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SCRAP TIRE RECYCLING: PROMISING HIGH VALUE APPLICATIONS

FINAL REPORT

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entitled UTILIZATION OF WASTE TIRES EMPLOYING NOVEL SURFACE MODIFICATION TECHNOLOGY

by:
Bernard D. Bauman,
Paul J. Leskovyansky, and
Henry Drela

Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195

For
U.S. Department of Energy
Office of Industrial Technologies
Washington, D.C.

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CONTENTS

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EXECUTIVE SUMMARY

The abundance of scrap tires has long been a problem, both from an environmental and a health standpoint. Approximately 242 million scrap tires are available each year and of these only 56 million are recycled in some fashion, leaving 186 million to be discarded in landfills and stockpiles. Landfills are disrupted by whole tires that float to the surface and stockpiled tires are breeding grounds for disease-spreading rats and mosquitoes.

Surface modification of scrap tire rubber, which enhances the properties of the rubber and allows for the use of the treated rubber as a component in high performance, high cost polymer systems, shows promise to ameliorate and possibly even eliminate the scrap tire problem. This approach, in which the rubber particles are treated with gaseous chlorine, was developed by Air Products and Chemicals, Inc. under contract with the Department of Energy.

To date, this program has progressed through a Phase I: Feasibility Study, and a Phase II: Engineering and Product/Market Development Study. In the Feasibility Study, a surface treatment was developed that enables scrap rubber particles to be blended with and to replace virgin polymers to yield composite materials with performance characteristics comparable or superior to pure polymers.

The Phase I Study, completed and reported in October 1991, demonstrated the following:

- Stable surface treatment chemistries.
- Favorable processing requirements.
- Successful cast polyurethane composite products with major market application potential.
- Favorable process economics.
- Potential for very large energy savings on a national scale; if all scrap tires in the U.S. were processed via this technology, 276 trillion BTU's would be saved.
- Strong industry support and interest by state and local agencies.

In Phase II, two main objectives were accomplished. A viable process scheme for scrap tire rubber treatment was designed and cost estimated, and applications and markets for treated scrap tire rubber were developed.

Key notes from the process studies of the scrap tire rubber treatment facility include:

- Reaction kinetics are very fast, allowing for short cycle times, and the heat of reaction is small, eliminating the cost of a cooling system.
- Chlorine consumption is essentially 100%.
- The Forberg design mixer is the best choice for the reactor.
- The capital cost for producing treated rubber is only $0.05 per pound versus $0.50 to $2 per pound for polymer production.
- The economics of a rubber treatment facility are very attractive because the equipment needed is inexpensive and the applications for treated rubber are high value.
- There are no adverse safety, health or environmental effects from this process.

The applications and market development work demonstrated the following:

- Treated rubber particles were successfully incorporated into fast-gelling void free polyurethane wheels and tires, with minimal reduction in product properties and in some cases property enhancements of the wheels and tires.
- The use of treated rubber particles in polyurethane industrial enclosures improved some of the properties of the enclosure and reduced the raw material costs.
- Polysulfide elastomer solvent-impermeable membranes for secondary containment in tank farms and polysulfide roof sealant were improved, especially with respect to tear strength, with the addition of treated rubber to the fomulations.
- The fracture toughness of expoxy resins was enhanced by the use of treated rubber.
- Treated rubber particles were successfully incorporated in shoe soling materials.
- Polyurethane foam products have also been improved with the use of treated rubber particles.

The applications just described are only the tip of the iceberg. Many more potential applications exist and as new ideas are tested still more concepts will arise.

Future development will include pursuing these myriad application ideas, as well as, further defining the process through pilot scale studies using the Forberg design mixer reactor.

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LIST OF FIGURES

LIST OF TABLES

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POLYURETHANES

Air Products and Chemicals Inc., Allentown PA
    Kenneth R. Oster, Steven J. Stocker, Sabrina K. Wetzel, Susan M. Clift, Edwin L. McInnis,
Miles Polymers Div., Pittsburgh PA
    Neil H. Nodelman, Clifford J. Lau, Ashok M. Sarpeshkar, Mel S. Coons, Bin Lee, Tracy Estabrook
Ethyl Corporation, Baton Rouge LA
    J. J. Karlin, Fran Grace
Synair Corporation, Chattanooga TN
    Robert Rose

