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RECOVERY AND SEPARATION OF HIGH VALUE-PLASTICS FROM DISCARDED HOUSEHOLD APPLIANCES

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Abstract

Argonne National Laboratory is conducting research to develop a cost-effective and environmentally acceptable process for the separation of high-value plastics from discarded household appliances. The process under development has separated individual high purity (greater than 99.5%) acrylonitrile-butadiene-styrene (ABS) and high-impact polystyrene (HIPS) from commingled plastics generated by appliance-shredding and metal-recovery operations. The process consists of size-reduction steps for the commingled plastics, followed by a series of gravity-separation techniques to separate plastic materials of different densities. Individual plastics of similar densities, such as ABS and HIPS, are further separated by using a chemical solution. By controlling the surface tension, the density, and the temperature of the chemical solution, we are able to selectively float/separate plastics that have different surface energies. This separation technique has proven to be highly effective in recovering high-purity plastics materials from discarded household appliances. A conceptual design of a continuous process to recover high-value plastics from discarded appliances is also discussed. In addition to plastics separation research, Argonne National Laboratory is conducting research to develop cost-effective techniques for improving the mechanical properties of plastics recovered from appliances.

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Introduction

It is estimated that more than 2.8 million tons of household appliances (such as refrigerators, freezers, washers, dryers, ranges, dishwashers, water heaters, dehumidifiers, and air conditioners) are being discarded annually and become available as obsolete scrap (1). Discarded appliances, commonly called "white goods" contain significant quantities of recyclable materials; however, not all appliances are recycled for their scrap value. In 1993 only about 62% of the discarded appliances were recycled (2). The recycling of appliances is driven primarily by the value in the steel contents. To recover the steel, appliances go through a shredding or disassembly operation. Currently metals represent more than 75% of the total weight of the processed scrap.

A by-product of the metal recovery operation is the nonmetallic fraction, which is rich in plastics and is commonly called "fluff". The fluff is disposed of in landfills at a cost of \$10-\$40 per ton. The cost of disposal of the shredder fluff has become a significant cost element of appliance-shredding and metal-recovery operations, and current trends suggest that the use of plastics in appliance manufacturing will continue to increase, at the expense of metals.

The use of plastics in large household appliances has grown from less than 1% of material content in the 1960s to as much as 25% by weight today (3). The amount of plastic used in the appliance manufacturing industry now totals more than 1.2 billion pounds (4). In 1991, the largest applications of plastics in household appliances were in refrigerators (241 million pounds) and washing machines (134 million pounds) (4). These two appliances account for more than 45% of all plastics consumed by household appliances. Table I shows the major high-volume plastics used in appliance manufacturing. The most common household appliance, the refrigerator, has gone through considerable design changes over the years to improve its operating efficiency. Technological innovations in the engineering and applications of plastics materials have been major contributors to the increasing value in appliances. The increasing use of plastics and the changes in materials composition in refrigerators as a function of time are shown in Table II.

Table I Consumption of Specific Plastics in Appliance Manufacturing

	Annual Consumption (million pounds)		
Plastic	1980	1985	1990
ABS	143	180	213
Polypropylene	86	115	175
Polystyrene	115	122	225
Polyurethane	110	120	154
PVC	71	98	124
Other	257	283	343
Total	782	918	1,234

Source: Society of the Plastics Industry

Table II Materials Used in Refrigerator Manufacturing (lb/unit)

Materials	1972[a] (1991)[b]	1980[a] (1999)[b]	1988[a] (2007)[b]
Steel	147.6	138.3	129.0
Compressor	30.3	28.2	26.0
Plastics	14.0	21.6	29.0
Fiberglass	17.9	8.9	0.0
Polyurethane Foam	4.0	11.0	18.0
Aluminum	7.9	10.4	13.0
Copper	0.6	0.8	1.0
Miscellaneous	5.7	6.8	8.0
Total	228.0	226.0	224.0

