SEPARATION AND RECOVERY OF THERMOPLASTICS
BY FROTH FLOATATION

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Abstract

This paper describes efforts by Argonne National Laboratory to develop a froth flotation process for separating and recovering plastics from mixed plastics waste streams generated from shredding obsolete appliances and automobiles. A process for recovering and separating equivalent-density ABS and HIPS from obsolete appliances was developed and pilot-tested with a throughput of 1,250 lb/hr. The basic process is outlined: unit operations and equipment are discussed, and material balances are presented. The resulting ABS product was analyzed and its physical and mechanical properties were established. Its properties resembled those of virgin, mid-grade ABS that is commercially sold today and is widely used by the automotive industry. Injection-molding tests were also conducted by automotive-components suppliers, using the 100% recovered ABS. Headlamp "back-cans" and automotive ventilation-system duct components were injection molded and the results showed that the recovered ABS met the specifications for these applications. These results confirmed that the recovered ABS can be used as an substitute for virgin plastic materials for molding highly complex automotive component designs, and in parts for other durable goods. Economic analysis of a commercial-scale system was also performed using manufacturers' equipment quotes and operating data from the pilot plant, and it predicts a simple payback of less than 2 years for plants producing about 850 tons per year of ABS.

Definitions and Acronyms

ABS- Acrylonitrile-butadiene-styrene.
APC- American Plastics Council. A membership organization comprised of about 25 major plastics producers.
ANL- Argonne National Laboratory.
Appliances- Often referred to Collectively as "White Goods" Includes: Refrigerators, Freezers, Clothes Washers/Dryers, Dishwashers, Room Air conditioners, Range/Ovens Microwave Ovens.
ARCA- Appliance Recycling Centers of America Inc.
ASR- Auto Shredder Residue. The reject material that is landfilled after processing scrap such as obsolete cars and appliances for recovery of metals.
ARA- Automotive Recyclers' Association. The trade association that represents about 12,000 auto dismantlers - companies that typically recycle cars for used parts.
EPDM- Elastomeric terpolymer from ethylene propylene and a non-conjugated diene.
Fines- Materials in ASR less than 0.25 in. Typically fines are comprised of metal oxides (e.g. rust), glass, dirt, wood, and small particles of plastics, rubber and other materials.
HIPS- High Impact Polystyrene.
ISRI- Institute of Scrap Recycling Industries. The trade association that represents scrap material recyclers including about 200 shredder operators who recover recyclable metals and materials from obsolete cars.
Obsolete Scrap- Post-consumer scrap such as obsolete cars, appliances and other household items.
PC- Polycarbonate.
PCB- Polychlorinated Biphenyl.
Polyolefins- Polyethylene and polypropylene.
PE- Polyethylene.
PP- Polypropylene.
Prompt Scrap- Scrap generated during the manufacturing process; industrial scrap.
PVC- Polyvinyl chloride.
SMA- Copolymer from styrene and maleic anhydride.
VRP- Vehicle Recycling Partnership. An organization formed by GM, Ford, and Chrysler to promote the recycling of obsolete automobiles.

Introduction and Background

Argonne National Laboratory, in collaboration with ARCA, APC, VRP, and others has developed processes for
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recovery of plastics from waste streams generated by appliance and automobile shredding and metals recovery operations. Argonne has patented this pilot-plant tested froth flotation process for separating equivalent-density appliance plastics ABS and HIPS.

Consumer durables such as household appliances and automobiles are manufactured from a mix of materials including metals, synthetic polymers, fibers, and glass. Typically, metals represent more than 75% of the total weight of these items. Over the last 15 years, however, the use of polymers in durables has increased substantially at the expense of metals, and current trends indicate that the use of plastics in such items will continue to increase. In 1996, the amount of plastics consumed by the appliance and automotive industries is estimated to be about 4.3 billion pounds. In year 2006 this figure is expected to reach 5.5 billion pounds.

In 1998, over 95% of the obsolete automobiles and about 70% of the obsolete appliances were shredded or dismantled to recover their metals. The shredding operation also produced between 3 and 5 million tons of nonmetallic residue, which is rich in plastics. As the portion of metals in appliance and automotive materials is reduced and the plastic content is increased, the economic incentive for using appliance and automobiles scrap as a source of steel will be reduced, because the plastics fraction constitutes a negative value to the shredding operation. Plastic materials used in appliance and automobile manufacturing are of high quality and have the potential of being recycled to high-value applications. Current technologies for recovering individual high-purity plastics, such as ABS, ABS/PC, PS, Nylons, PVC, PE and PP are not cost-effective, and as a result, all plastics end up in landfills. The Argonne plastics separation processes can be used in combination with other conventional (sink-float) methods to separate and recover these plastics from plastic waste streams.

