C. Development of Technology for Removal of PCBs and Other Substances of Concern (SOCs) from Shredder Residue

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Objective

- Develop viable strategies and technology for the control and minimization or elimination of polychlorinated biphenyls (PCBs) and other substances of concern (SOCs) from recycled automotive materials.

Approach

- Identify efficient and environmentally-acceptable process solutions for removal of contaminants, including PCBs, from materials recovered from shredder residue.
- Define variances in analytical procedures/test results for PCB analysis.
- Accomplishments During this Reporting Period (FY 2006)
- Argonne developed a two-stage cleaning process which in bench-scale tests has consistently produced plastics from the PP/PE product with <2 ppm PCBs.
- Completed tests in the commercial-solvent washing equipment using proprietary solvent-based solutions and in CO_2.
- Cooperated with the Bromine Science and Environmental Forum (BSEF) in preparing the BSEF brochure entitled "Deca-BDE Flame Retardant."

Prior Accomplishments

FY 2005

- Completed the study to explain discrepancies in PCBs analytical results.
- Initiated testing of commercial-solvent washing processes for cleaning plastics.
- Conducted a study to understand the interactions between PCBs and plastics.
- Identified and initiated testing of alternative methods for PCB removal.

FY 2004

- Completed the solvent/detergent screening study for removing PCBs and heavy metals from plastics.
- Completed aqueous cleaning tests in commercially-available equipment.
- Initiated a study to explain discrepancies in PCBs analytical results.

Future Direction

The FY 2007 plan includes:

- Develop experimental design and test Argonne's two-stage process at a larger scale (1-pound test) for the cleaning of the polyolefin concentrate.
- Develop a conceptual design and perform cost analysis of the process.
- Incorporate the process into the overall process design for recovering materials from shredder residue.

Argonne's two-stage process has successfully produced recovered plastics, at least PP/PE materials, with less than 2 ppm PCBs in multiple tests. However, this has been shown only in small-scale experiments. In FY 2007, larger-scale experiments will be conducted to investigate the scalability of the process including required residence time and operating temperatures.

Summary

The objective of this project is to develop techniques and/or technology to identify and/or cost-effectively remove polychlorinated biphenyls (PCBs) and other substances of concern (SOCs) from recycled automotive materials.

SOCs can impact the recyclability of automotive materials in a number of ways. Certainly, their presence in either recycled materials and/or materials source stream impact the overall costs of recovering recyclable materials. In some cases, their presence at parts-per-million levels, such as in the case of PCBs, can prevent the reuse of the recovered materials.

The strategy that is required for control of the SOCs may vary regionally. For example, requirements are different in Europe, North America, and Asia for various SOCs. Strategies for controlling SOCs can also depend on the technology used for recycling the automotive material.

The presence of SOCs in current vehicles and/or in other durable goods that are presently recycled with end-of-life vehicles is likely to impact the materials recycle stream for the foreseeable future. Consequently, the control of certain SOCs will require technology that will effectively remove the SOCs from recovered materials consistent with current regulatory requirements and consistent with the market requirement for the recovered material.

The focus of the work in this project is on the development of options and technology for the removal of PCBs from potentially recyclable materials recovered from shredder residue. PCBs, at parts-per-million levels, are routinely found in shredder residue. The source of the PCBs is not completely understood, but historically it has been associated with liquid PCB-containing capacitors and transformers that inadvertently escape the scrap inspections and control process at the shredders.

Development and Testing of a 2-Stage Process at Argonne

The work done so far on washing of polymers recovered from shredder residue suggests that different washing methods appear to reduce the PCBs concentration down to about 5-10 ppm in a reasonably short time. Further reduction in the concentration of PCBs requires more extensive and prolonged washing in fresh solution, Figure 1. The prolonged washing is further complicated by the adsorption of the cleaning solution by the plastics. This suggests that the PCBs on the plastics are adsorbed by two different mechanisms. First, some are in the oils and dirt that are on the plastics. Second, some of the PCBs are adsorbed on the plastics and they do not desorb easily during washing. We tested this hypothesis in the lab. We conducted washing tests using a non-flammable solvent to wash the plastics under conditions that minimized the absorption of the solvent by the plastics. This reduced the concentrations of PCBs from about 30 ppm to about 5 ppm under a range of operating conditions. The washed plastics were then processed in an environment that induces desorption. The PCBs concentration in several tests was reduced to below 2 ppm. Tests were also conducted where unwashed samples were exposed to the same environment that induces desorption. The PCBs concentration could not be reduced below 2 ppm. We are filing for a patent on the process.