[a] Year of manufacture

[b] Year of disposal

Source: American Plastics Council

As the portion of metals in appliance materials is reduced and the plastic contents increase, the economic incentive for using appliance scrap as a source of steel is also reduced, since the plastics fraction constitutes a negative value to the shredding operation. Plastic materials used in appliance manufacturing are of high quality and have the potential of being recycled in high-value applications. The key plastic materials contained in appliances include acrylonitrile-butadiene-styrene (ABS), high-impact polystyrene (HIPS), polypropylene (PP), polyethylene (PE), polyvinyl chloride (PVC), and nylons. Current technologies for recovering individual high-purity plastics, such as ABS and HIPS, are not cost-effective, and as a result, all plastics in appliance fluff end up in landfills. The ABS and HIPS, which are the most widely used plastics in appliances, are both high-value materials (virgin ABS:$1.20/lb, virgin HIPS:$.50/lb), and these two materials are currently targeted for recycling. ABS and HIPS are not compatible, and experiments conducted by Argonne National Laboratory indicate that the presence of small quantities of one in the other can result in significant degradation of properties. These experiments showed, that when 2.5 wt% virgin HIPS was added to virgin ABS, the Izod impact strength of the ABS dropped by about 45% and the tensile strength dropped by about 20% (see Figure 1). These findings suggest that in order to preserve the properties and consequently the market value of the recovered plastics, the separation technology must be capable of producing high-purity plastics (above 99% purity).

Argonne's research in plastics separation technologies is focussed on the development of processes for recovering high-purity ABS and HIPS materials from appliance fluff. This paper reports some of the results of this research.

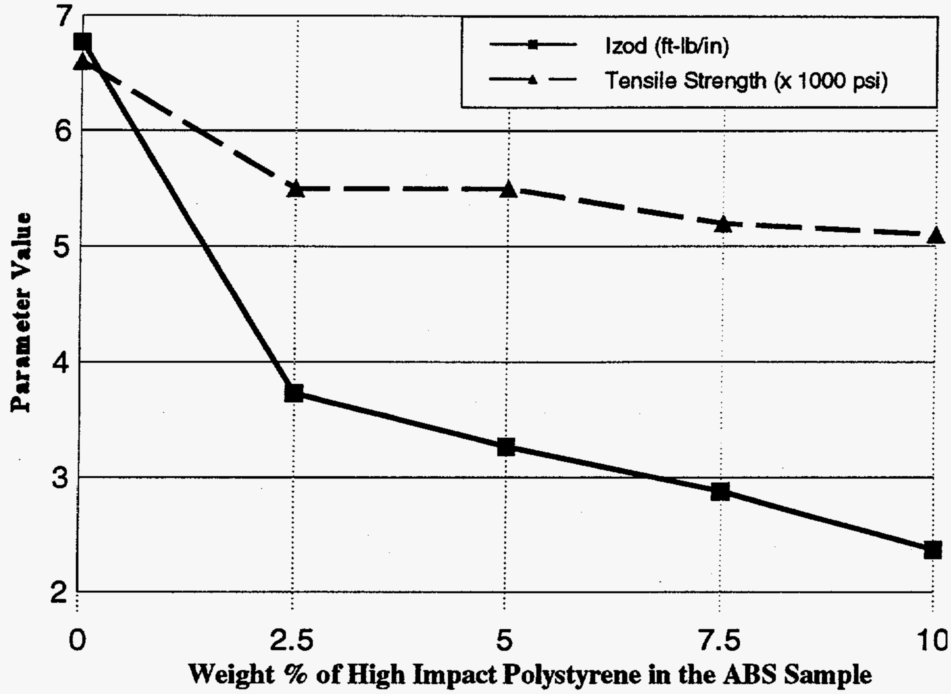

Figure 1 - Degradation of Virgin ABS Properties Resulting from HIPS Contamination

Potential Methods for Separating Plastics

Our first task in developing a process for separating pure ABS and HIPS was to evaluate different potentially viable methods to achieve this objective. In our research, we identified a number of possible methods, including optical color sorting (5), x-ray fluorescence detection (6), hydrocyclone classification, selective dissolution (7,8), and melt/stick.

Optical color sorting was ruled out because both HIPS and ABS can be present in the same colors. X-ray fluorescence detection methods are used mostly for household-plastic waste-stream separation to recover polyethylene goods and polyethylene terephthalate (PET) bottles. Selective dissolution techniques are likely to be costly when used to dissolve a plastic that is present in the mixture in a large fraction. Separation using hydrocylones is not expected to produce very pure fractions of ABS and HIPS because of the closeness of the relevant properties, shapes, and weights of the chips. Heating the mixture until the "tack" point of one of the constituents is reached to cause it to stick to a moving conveyor is technically feasible. A residual sticky film could result in the sticking of the undesirable materials, thereby reducing the purity of the recovered product.

Because of the potential shortcomings of the methods discussed above, we proceeded to develop other techniques that could enable us to produce very high purity products. Two methods were developed and tested: solvestick and froth floatation by using surface tension phenomena. Both of these methods are covered by invention disclosure documents.

