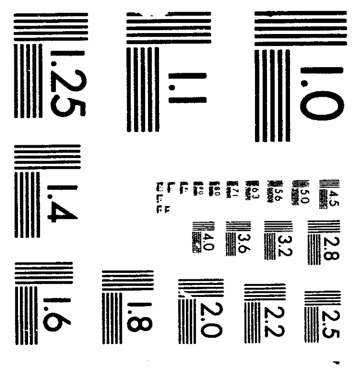

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PNL-SA-23361

CHEMI-MICROBIAL PROCESSING OF WASTE TIRE RUBBER: A PROJECT OVERVIEW

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December 1993

Presented at the
Pollution Prevention Technologies:
Industry Exchange Workshop
December 1-3, 1993
San Antonio, Texas

Work supported by
the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

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CHEMI-MICROBIAL PROCESSING OF WASTE TIRE RUBBER: A PROJECT REVIEW

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INTRODUCTION

Pacific Northwest Laboratory is developing a novel approach to diminish the enormous stockpiles of waste tires existing in this country. This process involves the use of thiophillic microorganisms to devulcanize the surface of ground rubber particles. The resulting material will have improved compounding characteristics and will be better suited for incorporation into virgin tire rubber compounds. This approach was born from the proliferation of interest in microbial-based processing of hazardous wastes and recycling technologies. Development activities evolved from a review of the literature involving biodegradation and biodesulfurization studies of polymers, coals, mining effluents, and crude oils.

The objective of this research is to develop a process to biodesulfurize (devulcanize) the surface of ground rubber particles. This process will introduce chemical reactivity to the surface of the ground rubber particles, thereby improving the chemical bonding and adhesion of the ground tire rubber into the virgin tire rubber matrix during compounding. The resulting product should have the same (or improved) level of quality as products manufactured with all virgin materials.

The Chemi-microbial processing approach, introduced in this paper, is targeted at alleviating the waste tire problem in an environmentally conscious manner. Furthermore, it is hoped that the results of this research may be applied to improve asphaltic materials and rubber and polymeric wastes to facilitate recycling of these materials. This research program is in its preliminary stages. The following discussions outline the logic and technical methods that will be used to accomplish this objective.

(a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO-1830.

PROBLEM

The effective collection and recycling of any waste material is an extremely complex issue. In most cases, the challenge of recycling materials involves the following interrelated components:

- societal issues,
- economic considerations and
- technical issues.

The issue of recycling waste tires comprises all three of these components. This problem alone could easily be the topic of a lengthy paper. This paper provides a basic overview of the problems associated with recycling waste tires and how each of these components relates to the scope of this project.

Handling waste automobile and truck tires is one of the most complex public policy issues facing our country. This problem involves elements of volume, safety and health. Currently, there are between 2 and 3 billion waste tires stockpiled in the U.S., with 250 million tires being added annually (U.S. Congress 1990). Large stockpiles of tires pose major safety (fires) and health (mosquito control and release of hazardous materials after fires) problems (Hall 1984; Moore 1986). Where, society views these stockpiles as liabilities to the public health and safety, the owners of these stockpiles consider the tires potential assets.

Lack of market volume is the primary economic consideration in the waste tire problem. The enormous stockpiles of waste tires exist because the markets for recycled tire rubber are not adequate to significantly reduce the volume of waste tires. It has been estimated that the total volume of ground rubber to be used in 1993 (200 million pounds) represents recycling less than 13 % of the total number of tires to be added to the waste stream in 1993 (based on 10 pounds of usable rubber from each recycled tire)(Smith 1993). Ground tire rubber will be used to produce materials ranging from rubber modified asphalt pavements to molded rubber products (Smith 1993). None of the current markets meet the criteria for an ideal market: high volume, long-term product life.

The primary technical issue concerning the use of ground tire rubber is that ground rubber particles are extremely chemically inert. The chemical inertness of the rubber particles limits the amount of ground rubber that can be successfully incorporated into most virgin rubber matrices. Increasing the reactivity of the surfaces of ground rubber particles should expand the range of types of virgin rubber matrices that can successfully incorporate ground rubber. Also, Chemi-microbial processing should allow for increases in the amount of ground rubber which could be incorporated into a given virgin rubber matrix.