POLYURETHANE WHEELS AND CASTERS

Faultless Caster Division, Babcock Industries, Evansville IN
    Charles A. Harris, Mike Keach, Dennis Garness
Elasco, Inc., Garden Grove CA
    Darryl C. Readshaw, Dan Walters, Henry Laruccea
Superior Tire and Rubber Corporation, Warren PA
    Bill LeMeur, Henrty LeMeur, Chuck Embry,
Air Products and Chemicals, Inc., Hometown PA
    William Gardiner, John Hosak, Ray Vespa, Stanley Treskolasky

POLYURETHANE MICROCELLULAR TIRES

Alshin Tire Corporation, Rancho Cucamonga CA
    Richard Alshin
Urethane Technologies, Inc., Irvine CA
    T. Roy McClellan, Dennis Hobbs, Rob Estrada, Dubravko Primar, John Mizulo

POLYURETHANE CANAL LINERS

Innovative Process Corporation, Billings MT
    Leroy Payne

POLYURETHANE PROCESS EQUIPMENT

Edge-Sweets Co., Inc. Grand Rapids MI
    Dario J. Ramazotti, Dave DeBoer, Steve Hoffman
Cannon USA, Mars PA
    Lisa M. Hufnagel, Bob Wingard,

POLYSULFIDE ELASTOMERS

Morton International, Woodstock IL
    A. R. (Tony) Fiorillo, A. Cindy Hanson,
Superior Environmental Products, Inc., Dallas TX
    Mike Cork
Air Products and Chemicals, Inc., Escambia FL
    Bob Gilbert, Brian Gebbia

EPOXY RESINS

Air Products and Chemcials, Inc., Allentown PA
    Dillip N. Shah, Andrea K. Smith, Peter A. Lucas, John B. Dickenson, Robert W. Thomas
Lehigh University, Bethlehem PA
    Raymond A. Pearson, Reza Bagheri

CONSULTANTS

Environmental Technologies Alternatives, Inc., Lima, OH
    Fernely G. Smith
Akron Rubber Development Co., Akron, OH
    Jerry J. Leyden
Composite Structures Technologies , Inc., Pennsauken, NJ
    William C. Tambussi

I. INTRODUCTION

In the United States, hundreds of millions of tires are discarded each year. Most of the rubber, steel, and fabric from these tires is not reused in any way and the majority of the tires are currently landfilled. This represents a lost resource in that useful products and/or energy could be recovered from these tires. The abundance of scrap tires has long been a problem, both from an environmental and a health standpoint. This report documents an approach that has promise to ameliorate and possibly eliminate this problem. This approach is surface-modification of scrap tire rubber. Surface-modification enhances the properties of the rubber and allows for the use of the treated rubber as a component in high performance, high cost polymer systems.

Surface-modification is the technique of treating rubber particles with gaseous chlorine. This causes chemical changes in the structure of the outer molecular layers of each particle, which in turn makes the surface more amenable to bonding with other polymers.

Since the inception of the surface-modification of scrap tire rubber program, much has been accomplished in Phase I and Phase II:

1. BONDING PROVED - The reactive gas surface treatment of scrap tire rubber particles or crumb rubber, results in superior bonding, as compared with no treatment, to the polymers (polyurethanes, etc.) investigated in the work so far.

2. ECONOMICS - The projected cost of surface treatment at commercial scale is sufficiently low to compete with polymer markets 4 times larger than all of the annual available tire rubber.

3. THE PROCESS is safe, environmentally clean, and very low in capital cost. The low capital cost and simplicity of the process make it possible to build plants of appropriate size to serve either a source of scrap rubber or a user of the treated rubber. Both horizontal and vertical integration are feasible and may offer cost and performance benefits.

4. MIXING PROPERTIES IMPROVEMENT may be important to other applications.

5. THREE GENERAL MARKET OPPORTUNITIES
    a. Existing polymer systems - partial substitution for polymers currently used in specific products; generally a pound for pound replacement where there are price and/or properties advantages. There is a 65 billion pound per year market in existing plastic or rubber parts or products. Color restricts many applications because tire rubber is always black.

b. Displacing polymers with a composite - products (or parts) that are now made of specific polymers, that can be made at lower cost and/or with better properties, with surface treated tire rubber and a different polymer matrix.

c. Displacing other materials - products (or parts) that are now made of wood, metal or other non-polymer materials, that can be made at lower cost and/or with better properties, with surface treated tire rubber in a polymer composite. The effect is to increase the use of polymers by using surface treated tire rubber.

In general, the market is diversified which is both a challenge and an opportunity. The challenge is that the treated rubber must be tailored for each application, but the opportunity is that the material can be tailored by variation in particle size, type, degree of treatment, and use of additives, etc.