The Solvestick Method

The solvestick method involves exposing the plastics mixture to a solvent that selectively attacks the surface of one of the plastics in the mixture, causing that plastic to stick to the surface of a moving conveyor while the other species are unaffected. To wash off any residual film of the sticking material on the conveyor surface, the conveyor belt is brushed while it is soaking in a bath of the solvent. This soaking step serves also to wet the belt surface for the second round of the conveyor. This concept was tested in our laboratory on a mixture of ABS and HIPS, and over 99.5% pure fractions of the two plastics were produced. Solvents that were tested on this mixture include acetophenone, diacetone alcohol, and acetone. The concept was also successfully tested on a mixture containing ABS, HIPS, PP, and PVC. For this mixture, three solvents and three steps were required.

The Floatation / Surface Tension Method

Separation based on density gradients is a well-known technique for separating solids and immiscible liquids. Froth floatation utilizing surface tension/density phenomena is also well- known and is widely used in the mineral-processing industry. Various particulate solids in addition to minerals have been extracted by using this method. Typical separation applications using floatation include treatment of wastewater, coal, clays, resins, corn, proteins, fats, rubber, dyes, glass, plastics, fruit juices, and cane sugar. There are a number of ways to float particulates, such as dispersed-air method, dissolved-air method, electrolytic floatation, and nonfoaming floatation. Comprehensive reviews of the floatation research are given by King (9) and by Matis (10).

The principle of the floatation process is that of a density difference between the particles and the floatation medium. In the simplest case, where particles are completely wetted by the floatation medium, two different particles with different densities can be separated by a fluid whose density lies between them. It is also possible to separate particles with close densities but with different surface wetting characteristics, where the effective density of one of the species can be reduced by the attachment of small gas bubbles on its surface. Due to the lower effective density of the bubble-particle agglomerate, those particles with nonwetting characteristics will float in a medium having a density higher than its apparent density.

The floatation medium used most often is water or aqueous solution. Therefore, the key parameter controlling the successful separation or floatability and nonfloatability of particles is whether the particle is hydrophobic or hydrophilic. The vast majority of plastic resins are hydrophobic in character. They have a tendency to float due to nonwetting characteristics (i.e., attached bubbles on the surface). It is therefore very hard to separate plastics with close densities. In the mineral-processing applications, the degree of hydrophobicity of a solid is controlled by direct surface-chemical action of floatation reagents, which could be collectors, frothers, activators, or depressants. Any solid can be rendered hydrophobic (by making the surface nonpolar), but it is hard to render a solid hydrophilic (by making the surface polar). For separation of close-density plastics, it is required to render one of the plastics hydrophilic.

Many factors affect the efficiency of froth floatation operations and the purity with which the different components of the mixture can be separated. Among these factors are size, stability, number of gas bubbles per unit volume, agitation intensity, density of the liquid phase, residence time of the bubbles, method of processing the froth layer, shapes, hydrophobicities, specific gravities of the solid particles, presence of thin layers of coatings or impurities on the surface of the particles, presence of viscous materials that can trap the particles or slow down their motion, presence of surfactant-type materials that prevents the sticking of the bubbles to the surface, and solution pH.

Matis et. al. presented an excellent review of the state of the art in floatation techniques for the separation of solid mixtures (10). Even though this technique is mainly used in the minerals processing industry, it has been used successfully in the separation of commingled PET, PP, PE, and PVC plastics (11).

Overview of the Argonne Process for the Recycling of Appliance Plastics

The process being developed at Argonne for recycling high-purity ABS and HIPS plastics from obsolete appliances is shown in Figure 2. In developing this design, we assumed that prior to shredding the appliances (such as refrigerators), the capacitors, which may contain PCBs and fluids (refrigerants, oils, etc.), are removed. State and federal regulations require the removal and proper disposal of these environmentally controlled substances. In addition, we assumed that such clear plastic components as shelves and containers are manually removed. These clear plastics parts may be polycarbonates, ABS, styrene acrylonitrile (SAN), or acrylics. Some of them are difficult to separate from each other by physical and mechanical means, while they are easily separable from opaque materials. We also assumed that the appliances are shredded in dedicated shredders and not with automobiles or with other obsolete durable goods. One of the largest appliance processors in the U.S., The Appliance Recycling Centers of America Inc., is dedicated to processing appliances only. They generate large quantities of appliance fluff, and they have been providing Argonne with important information for analyzing and characterizing the fluff waste stream.