TECHNICAL APPROACH

Many polymeric and rubber materials are vulcanized in order to impart desirable physical properties to the end-product. Rubber vulcanizates exhibit a number of desirable performance characteristics such as improved rheological properties, increased hardness, and decreased chemical reactivity. Vulcanization consists of the formation of a molecular network by a chemical bonding of independent polymer molecules. During manufacture, elemental sulfur (S_8) is added to tire rubber as a vulcanizing agent. As the rubber cures, elemental sulfur reacts with accelerators present in the compound to form mono and poly sulfide bridges, usually S_1-S_3, between independent rubber polymer molecules (Eirich 1978; Nordsiek 1987). Figure 1 illustrates the types of typical crosslinks and chain modifications in rubber vulcanizates.

The approach being studied in this project is to use thiophillic microbes or active enzymes from these organisms to selectively metabolize sulfur crosslinks in the ground tire rubber. Breaking these sulfur crosslinks represents one of the most significant problems to incorporating ground tire rubber into a new tire rubber matrix, because of the chemical properties vulcanization imparts to rubber vulcanizates. The use of thiophillic microbes for the selective degradation of sulfur crosslinks is being evaluated for three primary reasons:

- Vulcanization is largely responsible for the physical properties being targeted for modification.
- Two potential reactive sites will result for each sulfur metabolized.
- Biodesulfurization will inflict a minimum amount of damage to the polymer backbone.

Several bacterial strains have been identified for evaluation of their effect on ground tire rubber samples. These include *Thiobacillus ferrooxidans, Thiobacillus thiooxidans, Rhodococcus rhodochrous, Sulfolobus acidocaldarius*, and an unidentified mixed culture found in the American Type Culture Collection (ATCC). These strains were chosen based on the review of previous research in the literature involving biodegradation and biodesulfurization studies of polymers, coals, mining effluents, and crude oils (Torma 1990; Silverman 1959; Tsuchii 1985; Monticello 1985).

Dibenzothiophene (DBT) has been used extensively as a model compound in many biodesulfurization studies (van Afferden 1990; Krawiec 1990). Most of the microbes selected for these studies have been shown to metabolize DBT. If the microbes selected are not capable of metabolizing sulfur in the ground tire rubber, then DBT will be used to screen additional microorganisms isolated from soil under and adjacent to tire stockpiles and from extreme environment microorganisms. The use of DBT as a model compound is also helpful for predicting the surface chemistry of the bioprocessed ground rubber particles. The desulfurization mechanism for DBT has been shown to follow the

