RECOVERY OF POLYPROPYLENE FROM LEAD-ACID BATTERY SCRAP

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ABSTRACT

The recycling of metal containing scrap is a common practice in the industry and has a long tradition. In the last years this development was transferred also more and more to organic materials, in particular to thermoplastic polymers.

BSB Recycling GmbH, a company with a long experience in the treatment and recovery of lead from battery scrap, had recognized this exploitation at an early stage and challenged it by a consequent continuation of the idea to recycle materials other than metals without degradation and maintaining the quality. These efforts resulted in an economic and environmentally complying solution producing high quality polypropylene compounds at BSB beside lead and lead alloys from battery scrap.

The raw material for the production of polypropylene compounds is shredded plastics from the separation of the casings of lead-acid battery scrap. The production of polypropylene with specific physical and mechanical properties is carried out by the accurate dosing of organic as well as inorganic additives. The result of the procedure is a novel product group “Seculene PP”, a registered trademark of BSB Recycling GmbH.

INTRODUCTION

The recovery of lead and silver by means of mining, smelting and refining in Braubach, Germany has a very long tradition. Favorable geological conditions made it possible to mine ores in the Braubach region as far back as 2000 years ago. First smelting operations can be traced back to 1691, which is the founding year for the silver smelter Braubach. In the following centuries the emphasis shifted from silver production to lead smelting. Since 1977, the current BSB (former Blei- und Silberhütte Braubach) Recycling GmbH operates a secondary lead smelter with a current annual production of approximately 30,000 t of lead and lead alloys. The smelter converts decommissioned automotive battery, lead scraps, lead-bearing wastes, blasting sands and plated lead foils using environment friendly technologies. BSB Recycling is a pioneer in Germany in the field of environmental protection and became the first German secondary smelter to be certified to DIN EN ISO 9002.