**Characterization of Plastics Waste Streams**

**Plastics in Appliances**

Plastics used in appliance manufacturing are high-quality engineered materials and have the potential of being recycled to high-value applications. The key plastics used in appliances are: ABS, HIPS, PP, PE, PVC, and Nylons. The ABS and the HIPS, which are the most widely used plastics in appliances, are both high-value materials (virgin ABS: $1.00/lb, virgin HIPS: $.50/lb), and therefore we targeted them for recovery. Obsolete refrigerators contain, per unit, the largest quantities of ABS and HIPS plastics and in our research, refrigerator fluff was used, primarily, for demonstrating the viability of froth flotation for recovering and separating ABS from HIPS plastics. In 1992, more than one billion pounds of plastics were used in appliance manufacturing.

**Plastics in Automotive Shredder Residue**

About 3-5 million tons of ASR is produced annually in the United States, and it is about 30% (by weight) synthetic polymers. The list of polymers in ASR include in descending concentration order: PP, ABS, PVC, polyurethane foam, polyester thermoset, Nylons, PE, other urethanes, PPO styrene, polyester thermoplastics, SMA, HIPS, polyurethane rigid foam, PC, acrylics, phenolics, PP EPDM modified, acetals, PC PBT, ionomers, butyral, SAN, ABS/PC alloys, PPO Nylons, epoxies, polyester elastomers, and alkydes. Many others are also present in smaller quantities and new ones are added to the list every year. These polymers are coming primarily from shredding automobiles and home appliances. All of ASR is essentially landfilled, because current technologies for recovering plastics from it are not cost-effective. It contains over 3 billion pounds of synthetic plastics a year worth about 1.4 billion dollars, assuming the value of the recycled material is 50% of the value of the virgin material.

**Appliance Plastics Separation Processes**

Argonne’s research in plastics separation technologies was focused on the development of processes for recovering high-purity ABS and HIPS materials from appliance fluff. Upon achieving this goal, research was conducted to determine the applicability of this technology to mixed plastics derived from ASR.

Compatibility of plastics was an essential consideration in the development of separation technologies. It dictates the level of separation that is required to produce a value-added product. ABS and HIPS, the two major plastics in appliances, are not compatible. Experiments conducted by Argonne indicated that the presence of small quantities of one in the other results in significant degradation of its properties. When 2.5 wt % of virgin HIPS were added to virgin ABS, the Izod impact strength of the ABS dropped by about 45% and the tensile strength dropped by about 20%. Therefore, in order to preserve the properties and consequently the market value of the recovered ABS, the separation technology must be capable of producing high-purity plastic material (> 98%).

**Process R&D**

**Bench-Scale Testing**

Froth flotation has been successfully used in the mineral-processing industry for many years. To adopt this principle for the separation of equivalent density plastics, froth solution conditions that would render one of the plastics hydrophilic and the other hydrophobic (i.e. ABS hydrophilic and thus sinks while HIPS remain hydrophobic and thus attracts air bubbles and float) must be determined. The wetting characteristics of plastics can be selectively adjusted by controlling the pH, surface tension, density
and the temperature of the conditioning solution. By changing the surface wetting characteristics of equivalent-density plastic materials, the effective density of one of the plastics can be reduced by the attachment of a small gas bubble on its surface. Due to a lower effective density of the bubble-plastic particle, those plastics with non-wetting characteristics will float in the medium that has a higher density than the agglomerate's apparent density. Argonne conducted experiments which identified ranges of values of pH density and surface tension that resulted in the separation of ABS and HIPS from the plastics mixture at greater than 98 wt % purity. The yields were also greater than 80 %.

**Semi-Continuous Small Scale Testing**

Development of the froth flotation process for separating equal-density plastics required that the purity and yield be demonstrated under more practical conditions which take in consideration, among others, conveying slurries containing 0.25 inch hard plastics through pipes, valves and pumps. Therefore, a 50 lbs/hr semi-continuous froth flotation apparatus was designed, built and operated. We produced over 600 pounds of ABS with a purity greater than 98 wt %. We also tested many chemicals that can be used to produce the desired specific gravity, pH and surface tension effects in order the select the most environmentally acceptable and cost-effective agents. Samples of the recovered ABS were submitted to resin producers and to The University of Akron Polymer Research Center, for evaluation. The results of the semi-continuous lab scale testing campaign, confirmed that the process is technically feasible and that the physical properties of the ABS product met the specifications for high-value applications.

**Pilot-Scale Testing**

To demonstrate the commercial viability of the Argonne's froth flotation process, large-scale tests were necessary to confirm: a) process economics, b) establish product performance and market opportunities, and c) develop engineering/design data for a commercial-scale operation. To meet this objective a pilot plant with a 1000 lbs/hr design capacity was designed and built at Argonne and installed and operated at the appliances recycling facility of ARCA, our industrial partner, in Minneapolis, MN. The feed material was mixed plastics that were generated by shredding obsolete appliances.

The pilot plant consists of three processing stages. Stages 1 & 2 employ conventional density separation methods to isolate the ABS and HIPS as a single fraction. In stage 3, froth flotation is employed. Figure 1 is a simplified block diagram of the process.