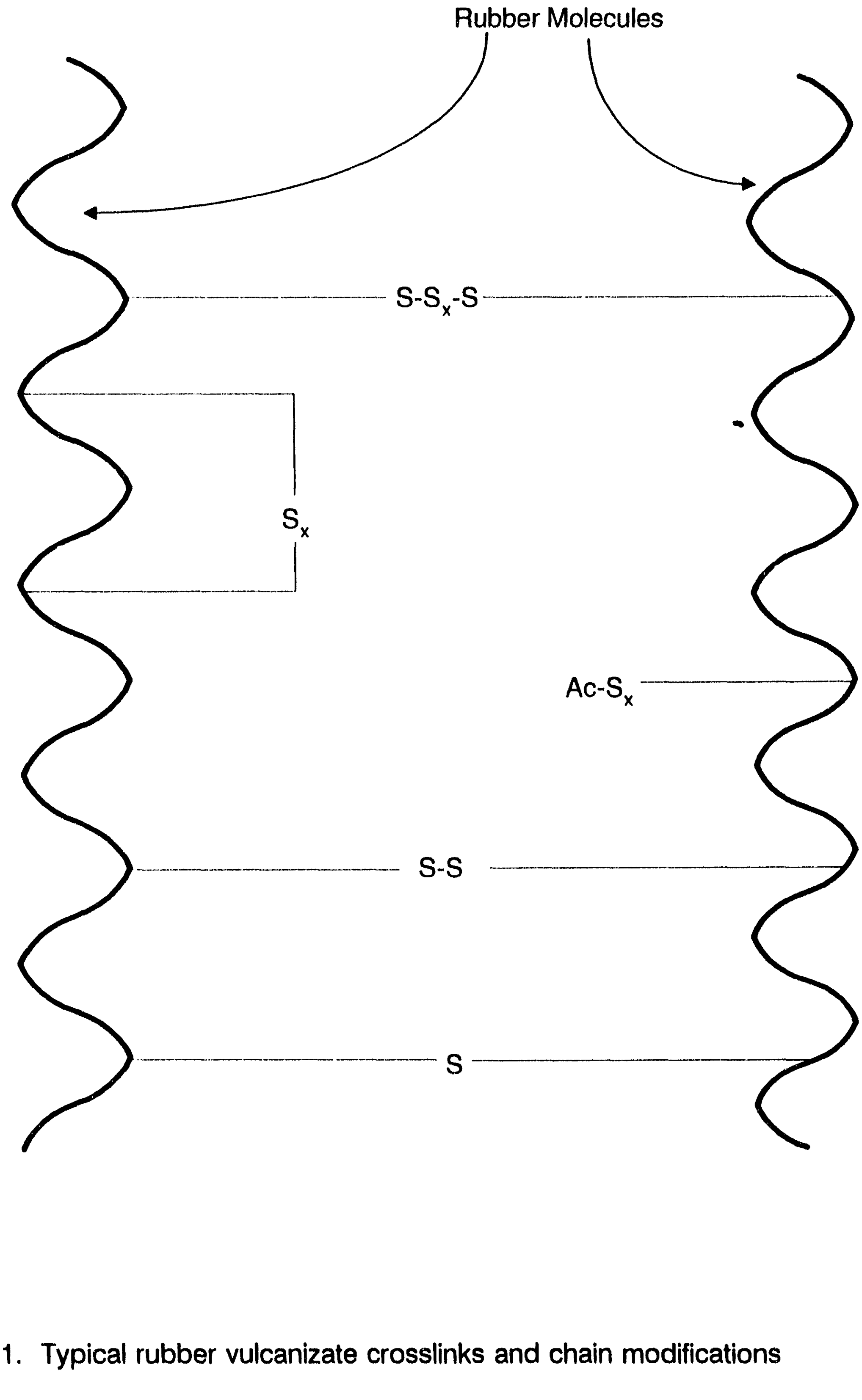

Figure 1. Typical rubber vulcanizate crosslinks and chain modifications

"4S" pathway, which represents a progressive oxidation of sulfur. Figure 2 illustrates the proposed "4S" desulfurization pathway for DBT. The sulfur crosslink is metabolized through sulfoxide/sulfone/sulfonate/sulfate in this degradation pathway. During these steps the sulfur is released from the organic frame as a sulfate ion, while the carbon frame is not severed and is only slightly oxidized.

The second phase of this project is to incorporate the surface modified ground rubber into virgin tire rubber compounds and evaluate the physical properties of the resulting cured rubber compounds. The results of these experiments will be compared with control experiments (unmodified tire rubber compounds and tire rubber compounds with unmodified ground rubber) to determine the influence of the surface modified ground rubber on physical properties. This phase of the project will use concepts developed in the following areas of rubber compounding and curing research:

- recuring of rubber vulcanizates,
- use of ultrafine rubber powders in rubber compounding and
- cure behavior of rubber compounds containing ground vulcanizates.

Concepts from these research areas will be used to develop particle introduction and compounding strategies to successfully introduce the surface-treated rubber into new rubber matrices.

Each of the areas of rubber research outlined above provides important information to help in developing compounding strategies. Work performed by Rouse (1992) describes the use of ultrafine ground tire rubber in rubber compounding. The results of this work show that there is a positive relationship between reduced particle size and physical properties. The author concluded that one of the key technologies requiring development was surface modification of the ultrafine ground rubber powders.

