A Sustainable solution for HBCDD containing PS foam via A dissolving technique with bromine recovery

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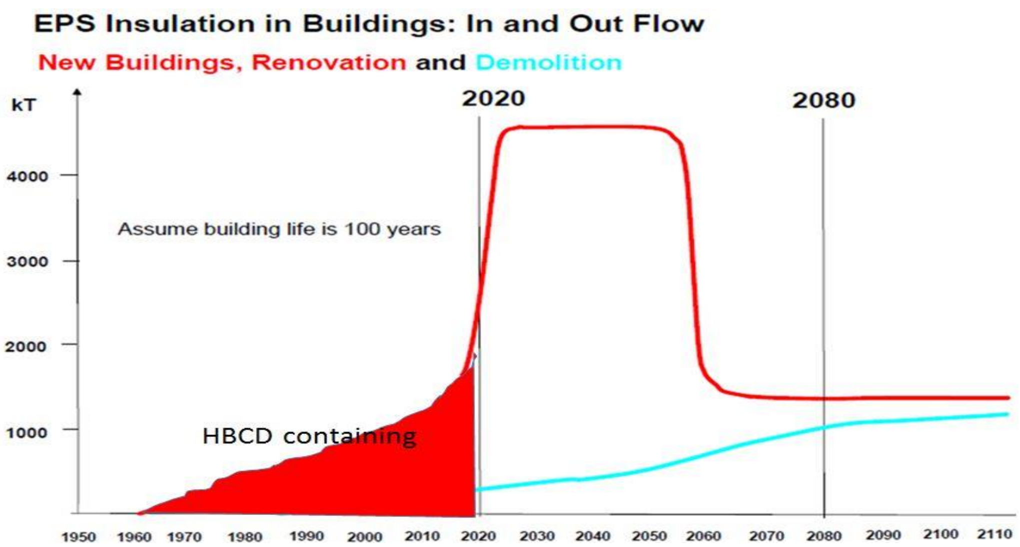
Introduction

Since many years Polystyrene foam is used for insulation of buildings. To enable the foam to fulfill fire safety requirements the Flame Retardant (FR) hexabromocyclododecane (HBCDD) was used. Since the Sixties more than 200.000 mtons of HBCDD were used in this application worldwide. The PS foam will only become waste after demolition of these buildings around 30-100 years after their construction. From 2020 onwards an increasing amount of PS foam waste can be expected, which needs to be safely handled. For a circular economy, the preferred option is material recycling and reuse as it has the smallest environmental footprint.



Picture 1 PS foam used incl HBCDD plus the upcoming release of B&C insulation foam during demolition

Legislation for POPs and SVHC: HBCDD is today classified as a substance of very high concern (SVHC) under REACH. HBCDD was also listed as a persistent organic pollutant (POP) under the UNEP Stockholm convention in 2013 and recycling was prohibited. It is now an Stockholm Convention Annex A substance and its usage, shipment and trade is globally forbidden in those countries that subscribed to this convention. Moreover, all HBCDD waste and its disposal is strictly regulated as HBCDD has to be destroyed in an environmental sound manner. According to the EU POP regulation HBCDD amendment recyclates with more than 100 ppm HBCDD are not allowed to be put on the market [1].