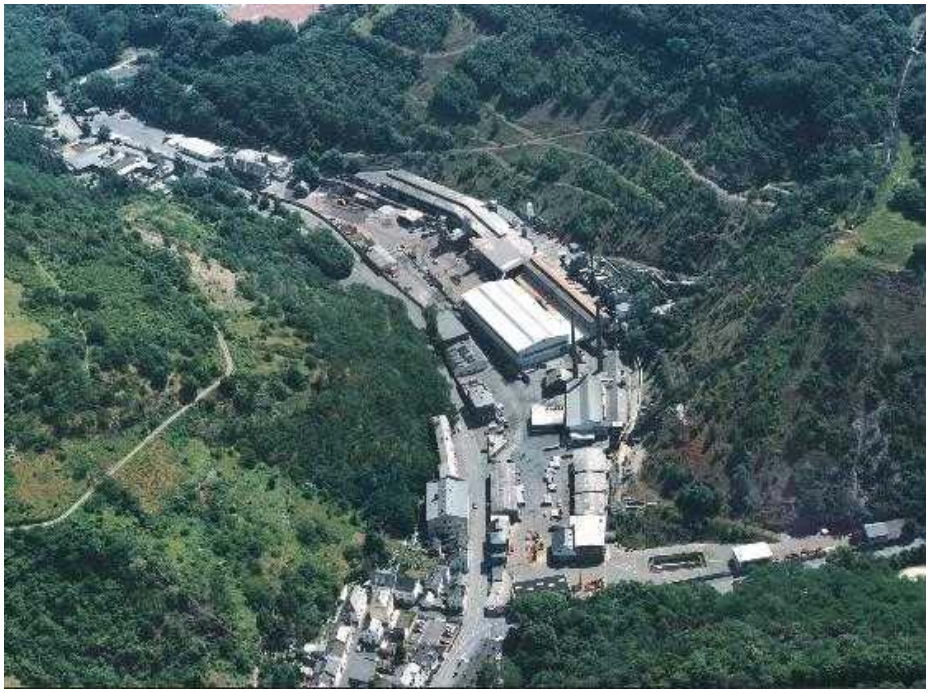

Figure 1 Photograph of BSB Recycling GmbH in Braubach/Germany

OVERALL PLANT CONCEPT

Main source of raw materials in the BSB smelter is automotive battery scrap, which is stored in an acid-proof, covered warehouse. In order to achieve the maximum utilization of the spent batteries and recovering most of their constituents, a separation of all constituents is required followed by an upgrade to high value products. As illustrated in figure 2 it is, therefore, current practice to process the batteries by draining the sulfuric acid for collection, crushing the whole battery in a breaker and subsequently separate the different components of the batteries, which are grid metal, lead paste, ebonite as well as various plastics. A settling-floating process using a hydroseparator is applied for the latter purpose. The separated lead bearing fraction paste is either desulfurized and metallurgically treated in one of the existing short rotary furnaces to recover lead bullion and generating a discardable slag or sold in the non-desulfurized form to the primary lead smelter of Berzelius Metall in Stolberg. The

desulfurization of the lead paste is performed by means of soda or caustic soda solution generating lead carbonate or lead oxide and also yielding anhydrous sodium sulfate minimizing SO_2 emissions and a high slag fall in the smelting process. The grid metal is molten in a short rotary furnace to obtain lead bullion. The obtained lead bullion is refined in a pyrometallurgical refinery removing all undesired impurities accompanying the lead in the bullion and, if required, alloyed to meet the various specifications of lead and lead alloy customer. The refined lead or lead alloy is then cast to 50 kg pigs.