Work by Layer (1992, 1992) on recuring rubber vulcanizates shows that, after curing, zinc-based accelerators remain as a zinc salt. This was not consistent with the view that these accelerators are irreversibly bound to the rubber at the end of curing. This phenomenon is significant when viewed with the results of work performed by Gibala (1993), which supports the observations of Layer. This work shows that there is diffusion of accelerators from ground vulcanizates into surrounding rubber matrices and that sulfur from the new rubber matrices diffuses into the ground rubber particles. These results suggest that the rubber compounds to be used with surface modified rubber particles should be heavily accelerated to minimize the effect of the diffusion of accelerators out of the ground rubber particles. This should help prevent decreased scorch times. Adjusting the content of elemental sulfur to account for diffusion into the ground rubber particles should help provide optimum network development during the cure. Utilizing these advancements in rubber compounding and curing should help facilitate incorporating surface modified ground rubber into virgin tire rubber matrices.

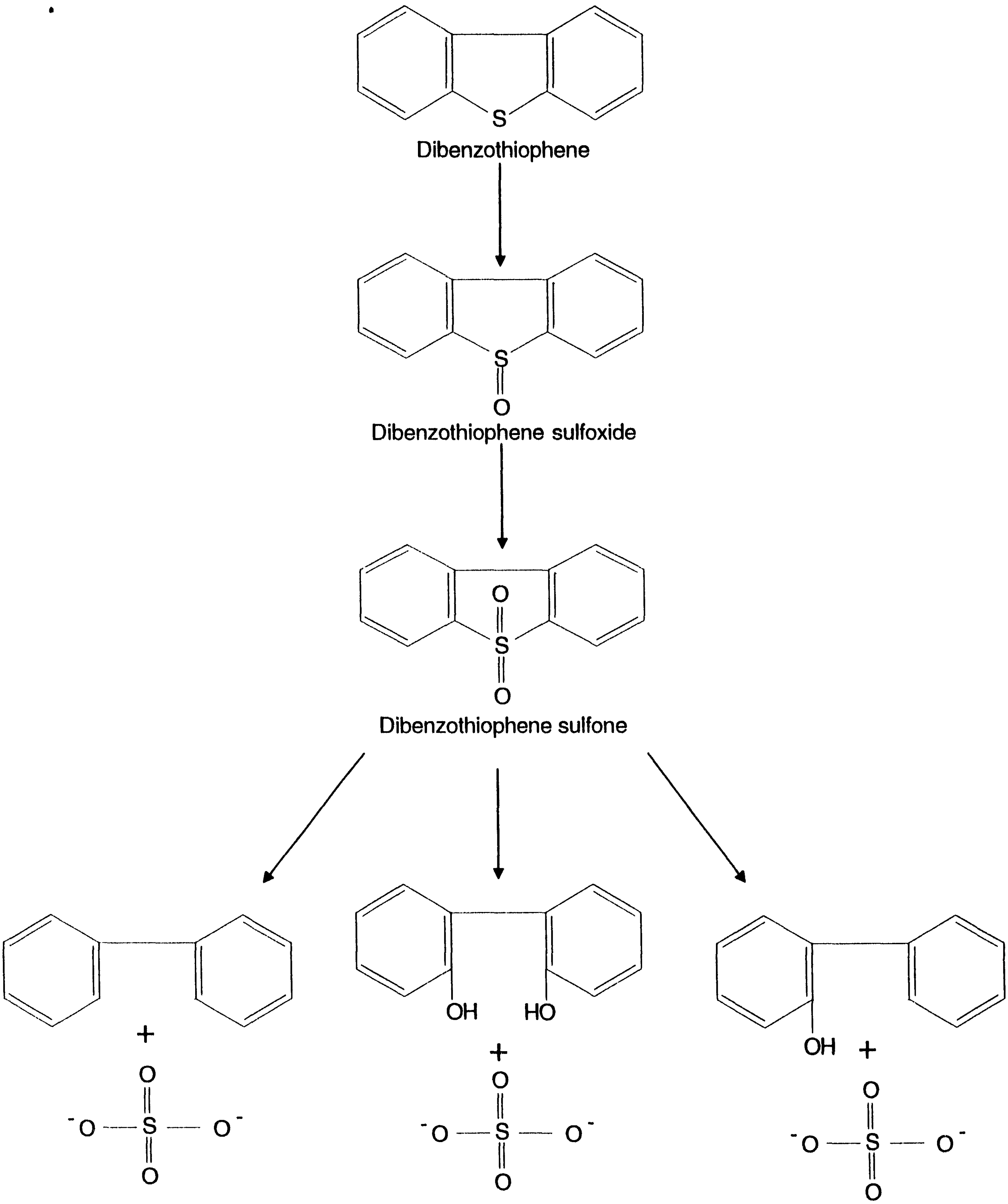

Figure 2. Proposed "4S" desulfurization pathway for dibenzothiophene

There is ample evidence in microbiological, polymer and rubber sciences literature to support the individual components of the Chemi-microbial processing approach to surface modification of ground rubber. The challenge of this research is to effectively combine these components to produce a commercially viable process. This research project is in its first year. It is anticipated that it will take three years to complete the project and deliver a commercially viable technology to the market place.