A 2-stage process, based on this concept, has been developed and tested at Argonne which has repeatedly reduced the PCBs concentration in polypropylene/polyethylene samples recovered from shredder residue to less than 2 ppm. We are filing for a patent on the process.

Evaluation and Testing of Solvent-Based Washing Systems

Three companies with equipment and/or proprietary washing solvents and solutions that could potentially be used for non-aqueous removal of PCBs from plastics recovered from shredder residue were identified by Troy Polymers, Inc. (TPI):

- Environmental Technology Unlimited (Wilmington, North Carolina);
- Cool Clean Technologies, Inc. (Burnsville, Minnesota); and
- itec Environmental Group, Inc. (Oakdale, California).

Each company was supplied with a sample of plastics with the determined concentration of PCBs of 11 ppm. Samples were washed at the three companies, and the washed samples were evaluated for PCB levels.

Environmental Technology Unlimited uses a proprietary METHEX solvent-based system and aqueous-based systems. Environmental Technology Unlimited performed six treatments of shredder residue plastics, and five out of the six washed samples reduced the PCBs concentration to below 2 ppm. The METHEX solvent-based system was superior to the aqueous system. Unfortunately, the company does not have equipment to conduct large-scale testing of the process using plastics.

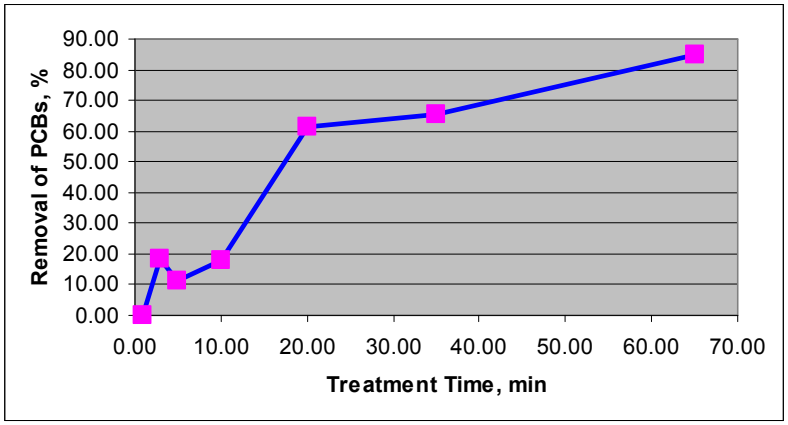

Figure 1. Removal of PCBs with time using a non-flammable organic solvent.

Cool Clean Technologies technology used CO_2 only. The washing failed to remove the PCBs. itec Environmental Group reduced PCB levels in the plastics from 11 ppm to 2.8 ppm via solvent washing; no CO_2 treatment, which normally follows the basic process, was used.

Further testing was conducted by itec in their new facilities in California, using plastics recovered by the Argonne process. The plastics were washed using itec's proprietary solvent and then with liquid CO_2. Two samples received by Argonne were analyzed and both showed residual PCBs concentration on the order of 5 ppm. Another series of trials were conducted at itec using different process conditions. Analysis showed the residual concentration of PCBs was still higher than 2 ppm.

Evaluation and Testing of Commercially-Available Aqueous-Based Washing Systems

Before testing the solvent-based systems, large-scale cleaning/washing tests were conducted using plastics from shredder residue by means of aqueous solutions and a surfactant previously identified earlier as the most promising from among many tested. The objective was to identify the limitations of the various types of existing washing equipment. Testing was done by using an ALMCO rotary-drum washer equipped with a dryer and SeKoN centrifuge equipment. The tests were carried out on about 100 lbs of plastic chips each. The particles were between 0.2 and 0.5 in. in size. Under a CRADA contract, GraPar Corporation built, for Troy Polymers, Inc. (TPI), and tested a specially-designed machine that has a design capacity of about 300 lbs/hour of plastics. TPI conducted further testing on this machine in its facilities.