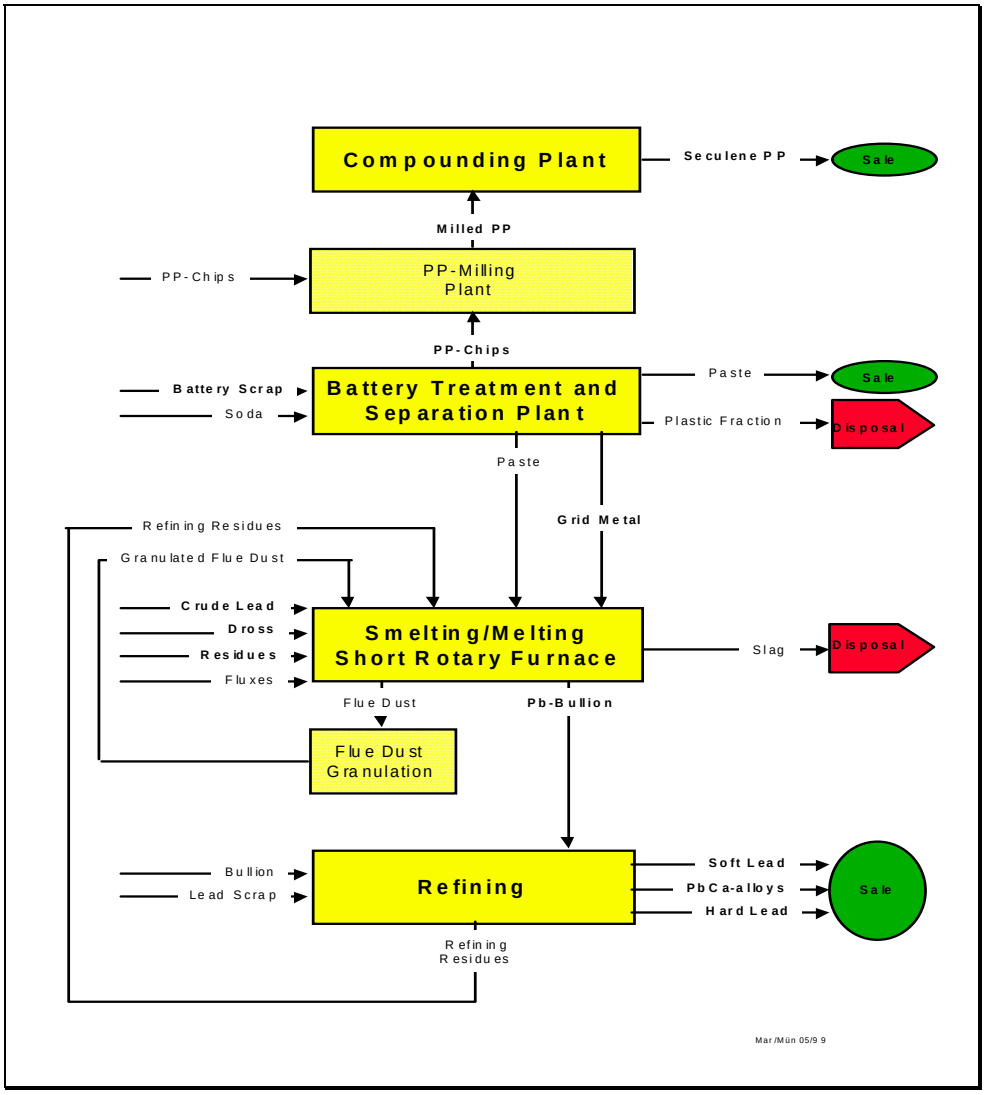

Figure 2 – Process Flowsheet at the Secondary Lead Smelter BSB Recycling

One of the various plastics, which became more and more dominant over the last two decades, is polypropylene. Until the mid eighties, the plastics fraction recovered during the separation process contained about 50% ebonite and had been discarded at a landfill. Based on the observed trend of an increasing amount of polypropylene entering the plant the management realized the importance of the exploitation of polypropylene at an early stage and challenged it by embedding a polypropylene compounding plant into the traditional flowsheet of recovering lead from scrap material.

The raw material for the production of polypropylene compounds is the shredded polypropylene fraction from the separation of the casings of lead-acid battery scrap in the battery breaking area. Before being transferred to the compounding plant the collected

polypropylene chips actually undergo intensive preparation steps. In a milling unit they are washed to remove any remaining paste and dust, shredded to a smaller and more homogenous fraction in a knife mill and dried to evaporate all remaining moisture. The design of the existing milling unit also permits to integrate raw polypropylene chips from other operations into the process. Figure 3 depicts the current material flow balance of the milling unit and the compounding plant at BSB. The resulting polypropylene pieces with a purity of more than 99.5% are then being pneumatically conveyed to the storage bins that feed the compounding unit.