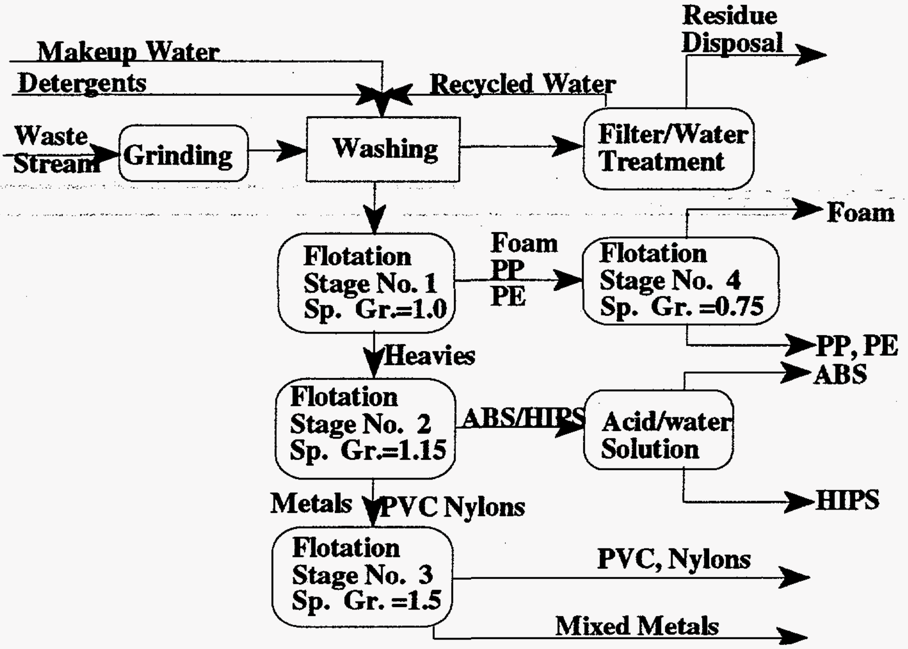

Figure 2 - Schematic Diagram of the Argonne Process for Separating Plastics from Appliance Fluff

The waste stream is first ground up to a particle size of about 0.25 in. The grinding process facilitates the complete liberation of rigid foam from refrigerator plastic-liner materials. The downsizing of the plastic materials also facilitates the handling of the material because the shapes and sizes of the pieces are more uniform. After grinding, the material is washed with water and detergents to remove the dirt and any residual oils. To enhance this cleaning process, the waste stream is agitated during washing. The wastewater resulting from the washing process is first filtered to trap its solids contents and then treated and reused. This procedure is intended to minimize the generation of wastewater.

The treatment process depends on the contaminants present in the water. A rinse stage, after the washing tank, is recommended, even though it is not shown in Figure 2. Separation of such light materials as foam, PP and PE can be achieved in the rinse tank, since the liquid specific gravity in that tank is about 1.0; paddle wheels or wipers can be used to skim the floaters out of the tank and drop them on a screen to drain. The water that drains from the lights can be pumped back into the tank. The foam can be separated from the PP and PE in a tank having a specific gravity between 0.7 and 0.85. Because of the limited volume and market value of the rigid foam and the PP/PE generated from this process, we have not yet addressed the upgrading of these streams.

The washed heavies can be separated further into two fractions. The first fraction contains the high-value plastics: ABS and HIPS. The second fraction contains the heavier constituents of the waste stream, such as PVC, nylons, and the residual metals. This separation can be achieved in a tank where the specific gravity is maintained at about 1.15. Lower densities in this tank may result in some loss of the ABS, even though it will minimize the potential of contamination of the ABS/HIPS stream with other plastics. The sinkers in this last tank can be separated further in a tank where the specific gravity is maintained greater than about 1.3.

Separation and recovery of the ABS and the HIPS is the primary objective. Both of these plastics have specific gravities in the range of 1.045 to 1.15. These effective specific gravities are for these plastics as they are used in the final product; the plastics still include all additives that may have been added to the virgin resin to produce application-specific formulations. Therefore, these two plastics cannot be separated from each other in high purity by using conventional gravity-separation techniques.

