100/te feed cost		
	60% £560/te	80% £750/te	100% £940/te	60% £560/te	80% £750/te	100% £940/te
Creasolv						
Project IRR	-ve (just)	17%	31%	-ve	-ve (just)	17%
Capital equipment cost (£m)	11.8	11.8	11.8	11.8	11.8	11.8
Working capital required (£m)	5.0	4.0	4.0	5.0	5.0	4.0
Centrevap						
Project IRR	-	-	-	16%	41%	
Capital equipment cost (£m)	-	-	-	6.0	6.0	6.0
Working capital required (£m)	-	-	-	2.5	2.5	
Creasolv-Centrevap						
Project IRR	-ve	11%	24%	-ve	-ve	9%
Capital equipment cost (£m)	14.0	14.0	14.0	14.0	14.0	14.0
Working capital required (£m)	5.0	4.5	4.5	-	-	5.0

The Creasolv and Creasolv-Centrevap processes will provide satisfactory investor returns when they can charge a gate fee of £45/te for the input material and 80% or more of virgin price for the final product.

The Creasolv process should be just profitable at 60% of virgin price for the product but the project IRR will not be attractive.

Centrevap will not remove BFRs but it should be able to compete with exports of BFR-free polymer to China at £100/te and produce attractive returns when treating BFR-free input polymers if it can achieve a product price of 60% or more of virgin polymer price.

The projections used in this analysis assume a process yield of 80%. This estimate is based on removing 10% inerts and 10% BFRs in the case of the Creasolv process and removing 20% inerts in the case of Centrevap. In practice it should be possible to do better than this with careful pre-treatment of the feed. This will improve commercial returns significantly

Improving the process yield for Creasolv to 90% makes the project IRR positive (7%) at a product price of 60% of virgin polymer (£45/te gate fee) and raises the IRR to 27% at a product price of 80% virgin polymer.

23. Conclusions and recommendations

Overall this project concludes that mechanical separation followed by a chemical process that removes brominated flame retardant additives from BFR-containing polymers is likely to be a better environmental and commercial option for treatment of WEEE plastics than landfill, incineration with energy recovery or feedstock recycling

Mechanical separation trials conducted during Phase 2 of the project demonstrated that:

- Identification of BFR-containing polymers by both BFR content and polymer type at WEEE dismantling facilities is technically feasible using relatively low cost, fast-acting hand-held instruments.
- Separation of polymers by type at dismantling facilities adds greatly to polymer value and should be commercially viable for WEEE items over about 0.5Kg weight, providing the UK authorities enforce the requirements of Annex 2 of the WEEE Directive regarding separate treatment of hazardous materials prior to shredding.
- Bulk separation of a clean mixed styrenic polymer fraction from mixed WEEE polymer by density is technically feasible and should be commercially viable in the UK.
- X-ray based polymer chip sorting is extremely promising as a commercially viable technique for bulk separation of polymers containing bromine, and other elements such as chlorine, lead and cadmium.

The more detailed and larger scale test work conducted during Phase 3 of this project has confirmed that the Creasolv process can remove all BFR types commonly found in WEEE polymers close to the 0.1% target set for this project.

The test work in Phase 3 has demonstrated that the Centrevap process option will not be able to achieve the BFR removal target set for this project. It can only remove impurities and polymer additives which are insoluble in the types of solvent required to dissolve the polymer.

However in other respects Centrevap is the most commercially viable solvent-based recycling process that has been tested in the course of this project. It is a flexible, easy to control and robust process design which is capable of removing insoluble polymer impurities and additives down to micron scale with a very short process residence time.

Business modelling indicates that both the Creasolv and Centrevap process options should be capable of operating at a profit and competitive with landfill or incineration under current UK economic conditions at a throughput of 10,000te/yr and with a recycle price of 60% of virgin polymer. However Creasolv is only marginally profitable and the overall project IRR is projected to be negative at this product price.

If demand for high grade recycle grows and the recycle price increases to 80% of virgin polymer then the financial models created for this project indicate that both process options will be attractive investment propositions, provided the Creasolv option can attract a gate fee for segregated BFR-containing input material of about £45/te.

The Creasolv process option will generate attractive returns and be able to pay a positive price of £100/te for its input material to compete with exports to China if it can achieve a sales price of 80-90% of virgin polymer. Recent market research by Axion indicates that end users are increasingly prepared to pay prices in this range for top grade recycles

Both the Creasolv and Centrevap process options should be considered in the context of the overall waste management picture for WEEE. Neither process is appropriate for treating all WEEE polymer types.

Creasolv will remove most BFRs efficiently from most styrenic polymers found in WEEE. It will not remove antimony trioxide.

Centrevap will remove very small insoluble impurities, including fillers and antimony trioxide, from styrenic and other solvent-soluble polymers but it will not remove BFRs because most BFR types are partially soluble in the solvents used in this project.

Both process options require sorting or mechanical separation of WEEE polymers by type before treatment. However, with further process development, both processes offer the potential to produce very high grade recycles, suitable for immediate re-use in new electrical and electronic equipment.

Combining the best features of the Centrevap and Creasolv processes has potential to produce a process which can remove not only the majority of BFRs but also the majority of other fine particulate contaminants, such as antimony trioxide, that are not soluble in the Creasolv solvents. However the capital cost of this option is higher.

WRAP and Fraunhofer IVV have entered into a technology sharing agreement which will make the Creasolv process technology available for license in the UK via WRAP.

Axion Recycling
November 2006
www.axionrecycling.com