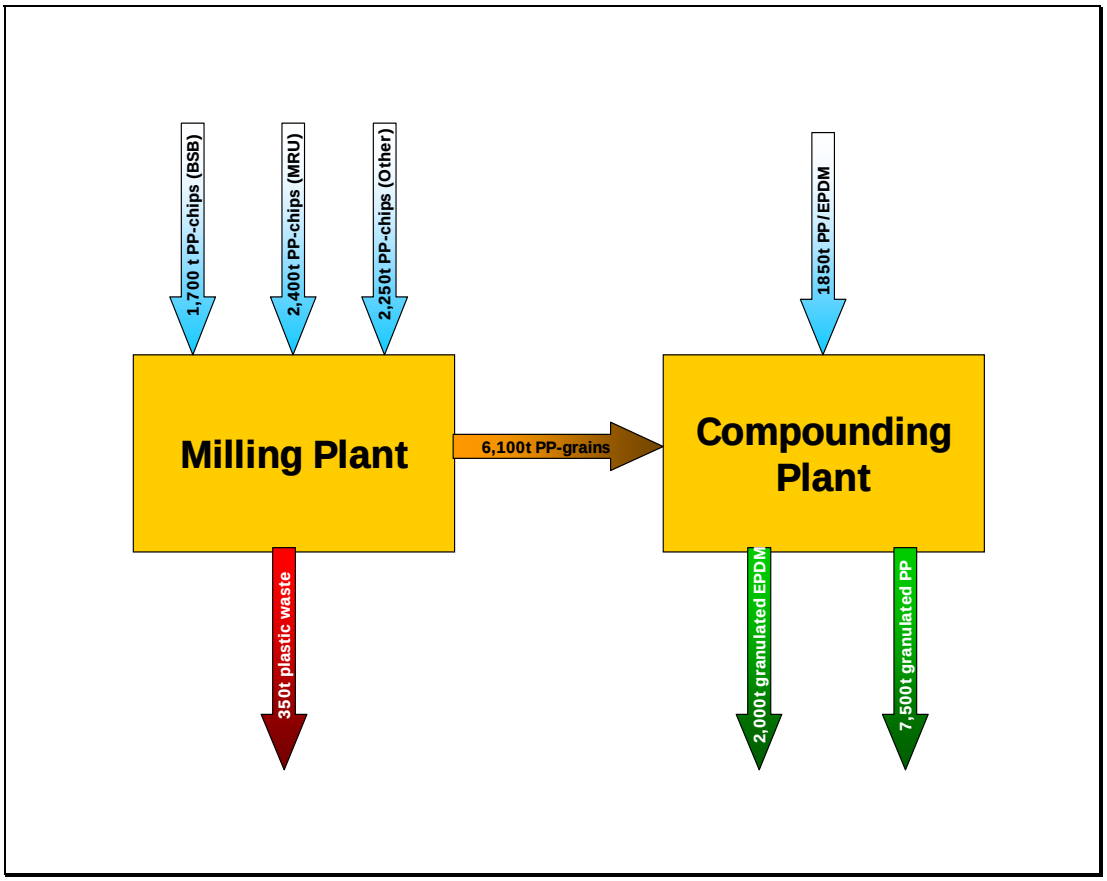

Figure 3 – Anticipated Polypropylene Material Flow Balance for the year 2000

The compounding plant was constructed in 1987 to process the polypropylene fraction collected from the battery breaker. Based on the prevailing quality of the polypropylene fraction from the milling unit it can be either processed to a lower quality product or upgraded to a highly valuable product by the application of specific refining procedures. BSB concluded after a detailed economic and ecological analysis that the high valuable product route was the more suitable application of the two technically viable choices for their purposes. Today, the consequent continuation and permanent improvement of the refining process of recycled polymers resulted in an economic and environmentally complying solution producing high quality polypropylene compounds at BSB beside lead and lead alloys from battery scrap. An on-line control system guarantees the high quality standard of PP compounds manufactured at Braubach and sold under the trade name of “SECULENE®”.

COMPOUNDING PLANT

The overall process concept of the compounding plant is illustrated in figure 4. Main equipment of the plant is a twin screw extruder, a filter system, a granulator and a dryer.