In each of these tests, the washed material was "visually" clean. However, PCBs analyses were highly variable and indicated that, in some cases, the PCBs concentration had increased after washing. As a result, it was determined that the PCBs analysis procedures should be reexamined, as is discussed in the next section.

The results suggest that existing aqueous-based equipment, as is, is not likely to reduce the concentration of PCBs to acceptable levels. Modifications are necessary to wash small chips (1/8 to 1/2 in.) of plastics — such as what will be recovered from shredder residue.

Evaluation of the Variability of PCB Sampling and Analytical Procedures

The large variability in the analytical results raised questions about the analytical sampling and analyses procedures. Therefore, experiments were performed to develop an understanding of the variability in PCB analytical procedures, explain the variability in the results, and develop a consistent procedure for the determination of the concentration of PCBs.

The variability may be due to a number of factors including sample size, plastics particle size, PCBs extraction procedure, analytical procedures, and/or interference from other compounds. A one-day seminar was held and attended by analytical experts from the United States and overseas to develop recommendations for improved sampling and analysis techniques specific to plastics chips recovered from shredder residue.

To investigate the possible interference of phthalates in the PCBs analysis, a sample of plastics chips derived from shredder residue was thoroughly mixed and then divided into four parts. The first part was analyzed by using gas chromatography and an electron-capture detector (GC-ECD) and by using gas chromatography/mass spectroscopy (GC/MS). The other three parts were spiked with different quantities of phthalates, as shown in Table 1, and the spiked samples were analyzed by using the same two methods. The results show no interference of the phthalates in the PCBs analysis. Interestingly, the GC/MS results were always higher than the GC-ECD results.

Table 1. Effect of phthalates on PCBs analysis.

Weight-Percent of Phthalates added	PCBs Concentration (ppm) by GC/ECD	PCBs Concentrations (ppm) by GC/MS
0	4.6+/-0.3	7.9+/-1.0
0.5	4.7+/-0.3	7.4+/-0.2
1.0	5.1+/-0.6	7.0+/-0.4
2.5	4.8+/-0.3	7.4+/-0.3

To investigate the effects of plastics particle size on extraction efficiency of PCBs, a series of laboratory experiments were conducted at TPI on 300-g samples of plastics with two different particle sizes (one made of chips about 0.2 in. in size and the other was granulated to about 0.04 to 0.08 in. in size). Typically in PCBs analyses, extractions are done on a few grams of material, even though the dirt, oil, and the PCBs are not evenly distributed on the shredder-residue plastics.

Samples of the plastics before and after washing were analyzed directly by three different laboratories by using standard PCBs analytical procedures. Extracts from nine sonications of 300-g samples were also analyzed for PCBs by three laboratories. The results (Tables 2–5) show that:

1. The three labs are fairly consistent for each set of samples.

Table 2. Concentration of PCBs (ppm) in plastics before and after extraction with hexane (granulated and ungranulated) — analysis by standard PCBs analysis procedures.

	Aroclor 1232	Aroclor 1242	Aroclor 1254	Total
Designation	ppm	ppm	ppm	ppm
	Laboratory #1			
Ungranulated before extraction	10.34 +/-1.53	N/D	1.27 +/- 0.29	11.6 +/- 1.51
Ungranulated after extraction	1.06 +/- 0.32	N/D	0.07 +/- 0.01	1.13 +/- 0.32
Granulated before extraction	4.54 +/- 0.84	N/D	0.06 +/- 0.16	5.14 +/- 0.98
Granulated after extraction	0.54 +/- 0.33	N/D	0.07 +/- 0.01	0.60 +/- 0.34
	Laboratory #2			
Ungranulated before extraction	N/D	8.69 +/- 1.02	N/D	8.69 +/- 1.02
Ungranulated after extraction	N/D	2.8 +/- 0.98	N/D	2.8 +/- 0.98
Granulated before extraction	N/D	5.31 +/- 2.04	N/D	5.31 +/- 2.04
Granulated after extraction	N/D	0.75 +/- 0.18	N/D	0.75 +/- 0.18
	Laboratory #3			
Ungranulated before extraction	N/D	9.93 +/- 4.67	N/D	9.93 +/- 4.67
Ungranulated after extraction	N/D	1.57 +/- 0.17	N/D	1.57 +/- 0.17
Granulated before extraction	N/D	3.07 +/- 0.26	N/D	3.07 +/- 0.26
Granulated after extraction	N/D	0.68 +/- 0.27	N/D	0.68 +/- 0.27