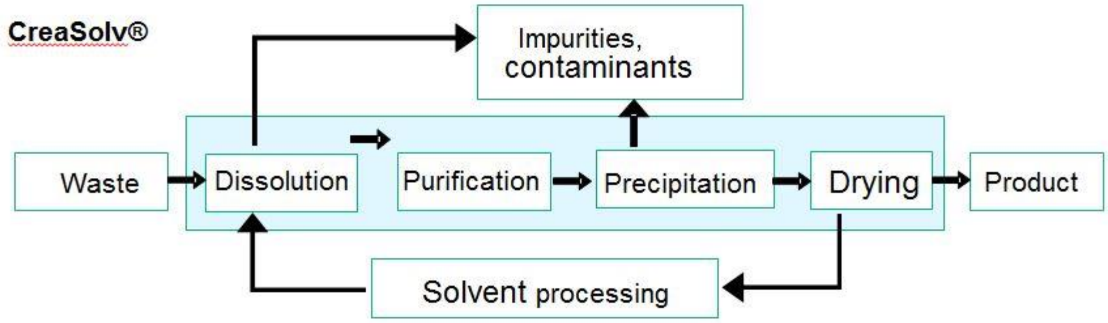
Co-combustion of PS insulation foam during incineration: The Plastics Industry performed an incineration trial with Polystyrene (PS) insulation foam [2]. PS foam was co-incinerated in a full-scale waste incineration plant. The co-feeding of 1 and 2 wt% of PS had no influence on the operation of the plant. The air emission, including dioxins and bromine, was not altered and so was the quality of the solid residues. The obtained destruction efficiency for HBCDD was >99.999%, independent of the amount of added PS . These results clearly indicate a virtually complete destruction of hexabromocyclododecane. Incineration at a state of the art incinerator is currently mentioned as the only environmentally sound solution to manage HBCDD waste, according to the UNEP Basel convention technical guidelines. This means, the preferred way to dispose of HBCDD containing material is advanced solid waste incineration.
However, incineration should not be the only End of Life option for a material. Firstly because across Europe there is insufficient incineration capacity. Secondly because the waste can be re-processed into a raw material. The whole value chain could benefit when polystyrene would be re-used during a second life.

Polystyrene Loop non-profit foundation: With a new initiative from the PS foam value chain a non–profit foundation under Dutch law "PolyStyrene Loop" was founded, with the aim to prepare the construction of a demonstration plant by 2018 for sustainable recycling of End of Life PS foams containing HBCDD. It was agreed to pursue the "CreaSolv® technique" developed and advanced by Fraunhofer IVV to recycle (End of Life) EoL PS foam into Polystyrene as part of the new Circular Economy strategy lauched in Europe in 2015.

The original core team that constituted representatives from Sunpor, Unipol, Synbra, ICL-IP Europe and EUMEPS, has now been extended into a project management core team with representatives from the entire value chain. It has received support from the Flame retardant producers (EFRA), the EPS bead producers (Plastics Europe-EPS/MC), XPS board producers (EXIBA), EPS converters (IVH, Stybenex and EUMEPS) and system applicators (Fachverband WDVS and EAE).

The objective is to demonstrate the technical and economical feasibility of closing the PS loop. This can be achieved by compacting and dissolving the PS foam and separating and destroying the HBCDD while recovering valuable bromine in an existing bromine recovery unit. The recycled PS can be re-used in the same application. The recovered bromine can be used to produce a new comparably sustainable FR (Polymeric FR) for PS foams.
In this way the industry is able to close the loop and to offer an industry concept that can deal with the growing volumes of construction waste, that will finally originate from the demolition of buildings in the coming decades. The purpose of the foundation is to prepare the ground work for a demonstration plant. The plant intends to have a capacity of maximum 3.000 tonnes annually and will be operated by a separately funded entity.

CreaSolv® process (CreaSolv® is a registered trademark of the CreaCycle GmbH, Grevenbroich.): Since 2002 Fraunhofer IVV studied solutions for the recycling of plastics containing additives. As a result of successive projects since early 2000's the CreaSolv® process was developed [3,4,5,6]. The proprietary solvent-based polymer recycling process dissolves PS coming from EPS and XPS waste, while maintaining the polymer chain. It offers a closed loop recycling solution for polystyrene foams within the newly emerging sustainable circular economy. The volume of solvents used is very small in relation to the treated plastic (<1%), because the CreaSolv® formulation is run in a closed-circuit and routinely recycled, whereas the relatively small volume of impurities is separated and concentrated. With its energy balance this process performs very well in environmental impact assessment studies [4].



Picture 2 CreaSolv process flow diagram

In 2004, the CreaSolv® process has been successfully applied to waste EPS [3], however, removal of HBCDD has not been an issue these days and has not been investigated in detail. For reason of some remaining technical issues and insufficient availability of PS foam from demolition the project was put on hold.
Since then performance of the CreaSolv® process has improved thanks to a number of finished research projects including a British WRAP project [4], the German PolyRessource project [6] and the European PolySOLVE project [7]. Project outcomes were an optimized technology on extractive cleaning on the one hand and an improved solvent recovery approach. However, none of these projects produced recycled PS that reached todays' specifications for use in new EPS / XPS producs, either due to HBCDD levels above 100 pmm (in 2004) or due to an incomplete drying of the polymer leading to an increased melt flow index (in 2013). Therefore, the company Sunpor and Fraunhofer IVV decided in 2014 to perform a small technical demonstration trial with the updated CreaSolv® technology, focusing on two targets: a) reaching the 100 ppm limit of the EU POP regulation and b) producing recycled PS ready for use in XPS/EPS production.