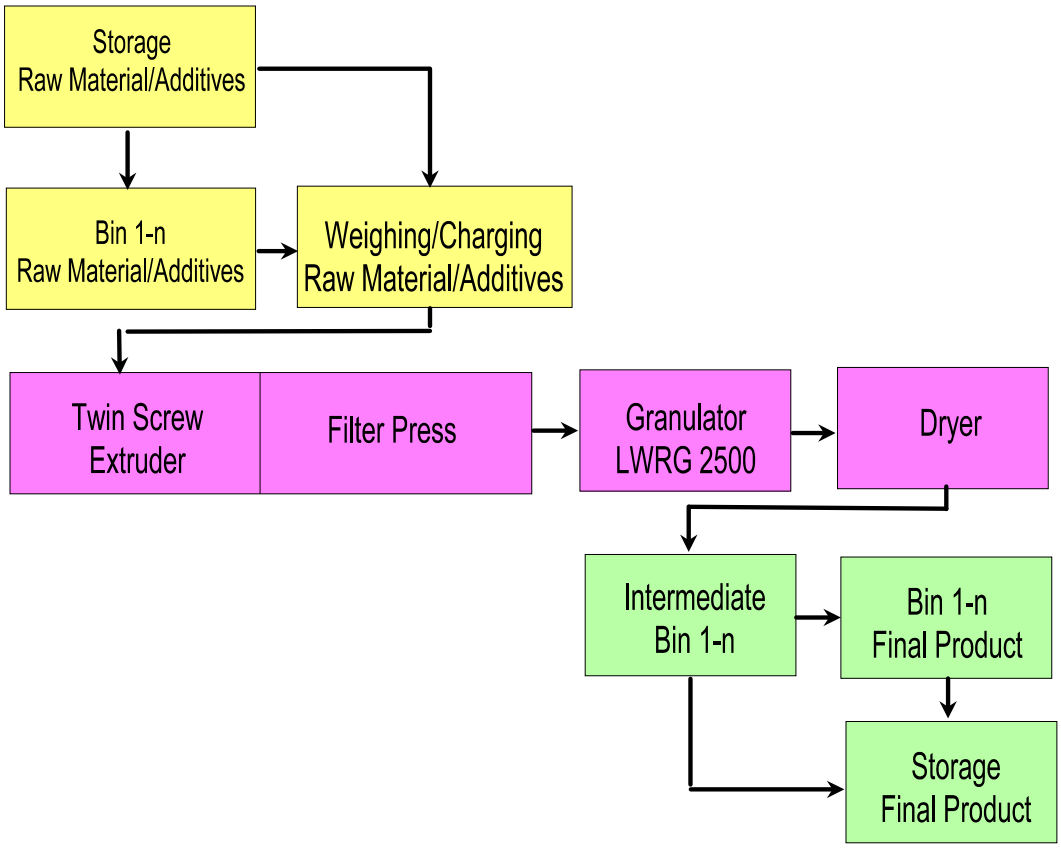

Figure 4 – Block diagram Compounding Plant

In contrast to most metallic materials it is a polymer specific peculiarity that the stress exposure during the production and further treatment as well as during its life cycle effects and changes its physical properties. Materials from different locations, for example, have diverse melting characteristics as shown in figure 5. Moreover, the existence and amount of impurities can have a negative effect on the matrix of the polymer. In case of polypropylene from battery scrap these impurities can consists of remaining polyvinylchloride (PVC) or rubber from the separators, traces of metal oxides, remainder of diffused sulfuric acid and glue. Extensive research and development work was carried out in order to eliminate these disturbances. The molecular disintegration of the plastic during the melting process as well as the material specific aging process during its life cycle could be significantly reduced by the employment of specifically developed stabilizers. The polypropylene pieces and the additives are fed separately by gravimetricely operating weigh feeders continuously to the twin screw extruder. The extruder is designed in particular for the requirements of the polypropylene material and consists of several individual heated chambers to maintain desired extruding conditions. The charge mixture is melted under carefully adjusted operating parameters applying external heat as well as internally released shear energy and subsequently mixed with additional components according to predetermined specifications in order to obtain a homogenous melt. Despite these distinct and permanent changing operating conditions it was possible to increase the overall melting volume rates at 230^0 C by approximately 20% from 6.8 cm^3/10min to 8.16 cm^3/10min over the last decade (Figure 6). Gases are removed through an intense degassing during the melting.