Table 3. Concentration of PCBs in the ungranulated samples, as calculated from the analysis of the hexane solution extracts.

	Aroclor 1232	Aroclor 1242	Aroclor 1254	Total
Designation	ppm	ppm	ppm	ppm
	Laboratory #1			
Extract 1	8.67 +/- 0.87	N/D	1.02 +/- 0.29	9.69 +/- 0.99
Extract 2	4.59 +/- 1.52	N/D	0.28 +/- 0.05	4.86 +/- 1.49
Extract 3	0.51 +/- 0.09	N/D	0.14 +/- 0.01	0.65 +/- 0.10
Total	**13.76 +/- 2.47**	**N/D**	**1.43 +/- 0.34**	**15.19 +/- 2.57**
	Laboratory #2			
Extract 1	N/D	7.62 +/- 0.58	N/D	7.62 +/- 0.58
Extract 2	N/D	1.44 +/- 0.04	N/D	1.44 +/- 0.04
Extract 3	N/D	0.62 +/- 0.04	N/D	0.62 +/- 0.04
Total	**N/D**	**9.67 +/- 0.65**	**N/D**	**9.67 +/- 0.65**
	Laboratory #3			
Extract 1	N/D	6.56 +/- 0.67	N/D	6.56 +/- 0.67
Extract 2	N/D	1.52 +/- 0.23	N/D	1.52 +/- 0.23
Extract 3	N/D	0.64 +/- 0.03	N/D	0.64 +/- 0.03
Total	**N/D**	**8.71 +/- 0.92**	**N/D**	**8.71 +/- 0.92**

Table 4. Concentration of PCBs in the granulated samples, as calculated from the analysis of the hexane solution extracts.

	Aroclor 1232	Aroclor 1242	Aroclor 1254	Total
Designation	ppm	ppm	ppm	ppm
	Laboratory #1			
Extract 1	18.62 +/- 8.99	N/D	2.20 +/- 0.61	20.81 +/- 9.59
Extract 2	2.30 +/- 2.56	N/D	0.25 +/- 0.06	4.86 +/- 1.49
Extract 3	0.62 +/- 0.14	N/D	0.11 +/- 0.01	0.65 +/- 0.10
Total	**21.52 +/- 11.69**	**N/D**	**2.55 +/- 0.67**	**24.07 +/- 12.25**
	Laboratory #2			
Extract 1	N/D	7.24 +/- 0.34	N/D	7.24 +/- 0.34
Extract 2	N/D	1.01 +/- 0.03	N/D	1.01 +/- 0.03
Extract 3	N/D	0.42 +/- 0.03	N/D	0.42 +/- 0.03
Total	**N/D**	**8.67 +/- 0.40**	**N/D**	**8.67 +/- 0.40**
	Laboratory #3			
Extract 1	N/D	6.29 +/- 1.98	N/D	6.29 +/- 1.98
Extract 2	N/D	1.10 +/- 0.06	N/D	1.10 +/- 0.06
Extract 3	N/D	0.48 +/- 0.03	N/D	0.48 +/- 0.03
Total	**N/D**	**7.87 +/- 2.06**	**N/D**	**7.87 +/- 2.06**

Table 5. Comparison of PCBs concentration (ppm) in the starting plastics samples by direct analysis and by calculation based on the amounts in the hexane extracts.