Material and Methods

Sunpor provided a sample of waste EPS containing 1.5% HBCDD. In addition, Stryrolution PS 156 F, a virgin PS type that is usually used for production XPS, was purchased from Biesterfeld Plastic GmbH, Germany.
Both samples were subjected to the updated CreasSolv® process in small technical scale (100-200L units) including a dissolution step, a mechanical cleaning unit for removal of undissolved material, an extractive cleaning unit for removal of HBCDD, a drying unit for production of PS granules and an internal solvent recovery unit for applied CreaSolv® formulation.

HBCDD was traced in input, intermediate and product samples in terms of bromine by X-ray fluorescence analysis (Spectro, Spectrolab 2000) and quantified using the standard calibration of the XRF system. Residual levels of HBCDD were quantified in final products by LC/MS. In brief, recycled PS was dissolved in tetrahydrofurane (10 wt%) and precipitated by addition of a fivefold amount of EtOH. Supernatants were separated from the PS gels and subjected to LC/MS analysis after passing a 0.45 µm PTFE syringe filter. LC/MS was performed in SRM mode (QuattroLC, Water) and qiuantifcation of HBCDd was based on an internal standard method (13C-γ-HBCDD) and reported as the sum of α-, β- and γ-HBCDD. Determination of molecular weights (Mw) was based on DIN 55672-1 using gel permeation chromatography (GPC). Determination of residual solvent amounts samples was performed by head-space gas chromatography coupled to a flame ionization detector (HS-GC-FID). Quantification was based on the principle of multiple headspace injection.

Results and discussion:

Separation of HBCDD and polystyrene: The extractive cleaning approach based on the principle of dissolution and precipitation, resulting in a polymer gel separated from an extract phase. XRF analysis of bromine concentrations in extracts and corresponding PS gels revealed a significant removal of the HBCDD from the PS gel, which was repeated until the HBCDD level in PS was reduced sufficiently (below 50 ppm according to customer specifications). This process was first studied in laboratory scale and then upscaled into small technical scale. HBCDD removal was quite well comparable in both scales and HBCDD distributon between extract and PS gel phase could be described very well by a simple distribution model. This allowed calculation of required purification steps from HBCD levels in the input stream.

Overall HBCDD removal was calculated by: Removal (%) = 100% x (1- conc(Br) product/conc(Br)input)
HBCDD removal varied from > 99,6% in technical scale trials to > 99,8% in lab scale trials and describe a sufficient separation of flame retardant and polymer.

Sufficient technical drying of the HBCDD free recycled polystyrene is crucial for production of marketable product that complies with strict specifications. Products from earlier projects ended with slightly too high residual solvent levels, that deteriorated the glass trasition temperature of the recycled material, Tg.
Small technical scale sample production reported here reached residual solvent levels of 600-800 ppm. 500 ppm is the requested performance indicator for industrial scale drying aggregates.