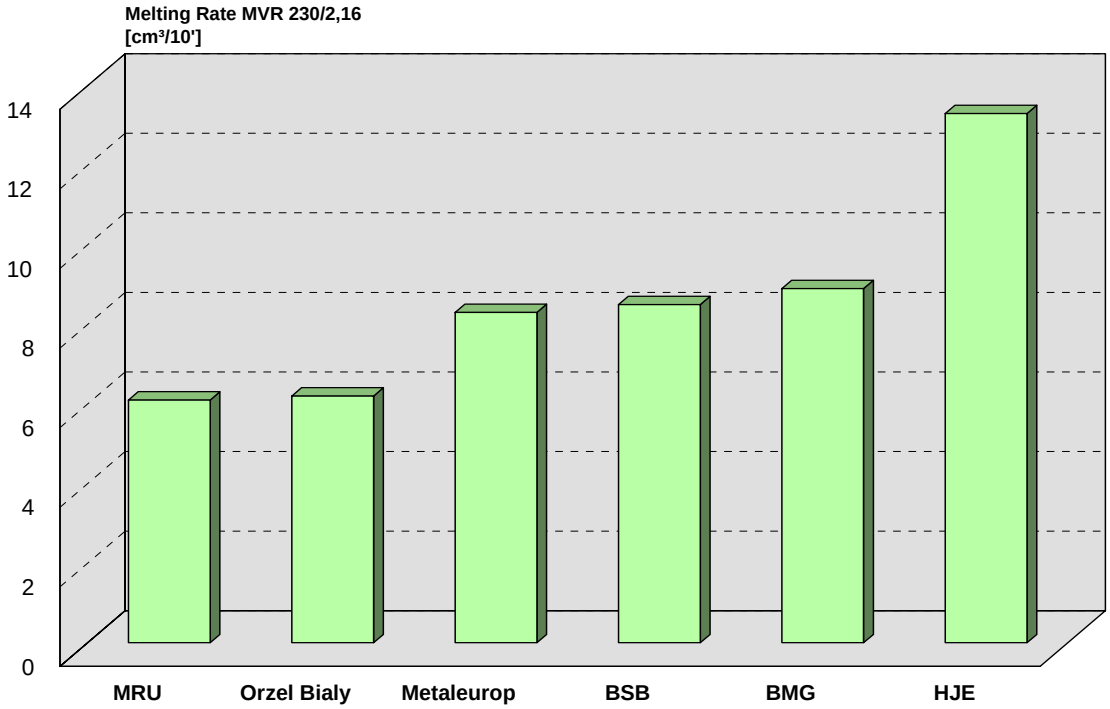

Figure 5 – Melting Rates of different Polypropylene Raw Materials in 1999

The molten polypropylene product is extruded out of the extruder into a filter press. The filter press is an automatic and continuously operating unit comprising of stainless steel filters on a rotating wheel. The melt is forced through the filter screens removing not molten materials like wood chips, paper and other non-propylene materials. At a certain pressure difference over the screen the wheel containing the stainless steel screens rotates to a clean filter. Depending on the amount of remaining impurities the occurring screen fouling is quite detrimental and the screens frequently had to be replaced in former times representing a significant cost factor of the operation. In 1999, this screen system was replaced by a back-flushing screen system and eliminated the excessive consumption of screens.

A pump generates the required pressure for the filtration in order to avoid undesired temperature increases. Extruder, pump and filter press are process controlled and interlocked. Following the filtration the melt is granulated with water in a granulator achieving a homogenous grain size distribution between 2 and 4 mm.

The granules are conveyed into storage bins where they remain until they pass the quality control requirements before they are packed in big bags, containers, octa-bins or container trucks in accordance to the customer requests. An on-line control system continuously reads and records more than 60 operating parameters covering every process step and making it possible to investigate the production data of each manufactured lot even at a later point in time.