Plastics Sample	PCB Concentration by Direct Analysis	PCB Concentration Calculated from PCBs in the Hexane Extracts
Ungranulated, Lab-1	11.6 +/- 1.51	15.19 +/- 2.57
Ungranulated, Lab-2	8.69 +/- 1.02	9.67 +/- 0.65
Ungranulated, Lab-3	9.93 +/- 4.67	8.71 +/- 0.92
Granulated, Lab-1	5.14 +/- 0.98	24.07 +/- 12.25
Granulated, Lab-2	5.31 +/- 2.04	8.67 +/- 0.4
Granulated, Lab-3	3.07 +/- 0.26	7.87 +/- 2.06

2. Direct analysis of the samples from the three labs showed that the concentration of PCBs in the granulated plastics was about 5 ppm, and for the un-granulated, it was 10 ppm. Obviously, the granulated samples have larger surface area per unit mass than the other samples. Therefore, more efficient extraction of PCBs from the plastics would be expected in the case of the granulated chips. Because this was not the case, the results indicate that the particle size does not affect the PCB results. Further, the results indicate that the PCBs are on the surface of the plastics and not absorbed in the plastics. After extraction, the samples all had less than 2 ppm of PCBs, except for one sample that showed 2.8 ppm.

3. Calculation of the concentration of PCBs in the original samples based on the determined PCBs in the hexane extracts (prepared via 9 sonications of 300-g samples) showed that the concentrations of PCBs in the granulated samples were comparable with those of the un-granulated samples. These results further indicate that the PCBs are predominantly on the surface of the plastics and not absorbed in the plastics, otherwise the granulated samples would have shown higher concentrations.

In addition, two of the laboratories identified Aroclor 1242 as the only PCB present, while the third laboratory identified Aroclors 1232 and 1254 as the only two present. TPI also conducted an analysis of various plastics samples by using GC-ECD and GC-MS methods. The results are compared in Table 6. Results from the two methods are in reasonable agreement, even though the GC-MS method showed higher values.

Evaluation of Soxhlet Method for PCBs Extraction

Successful commercialization of technology for recovering polymers from shredder residue depends on a reliable and inexpensive technique to analyze samples for PCBs in the field. The U.S. EPA and European protocols for PCBs analysis were reviewed and experiments were conducted to understand the requirements for on-site analysis. A Soxhlet-based method appears to be appropriate for testing because of its simplicity and because it is among the methods specified in both the U.S. EPA protocols and in the European protocols (Table 7). Limited experiments to define the operating conditions for the Soxhlet method were conducted. The results are discussed below.

Selection of a Solvent

Two solvents were tested: hexane and toluene. Three 120-g samples were extracted with hexane for 8 h, and another three 120-g samples were extracted with hexane for 24 hours. Similarly, three 120-g samples were extracted with toluene for 8 h, and another three 120-g samples were extracted with toluene for 24 hours. All extractions were carried out while maintaining the siphoning time at 8–10-min intervals. This procedure resulted in 24 samples of extracts and 12 samples of extracted plastics that were analyzed, Table 8. The results indicate that hexane is a better solvent than toluene.

Table 6. Comparison of PCBs analysis using GC-ECD and GC-MS methods (extraction was carried out using hexane at 2,000 PSIA and 100°C).

Sample Type	PCB Concentration, Using GC-ECD (ppm)	PCB Concentration, Using GC-MS (ppm)
Ungranulated Chips	7.55	9.67
Ungranulated Chips	3.70	5.07
Ungranulated Chips	1.50	3.3
Ungranulated Chips	1.35	2.66
Granulated Chips	7.56	9.37
Granulated Chips	0.93	1.82
Granulated Chips	0.82	2.11
Hexane Solution	9.93	9.50
Hexane Solution	8.3	11.13
Hexane Solution	1.41	1.72
Hexane Solution	0.78	0.92
Hexane Solution	0.53	0.65

Table 7. Protocols for PCBs analysis.