ECONOMIC POTENTIAL

The economics of utilizing surface modified ground tire rubber in new and retread tire manufacture is very favorable. Preprocessing waste tires by grinding, shredding, separating and sieving is required for effectively recycling waste tires. Preprocessing is required for practically every form of post-consumer processing of waste tires except whole tire derived fuel and boat bumpers. The cost for finely ground (200 mesh) tire rubber is approximately 0.25 cents per pound. (Rouse 1992) Virgin rubber stocks used in manufacturing new and retread tires cost between 0.60 and 0.90 cents per pound, depending on the end-product application. This provides a margin of 0.35 to 0.65 cents per pound for processing costs. Best estimates at this time show processing costs to run between 0.15 and 0.25 cents per pound. This provides a margin of profitability between 0.10 and 0.55 cents per pound.

The market volume for retread and new replacement and original equipment tires in this country is between 250 and 300 million units per year (U.S. Congress 1990). Incorporation of 15% surface modified ground tire rubber has been targeted as a goal. If this level of modification is achieved, then it is estimated that between 750 and 900 million pounds of ground rubber could be utilized in these markets. This volume of ground tire rubber represents the recycle of 112.5 to 135 million waste tires. The potential dollar volume for this market ranges between 300 and 450 million dollars per year.

ALTERNATIVE APPLICATIONS

Surface modified ground tire rubber could be used in a number of different applications to extend polymer materials. It is hoped that the increased reactivity of the surfaces of the rubber particles can be used to increase the amount of ground rubber incorporated into other polymers such as polyurethanes.

The use of surface modified ground tire rubber in rubber modified asphalt also holds interesting opportunities. Regular tire rubber incorporated into asphalt swells due to uptake of low molecular weight organic components in the asphalt (Shuler 1982; Stephens 1982). There is no conclusive evidence that the chemical moieties in asphalt bond with the surface of the rubber particles. It is hoped that because of the modification in the surface properties of the microbially processed rubber particles that certain polar species in the asphalt will preferentially bind to the rubber particles, establishing a true rubber-asphalt phase within the asphalt cement.

BASELINE TECHNOLOGIES

Comparable Tire Recycle Technologies:

Currently, there is only one technology comparable to the Chemi-microbial process for surface modification of ground tire rubber. This technology was developed by researchers at Air Products and Chemicals, Inc. (Bauman 1991). In this process the surface of ground tire rubber is modified by exposure to highly reactive gaseous atmospheres. The reactants (combinations of chlorine, fluorine, oxygen and sulfur dioxide gases) and operating conditions for the Air Products process are much harsher and hazardous than those for the Chemi-microbial processing. The Air Products process also requires thermal and or chemical post-treatment fixation to stabilize the surface of the modified particles. This technology has mainly been targeted towards modification of polyurethanes.

Alternative Tire Recycle Technologies:

Several rubber recycling technologies exist but none provides an ideal way for solving the problem of waste tire stockpiling.

- In the rubber modified asphalt cement process, unmodified ground tire rubber is added to asphalt to manufacture pavement surfaces. This technology is being heavily supported by the Intermodal Surface Transportation Efficiency Act of 1991. The Federal government is mandating to state departments of transportation to use rubberized asphalt in 5% of all federal highway projects. The percentage of projects using ground tire rubber will increase incrementally over the next years.

  There are some positive and negative aspects to this proposal. The positive aspect is that a relatively large volume of tires could be used in this application, but this is not a panacea. The research is not conclusive as to the true life cycle benefit of rubber modified asphalt pavements. Also, the chemistry of asphalts varies to an amazing extent, based on crude source and manufacturing practices. There are asphalts that are incompatible with modification by ground rubber.