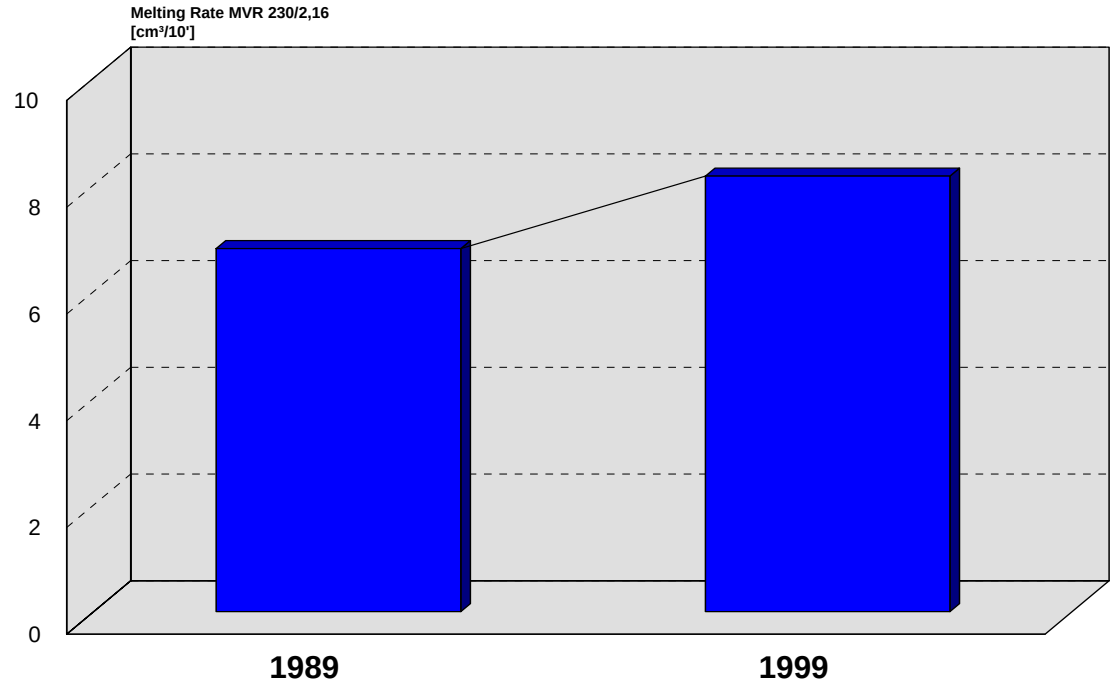

Figure 6 – Development of Overall Melting Rate of Polypropylene Product

PRODUCTS AND MARKET

The technological advantage in manufacturing polypropylene granules at BSB Recycling is not exclusively attributed to the design and operation of the compounding plant but also to the implementation of a customer oriented quality control system. The manufactured polypropylene products are combined under the trade name SECULENE PP and comprise various polypropylene compounds. Additives like talcum or caoutchouc are mixed in different amounts and ratios to the compounds modifying their individual properties depending on the area of application. The defined addition of a selected polypropylene containing recycle material from the reconditioning of used car bumper systems, for example, resulted in the development of a cold heading tenacious compound for the application in the car industry. It is possible to manufacture even more complex products custom made for special applications. In cooperation with German car manufacturers for example a compound was developed with sound absorbing properties. Today, BSB Recycling offers 10 to 15 different marketable product qualities.

The possibilities to modify the properties of SECULENE PP are manifold and only restricted by the availability of the polymer matrix in the battery casings. The polymer matrix is the foundation of all evolved formulas and achieved alterations. The careful and intelligent adaptation of existing formulas permits the application of SECULENE PP in a wide spectrum. Being capable to extensively modify the material properties allowed BSB Recycling to introduce SECULENE PP in many diversified industrial areas. The most dominant product group, however, consists of components for the car industry (85%). Popular applications in that area are fender liner, headlight and air suction filter casings, V-belt covers, cable covers, etc. Examples of different product qualities for the automotive industries and their diversified applications are shown in table 1. The continuous communication and cooperation with the German automobile industry and their component suppliers as well as the supply of quality products resulted in the acceptance of BSB Recycling GmbH as a competent partner for the car

industry. Projects have been carried out or are still ongoing with companies such as Daimler-Chrysler, BMW, VW and Opel (GM).

Producer	*specification*	*SECULENE*	*automotive part*
OPEL	QK 001 817	PPR 1240 TV20 S0	diverse cable covers
			holder of first-aid box
			holder of incandescent lamp
			motor casing
			fender liner
			water dismissing part
	QK 001 818	PPX 1210 S0	covers
	QK 001 803	PPT 8027 S0	fender liner
			side cover bumpers
	QK 001 802	PPR 1240 TV30 S0	air filter casing
BMW	BMW-N 601 00.0	PPX 8000 TV15 S0	cover control unit
	BMW-N 601 00.0	PPT 8027 S0	cable covers
	BMW-N 601 00.0	PPR 1240 TV20 S0	trunk liner
			cover spare wheel
VW / AUDI	VW-TL 52035	PPX 8000 BY 1.2 S0	fender liner with noise damper
	VW-TL 52221	PPX 8027 S0	fender liner
Skoda	VW-TL 52221	PPX 8027 S0	fender liner
			tool bag
	VW-TL 52035	PPX 8000 BY 1.2 S0	fender liner with noise damper
JAGUAR	-	PPT 8027 S0	fender liner

Table 1 – Examples for Technical Specifications for SECULENE PP in Automobile Industry

But SECULENE PP materials are also used in the electronic industry (12%) as components for washing machines, dryers, vacuum cleaners and dishwashers (Figure 7). Applications in other areas are gaining more and more importance because of the permanent extension of the product group by developing new materials with altered of improved properties.