Parameter	European Protocols	U.S. EPA's Protocols	Recommended Protocols
Particle size (mm)	0.5	Not specified	1
Sample size for extraction (g)	3	30	30
Extraction equipment	Soxhlet	Sonication Soxhlet Pressurized fluid	Soxhlet
Extraction time	Not specified	Not specified	>/= 4 h Siphoning cycles at 8–10-min intervals
Solvent	Toluene	Hexane 50/50 Hexane/acetone 50/50 Methylene chloride/acetone	Hexane
Analytical method	MS	GC/ECD MS	MS
Quantification method	6 congeners multiplied by 5	Aroclors	Aroclors

Table 8. Results of the extractions of the 120-g samples with hexane and toluene.

Solvent	Extraction Time (h)	Average PCBs in Extract (ppm)	Standard Deviation (ppm)	Average PCBs in Extracted Plastics (ppm)	Standard Deviation(ppm)
Hexane	24	9.4	1.5	N.D	0
Hexane	8	9.3	0.8	N.D.	0
Toluene	24	9.8	2.4	1.4	0.2
Toluene	8	9.7	0.9	3.0	0.6
Hexane	4	14.5	2.9	N.D. in samples no. 1 and 2; 1.0 in no. 3	1.0

Determination of Extraction Time

Three additional 120-g samples were extracted with hexane for 4 hours each. This procedure resulted in six samples of extracts and three samples of extracted plastics that were analyzed. The results are given in Table 8 and indicate that a Soxhlet extraction time of 4 hours is adequate because it reduced the PCBs concentration in the extracted plastics to below the detectable limits in two of the three samples and reduced it in the third to 1 ppm, even though these samples apparently had more PCBs initially, as evidenced by the higher level of PCBs in the solvent.

Determination of Adequate Sample Size

In addition to the six 120-gram samples extracted for 24 hours discussed above, six additional 60-gram samples and six additional 30-g samples were processed and sampled in the same manner as before (24-hour extraction time and same siphoning intervals) by using hexane. The results are summarized in Table 9. The results indicate that a sample size of 30 g appears to be adequate.

Sample preparation was also investigated. The results indicated that a well-mixed plastics sample of at least one pound should be granulated to a size of 1 mm and mixed before sampling is done.

Comparison of the U.S. EPA and the European Quantification Methods

Four of the extracts from the 120-g samples that were extracted with hexane for 24 hours and two of the 120-g samples that were extracted with hexane for 8 hours were also quantified by using the European method. The results were essentially identical within analytical errors (Table 10). These results lead to the following conclusions:

1. A conventional Soxhlet extractor using hexane is effective for PCBs extraction from plastics.
2. A total extraction time of 4 hours with siphoning intervals of 8–10 min is adequate for complete extraction of the PCBs.
3. The EPA and the European quantification methodologies yield very close results.

Publications

Overview of Washing Systems for Commercial Cleaning of Plastics Separated from Automotive Shredder Residue, Sendijarevic, I.; Sendijarevic, V.; Winslow, G.R.; Duranceau, C.M.; Simon, N.L.; Niemiec, S. F.; and Wheeler, C.S., SAE Paper No. 2005-01-0851.

Screening Study to Evaluate Shredder Residue Materials, Sendijarevec, V.; Simon, N.; Duranceau, C.; Winslow, G.; Williams, R.; Wheeler, C.; Niemiec, S.; and Schomer, D., SAE Paper No. 2004-01-0468.

Table 9. Results of the 24-h extractions with hexane of different size samples.

Sample size (g)	Average PCBs in Extract (ppm)	Standard Deviation (ppm)	Average PCBs in Extracted Plastics (ppm)	Standard Deviation (ppm)
30	10.8	1.9	N.D	0
60	25.5	12.6	N.D.	0
120	9.4	1.5	N.D.	0

Table 10. Comparison of the U.S. EPA and the European quantification methods.

Extraction Time (h)	PCBs According to the EPA Method (ppm)	PCBs According to the European Method (ppm)
24	10.8	9.8
24	9.8	10.9
24	8.0	10.7
24	11.2	11.5
8	11.7	12.3
8	10.8	10.8

[i] One of the formal consortia of the United States Council for Automotive Research (USCAR) set up by the "Big Three" traditionally U.S.-based automakers to conduct joint pre-competitive research and development.