In this report, key results from Phase I, highlighting the incentives for continuing the program through Phase II, are summarized, and all the aspects of Phase II, including market and applications development, process development, plant design, economics, and environmental, energy, and safety impact, are detailed.

II. BACKGROUND

A. The Scrap Tire Problem

It is often quoted that there is approximately one scrap tire generated per year for each U.S. resident. The infrastructure in place for handling this vast number of scrap tires is noteworthy. There are 150,000 - 180,000 retail stores that sell replacement auto and pickup truck tires. These are gas stations, independent dealers, tire manufacturer owned stores, and mass merchandisers. The 20 inch tires used on highway trucks (18 wheelers) are generally sold/replaced at fleet maintenance shops, which are not as visible.

The predominant practice is for the retail store to pay an independent tire hauling firm, "casing jockey", to remove the worn-out tires. Approximately 35% of the "worn-out" tires have some use as tires:

- As a marketable used passenger car tire having greater than 2/32 inch tread ("high-tread") or

- As a retreadable casing. The inspection of the tires to remove these is done by the retailer or by the casing jockey.

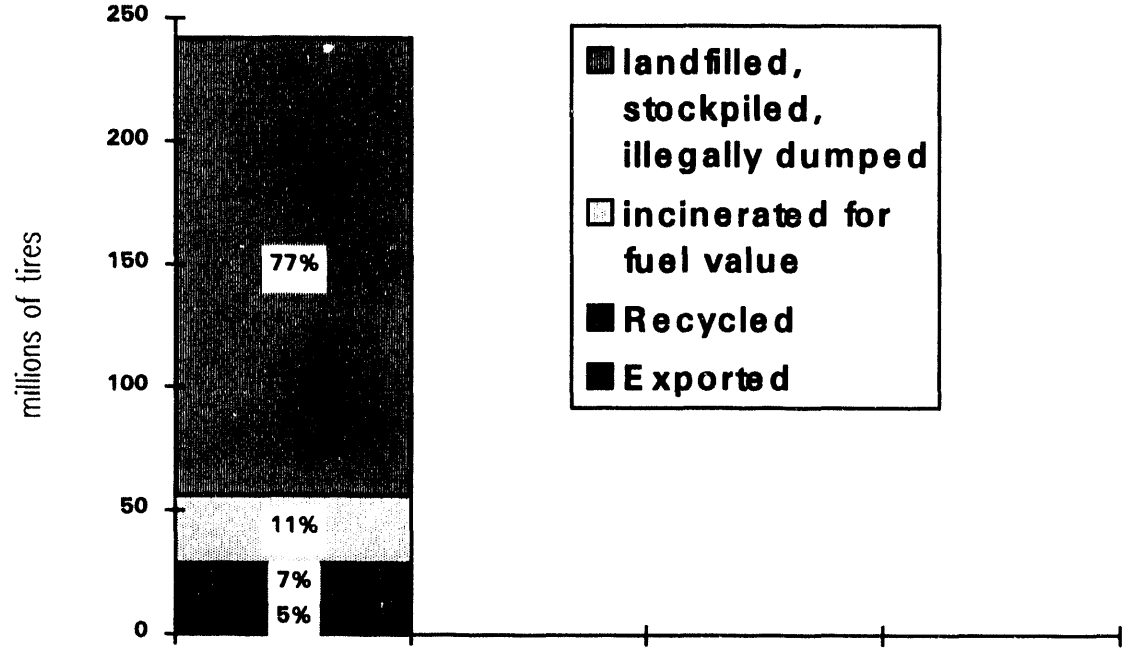
Therefore, there are three streams from the turned-in tires:

1. The "high-treads" generally move from the more affluent neighborhoods to the less affluent neighborhoods, in the same city.
2. The retreadable casings are usually trucked substantial distances to the retreading plant.
3. What is left, in the casing jockey's possession, is the "scrap tire" which must be disposed; these tires are typically landfilled or stockpiled simply because very few of the existing utilization technologies can afford to pay for the tires. Whole tires cannot be used in most of the processes as is and it costs money to either grind the tires for use and/or to retrofit the operation to accomodate the tires. The highway truck tires, when they are no longer suitable for retreading (on the average they are retreaded 2 times before the casing is damaged), also become "scrap tires" for disposal.

Figure 1 shows the fate of the scrap tires.

Figure 1

U.S. EPA Summary of Destination of Scrap Tires (Oct 1991)



Using the numbers from the U.S. EPA report, "Summary of Markets for Scrap Tires," 1991 data, after the sale of "high treads" (to be sold as used tires) and the sale of retreadable casings to retreaders, 242 million tires per year are "scrap tires." (The National Tire Dealers and Retreaders Association (NTDRA) indicates 270 million tires.) Of the 242 million tires, 56 million are recycled in some fashion as shown in Figure 1.