**Pilot-Plant Tests Campaigns**

Pilot testing of the process was done in staged campaigns, and it was focused primarily on the froth flotation process, because stages 1&2 are conventional technology. Studies were also conducted to assess the impact of variations in key parameters on process performance.

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**Figure 1. Simplified Block Diagram of the ABS/HIPS Recovery Process**
The first campaign was a parametric study conducted in the laboratory to determine the impact of the various froth solution properties (specific gravity, pH and surface tension) on the process performance. The data were necessary for establishing the operating conditions in the field. The results established that the optimum solution parameters for maximizing purity and yield are: specific gravity=1.067, surface tension=35 dynes/cm, and pH=1.76. The performance was not sensitive to changes in pH in the range of 1.25-2.60 while the surface tension and density were maintained at the values given above.

The second test campaign was designed to test the pilot plant design parameters and to establish process performance (changes in the recovered ABS/SAN yield and purity) as a function of time at different process parameters such as throughput rate. We tested three through put rates (1000 lbs/hr, 1250 lbs/hr and at 1500 lbs/hr). These test runs were also necessary to determine the time required to reach steady state operation for proper sampling, and are important for scaling up the design. In these tests, froth solution conditions were maintained at the conditions identified in the first campaign: density 1.067 g/mlcm³, surface tension 35 dynes/cm and pH 1.76. At 1000 lbs/hr infeed rate, the recovered ABS purity was greater than 98% and the yield was above 82% during the entire test time of 90 min. As the infeed rate was increased to 1,250 lbs/hr, while all other operating parameters remained the same, the purity stayed above 98 wt %, but the yield increased sharply from 52% at 30 minutes to about 65% at 70 min. As the infeed rate was increased to 1,500 lbs/hr, while all other operating parameters remained the same, the purity dropped from 98 wt % at 30 min down to about 93% at 40 min. The change in purity at the higher throughput rates may be attributed, at least in part, to the rapid built-up of materials (floaters and sinkers) in the tank, at this higher flow rate. This built-up reduces the extend of the separation zone as the turbulent boundary layer thickness increases, and as a result, not enough time for some of the floaters to rise. As the built-up of plastics on the bottom of the tank increased further, it blocked the horizontal flow of the slurry and increased its downward flow. This pulled some of the material that normally floats downward thereby increasing the yield.

These results confirmed our design criteria for the pilot plant of 1000 lbs/hr.

**Properties and Product Testing**

To assess the performance and, ultimately, establish the market value of the recovered ABS, tests were conducted to determine key physical and mechanical properties of the recovered material. The results of these tests will make it possible to match the recovered ABS properties to performance standards for premium applications. The properties of the recovered ABS were also compared with a mid-grade virgin ABS material that is used in large volumes by the automotive industry.

The properties of the recycled ABS place it in the intermediate range of engineering resins. This type of resin is used in durable products where its strength-to-weight ratio is an attractive alternative to metals. The major markets for virgin ABS are transportation, appliances and electronics. Basically, virgin resins set the price ceiling for post-consumer resins. Post consumer plastics can realize a value of up to 95% of virgin if they are upgraded and meet the performance requirements of the virgin application. Based on its properties, and color consistency, the recovered ABS could be used in a variety of premium applications including the automotive industry. The price (BLC, Inc.) of the recycled ABS, depending on market conditions, in projected to be in the range of $.50-.75 per pound.

**Molding Tests**

The single largest market for ABS is the automotive industry. The range of potential automotive applications for the recovered ABS include body panels (cowl vent grille, rear end panel), engine & functional components (interior speedometer housing components, steering column components), Interior & functional components (console components, instrument panel components, signal lamp housing, trim panel interior) trim, exterior ( radiator grille & headlamp bezel and Z-other exterior trim). Molding tests were conducted by automotive industry parts molders/suppliers and the results showed that the recovered ABS properties meets the processing performance requirements for using the ABS in selected automotive parts including in lighting assemblies and automotive ventilation system duct components.

**Conclusions**

A process for recovery and separation of equivalent density ABS and HIPS materials from appliance fluff was developed, tested and patented. Development of the process evolved from bench-scale proof-of-concept to process demonstration at a pilot plant that was successfully operated at an appliance processing and shredding facility. During the course of the development effort, samples of recovered ABS were supplied to potential users of the product. The ABS recovered by the Argonne process met the quality requirements of automotive parts molders/suppliers and its properties averaged about the same as the properties of virgin mid-grade ABS materials, which are used widely by the automotive industry.
A cost analysis based on pilot-plant operation using vendor quotes indicates that the capital cost for a 850-ton-per-year ABS producing plant is about $650,000. The payback period on this investment is estimated to be less than 2 years based on a ABS and HIPS market prices of $0.40/lb and $0.20/lb respectively. In summary, froth flotation is a very promising technique for separating durable plastics from appliance and automotive shredder waste streams efficiently and cost effectively. The process developed by Argonne is ready for full-scale demonstration using source materials derived from obsolete refrigerators and similar durable products.