  Finally, the volume of tires that can be used in a pavement should be put into perspective. Asphalt constitutes about 5% of a typical hot mix asphalt concrete pavement. For a ton of asphalt pavement, that is equivalent to approximately 100 pounds. Most rubberized asphalts contain between 15% and 25% percent ground rubber (by weight of asphalt binder). This correlates to about 15 to 25 pounds of rubber per ton. Based on 10 pounds of rubber recycled from each tire, this only adds up to about three tires recycled per ton of asphalt pavement.

- A number of different pyrolysis technologies are available that are targeted at extracting various hydrocarbon oil products, carbon black and gaseous byproducts.

- Tire derived fuel (TDF) or burning tires for their energy content is not an ideal recycling technology, because of its consumptive nature. However, TDF does have its place in helping to solve the waste tire problem. There is about 300,000 Btu in each tire. Tires contain more Btu per pound than wood, coke and coal (Farcasiu 1993). TDF and technologies such as waste tire-coal coprocessing are the appropriate answers to the disposal of waste tires which for one reason or another are not suitable for grinding and subsequent recycling.

- Ground tire rubber is used in a wide variety of moldable materials for low performance applications such as rubber mats and playground surfaces.

INDUSTRY PARTNERSHIPS

Many potential industry collaborations exist in the rubber processing, tire retreading and new tire manufacturing markets. Rubber processors could implement this technology in the future to expand their product lines. Retreaders could use this process "in house" to modify finely ground tire rubber removed during tire carcass preparation to extend rubber treadstocks. Finally, new tire manufacturers could implement this technology to "close the loop" and begin to recycle rubber on a much larger scale.

At this time, a Cooperative Research and Development Agreement (CRADA) is being pursued with one of the largest tire retreaders on the North American continent. Our objective is to have this CRADA agreement signed and in place early in 1994.

FY-94 ACTIVITIES

Biodesulfurization experiments will be conducted for the microorganisms selected from the literature. Ultrafine ground rubber (200 mesh) will be used in these experiments. This material is representative of typical finely ground tire rubber materials.

Shaker flasks will be used for culturing the microorganisms with the ground rubber as the primary source of nutrients for the microbes. Media and rubber samples will be analyzed as a function of time to determine growth and reaction kinetics. Electron Microscopy; High Pressure Liquid Chromatography (HPLC); Photoacoustic and Attenuated Total Reflectance Fourier-Transform Infrared Spectroscopy (PAS/FT-IR and ATR/FT-IR); and elemental analysis will be used to analyze the degradation products, the rate, and the extent of the desulfurization in these experiments. The surface modified ground rubber will be incorporated into virgin rubber compounds and cured. The physical properties of the cured rubber compounds will be evaluated by industry-accepted protocols (i.e., tensile and elongation, tear resistance, etc.). The most promising organisms for producing a devulcanized material at the most desired degradation rates wili be determined from these experiments. A report will be provided documenting the results of these experiments. The primary result of this task is to identify the most suitable organism (or combination of organisms) to focus on in the remainder of the work.

A final objective for the first fiscal year is to cooperate with our CRADA partner to produce a test set of retread tires that has surface modified ground rubber incorporated into the new tread material. We are faced with a number of technical and logistical obstacles to achieve this goal, but feel that these obstacles can be overcome and that this exercise is necessary to determine the processability of treadstocks treated with surface modified ground rubber.

CONCLUSIONS

Waste tires represent an enormous problem for this country. The tires that have been stockpiled over the last several decades are a wasted resource. Each tire contains the equivalent of 2 to 3 gallons of oil. Harnessing the energy, materials and human resources used in the original manufacture of these tires through recycling will provide significant long-term solutions to the health, safety and economic issues associated with waste tires.

To succeed at addressing the waste tire problem, it is will be necessary to develop the technology to "crack" into the new tire and retread tire manufacture markets. These two markets are simply the only markets large enough to handle the gigantic volumes of tires stockpiled in this country. Chemi-microbial processing of waste tire rubber could offer a unique opportunity to utilize "green" processing technologies to provide an environmentally responsible answer to solving the waste tire problem.

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