The total mass balance of the process of recovering appliance plastics is shown in Table III. Pure ABS fraction constitutes about 74% of all the plastics recovered. The next largest plastic stream recovered is the ABS-contaminated HIPS. Research is currently under way at Argonne to develop a technique to remove the ABS contaminant and produce a pure HIPS fraction by means of an aqueous-acid solution floatation process. Depending on the HIPS concentration in the appliance fluff, this fraction could represent an important revenue-producing fraction for the plastics recycling operation.

Table III Mass Balance of the Argonne
Floatation Process

Materials Streams	Weight %
Polyurethane foam and polyolefins	6
ABS-contaminated HIPS	19
ABS and SAN	74
Nylon, PVC, and other heavies	1
Total	100

Table IV shows the results from tests conducted to assess the effectiveness of the aqueous-acid solution floatation process for separating ABS from HIPS. The samples were prepared by using hand-picked ABS and HIPS plastics from obsolete appliances. Acetone and xylene were used in the initial evaluation of ABS-rich or HIPS-rich samples. These samples were shredded, washed with a surfactant-water solution, and separated by using the aqueous-acid solution. The

Table IV Analysis of Floaters and Sinkers from the Aqueous-Acid Floatation

Sample	Floaters	Sinkers
Test 1		
ABS rich	2 out of 19 dissolved	all dissolved
HIPS rich	1 out of 30 dissolved	all dissolved
Test 2		
ABS rich	11 out of 45 dissolved	89 out of 90 dissolved
HIPS rich	9 out of 75 dissolved	all dissolved

separated plastics were then tested by using a selective solvent that only dissolves ABS. The sinkers were almost pure ABS, with the exception of one flake out of over 250 flakes. The floaters contained about 3-25% ABS and 75-97% HIPS.

In a new set of tests, samples of ABS/SAN and HIPS contaminated with ABS were prepared by using the entire Argonne Floatation Process. The final ABS/SAN fraction was analyzed for possible HIPS contamination by using selective-solvent and Fourier Transform Infrared Spectroscopy (FTIR) techniques. There was no evidence of HIPS contamination according to the selective-solvent method of analysis. Samples of the floaters and sinkers fractions, each weighing about 7 lb, were independently analyzed by the Edison Polymer Innovation Corporation (EPIC) and the University of Akron by using FTIR. Table V gives results from this study. There was no evidence of HIPS contamination in the sinkers fraction; however, the floaters fraction had ABS contamination as expected. The EPIC report (12) concluded, "Various fractions in the sinkers fraction sample were all identified as ABS."

Table V Quantitative FTIR Analysis

	Weight Percent		
Sample	Acrylonitrile	Butadiene	Styrene
Floaters 1	20	8	72
Floaters 2	0	10	90
Floaters 3	0	10	90
Floaters 4	0	10	90
Floaters Blended	2-4	7-9	89
Sinkers 1	29	11	60
Sinkers 2	26	10	63
Sinkers 4	32	11	56
Sinkers Blended	32	11	56
	26	13	61

Compatibility Experiments

In order to quantify the compatibility of HIPS in ABS, Argonne submitted nine ABS, HIPS, and blended samples to the University of Akron for impact and tensile strength testing. The results, tabulated in Table VI, clearly show the severity of the HIPS contamination of the ABS. Impact strength and tensile strength of ABS dropped by 45% and 18% with only 2.5% HIPS content (Sample 2). The impact strength was recovered by addition of a compatibilizer (GE Blendex) (Sample 6), but at the expense of the tensile strength. It is also expected that stiffness and thermal stability will be adversely influenced by the HIPS contamination, and it may not be possible to recover them by the addition of the compatibilizer.

Table VI Impact and Tensile Strength of ABS with HIPS Contamination

Sample	% Weight of HIPS in ABS	Izod-Impact (ft-lb/in.)	Tensile Strength (psi)
1	0	6.77	6608
2	2.5	3.73	5461
3	5.0	3.27	5468
4	7.5	2.88	5251
5	10	2.37	5147
6	2.5[a]	6.73	4931
7	7.5[a]	4.73	4765
8	100	1.58	3415

[a] Compatilizer added

Conclusions

This paper describes an environmentally sound recovery process of valuable plastics from household appliances. The ABS recovered from obsolete appliances is projected to have a market value of $0.50-$0.60 per pound. A pilot plant is currently being designed and is planned to be in operation in the spring of 1996. The plant will be installed in an appliance processing facility in Minneapolis, Minnesota, and will have a processing capacity of appliance fluff of about 1000 lb/hour. Research for developing techniques to cost-effectively improve the properties of the recovered ABS are continuing.

Acknowledgment

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