Figure 7 – SECULENE PP components for the industry

FUTURE PERSPECTIVES

BSB Recycling GmbH successfully pioneered the recycling of polypropylene and converted it into a highly valuable product, which is proven by the rising number of competitors with similar business activities. This competition certainly will accelerate the growth of the product group SECULENE PP providing a large potential of new applications. From 1994 until 1999 the sales of SECULENE PP could be increased from annually 2,100 t to 6,700 t. In the year 2000 a growth of approximately 42% is anticipated and for the year 2001 an additional growth of more than 42% is expected (Figure 8). Taking this rapid development into account, the plants current capacity in Braubach will be reached in the foreseeable future and has to be expanded. Basis for the continuation and further development of the compound activities at BSB Recycling however is the recyclable construction of SLI batteries, i.e. their casings. For future consideration of product lifecycles each individual step has to be assessed and optimized. In Germany the authorities did provide the foundation for lifecycle assessments by introducing a legislation on recycling “Kreislaufwirtschaftsgesetz”, which urges the industry to recycle any kind of waste materials whenever possible. BSB Recycling GmbH understood their responsibility and realized new structures based on their long experience in the recycling business providing a economical and ecological sound future of lead and polypropylene recycling from battery scrap in the new millennium.

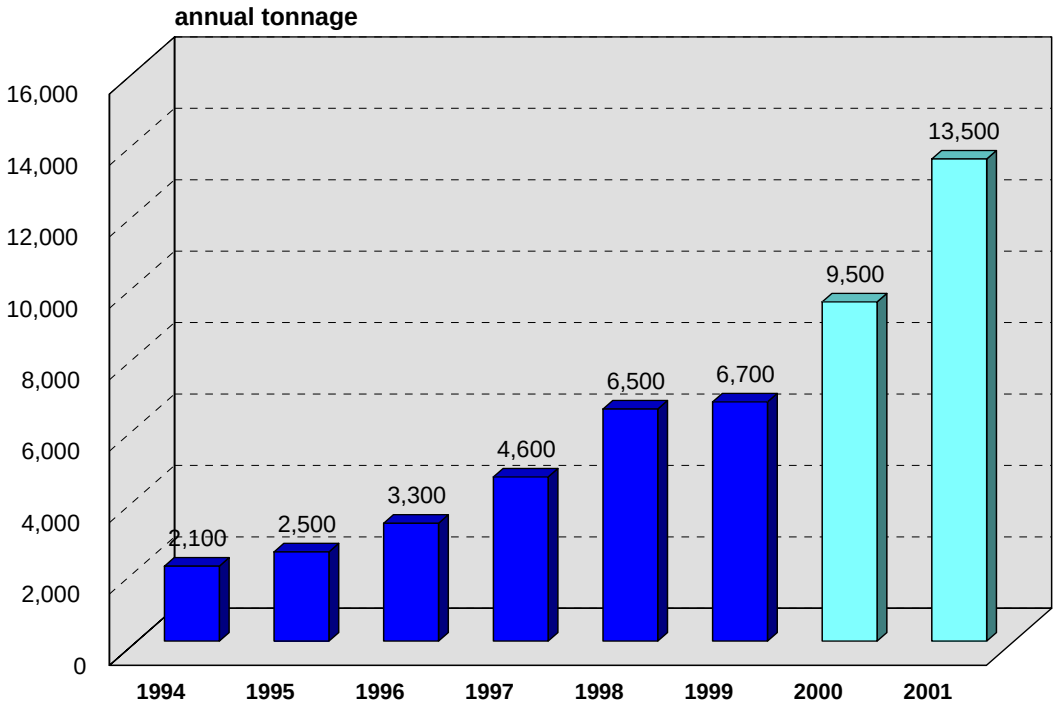

Figure 8 – Sales Development of SECULENE PP at BSB Recycling GmbH