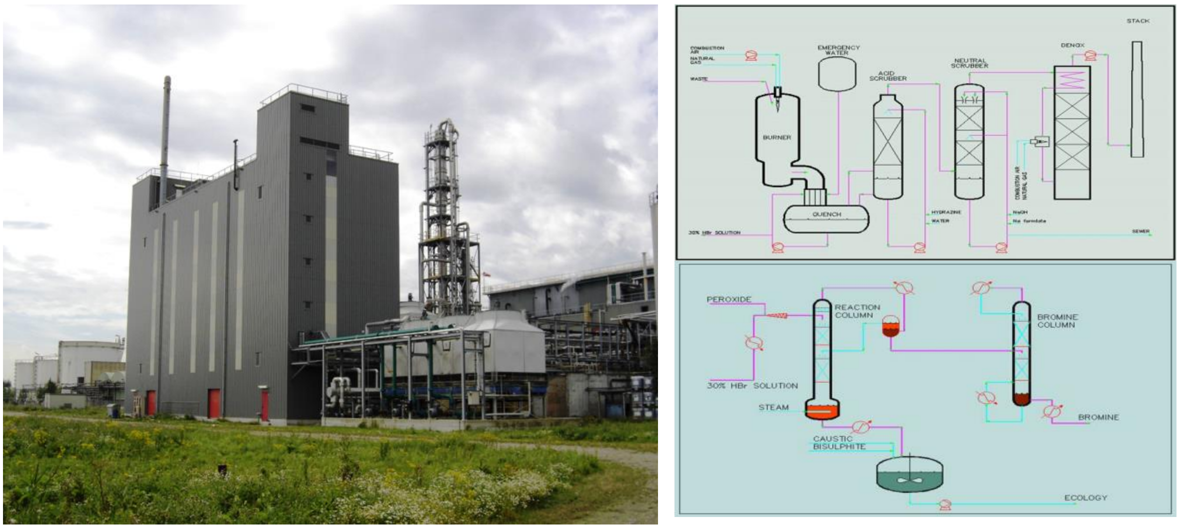
An interesting finding resulted from measuements of the molecular weight distributions (GPC). Mw was significantly higher in product samples compared to the input. This indicates that CreaSolv® removes not only HBCDD from the polymer but also oligomeric degradation products of waste components.

Sample	Mw	Residual solvent	HBCDD
Dimension	g / mol	[%]	[mg/kg]
Input	176.000	-	15.000
Dried PS product	196.000	2	n.d.
Final PS product	196.000	0.06 -0.08	< 50

In 2015 Sunpor Kunststoff GmbH, converted the recycled PS produced at small technical scale into new prime Lambdapor EPS foam. The new polymeric flame retardant polyFR was added to ensure fire safety and subsequently moulded into EPS foam, meeting all specifications for application in e.g. insulation applications.

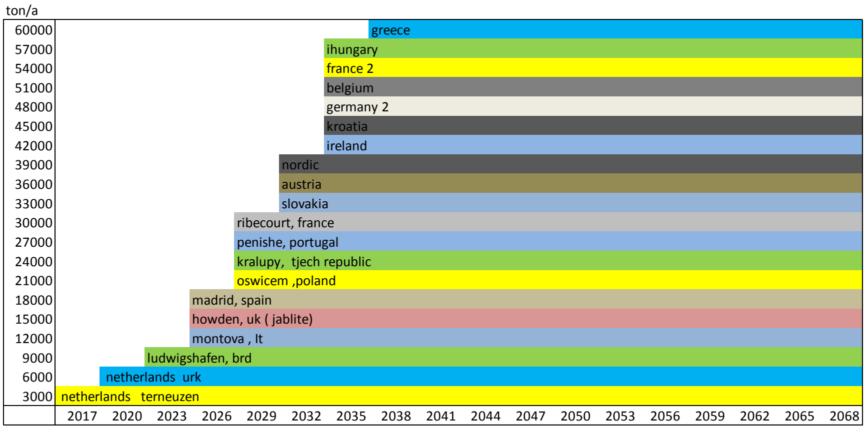
The HBCDD residue from the extraction step is concentrated and considered for treatment in the BRU of ICL IP in Terneuzen with a destruction efficiency higher than 99, 999% for HBCDD, bringing the outcome of the overall destruction efficiency in line with the Basel-Convention Technical Guidelines. Additionally a new PS recyclate containing residual HBCDD far below 100 ppm is obtained.

This proposed demo plant will need to recycle PS foam with HBCDD from building and construction waste into Polystyrene. At the same time a full bromine recovery will be realized in the **existing** Bromine recovery installation (BRU) at ICL-IP in Terneuzen, where the bromine that originated from the restricted Persistent Organic Pollutant (POP) flame retardant HBCDD, will be re-used to make the new polymeric flame retardant.



Picture 3 Existing Bromine Recovery Plant at ICL-IP in Terneuzen

Once more volumes of PS foam are becoming available, this technique can be used and further rolled out all over Europe to handle locally the HBCDD containing foam and convert it into clean PS so that the removed HBCDD can be transported to ICL-IP in Terneuzen for the recovery of the bromine.



Picture 4   Predicted role out upcoming B&C PS foam volumes in Europe

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Keywords:
CreaSolv® process, POP's, SVHC, co-combustion in incineration, HBCDD,Flame Retardants, bromine recovery