The remaining 186 million tires that are discarded each year are mostly a mix of automobile tires, light truck tires and medium and heavy highway truck tires; there is also a contribution from a variety of off-road and special use tires. Depending upon the assumptions with respect to the quantity distribution of tire sizes and weights, and depending on the assumed average rubber content and the recoverable percentage, the total U.S. scrap tire rubber that is generated, but not currently reused, is 3 to 6 billion pounds per year.

Automotive tires are highly engineered products designed to be durable and to withstand tremendous punishment during the performance of their intended function. Tires must be chemically inert such that they essentially do not degrade over long periods of time. This attribute of durability becomes a problem at the end of the useful life of the tire. They are difficult to grind up, and it is almost impossible to get tire rubber to undergo chemical reactions to form it into new products. So, most of the them are landfilled or stockpiled.

However, landfilling and stockpiling of tires is becoming a problem. Some states restrict the landfilling of tires whole or shredded as is shown in Table 1.

Table 1
SCRAP TIRE LAWS AND REGULATIONS (JANUARY 1993)

LEGEND: S = STORAGE P = PROCESS H = HAULER G = GENERATOR D = DISPOSAL
PP = PRICE PREFERENCE

STATE	FUNDING	REGS	LANDFILL	MARKET INCENTIVES
AL		S P		
AR	$1.50/tire disposal fee on retail sales $1/tire imported into state	S P H	tires must be cut and monofilled	30% equipment tax credit; 10% PP for retreads; Grants
AZ	2% sales tax on retail sale	S P H	bans whole tires	10% equipment tax credit; Municipal grants
CA	$0.25/tire disposal fee	S	effective 1/93 bans whole tires	40% tax credit for manufacturers using secondary materials; Grants and loans; 5% PP for tire materials
CO		S P		Tax credit for manufacturing using secondary materials
CT		S		10% PP
FL	$1/tire management fee	S P H G	bans whole tire - 1/95	
HI			Honolulu only -- bans whole tires	
ID	$1/tire retail sales	S	bans all tires	Grants to cities and countries; $20/ton end-user rebate; $1/retread reimbursement
IL	$1/tire retail sale and $0.50/vehicle title transfer	S P H	bans whole tires - 7/94	Rebates, grants and loans for manufacturing and marketing; Procurement goals
IN	permit fee tire storage sites	both proposed S H		10% PP and grants
IA		S P H	bans whole tires	Grants; Recycled content required for state purchases
KS	$0.50/tire retail sales	S P H	tires must be cut	Tax credits for equipment; Municipal grants
KY	$1/tire retail sales	S	tires must be cut	Tax credits for recycling businesses; Loans; Recycled content preference
LA	$2/tire retail sales - 2/92	S P H	tires must be cut	Tax credits; 5% PP
ME	$1/tire disposal fee	S P H		State should buy recycled; Loans and grants
MD	$1/tire first sale	S P H	effective 1/94, bans tires	5% PP
MA		S P		10% PP
MI	$0.50/vehicle title transfer	S P H G		Grants and loans; 10% PP
MN	$4/vehicle title transfer	S P H	bans whole and cut tires	Grants
MS	$1/tire retails sales	S P H	to be written	County and regional grants and loans; 10% PP
MO	$0.50/tire retail sales	S P H	bans whole tires	10% PP; grants
MT		S		Tax credits for equipment and products; State required to buy recycled

Table 1
(continued)
SCRAP TIRE LAWS AND REGULATIONS (JANUARY 1993)

LEGEND: S = STORAGE P = PROCESS H = HAULER G = GENERATOR D = DISPOSAL
PP = PRICE PREFERENCE

STATE	FUNDING	REGS	LANDFILL	MARKET INCENTIVES
NE	business assessment fee $1/tire retail sales			Grants
NV	$/tire on new tire retails sales	to be written		Grants for education and highway projects; 10% PP
NH	town administered graduated vehicle registration fee	S P	tires must be cut unless facility is exempt	State should buy recycled
NJ		S P		Grants; Tax credits; State should buy recycled
NY		S P H		Grants; DOT specification for crumb rubber
NC	1% sales tax on new tires	S P H	tires must be cut	Grants; Funds county tire collection
ND	$2/new vehicle sales	S H		
OH		S	tires must be cut	
OK	$1/tire on new tire sales	S P		Grants; Processor credits
OR		S P H	tires must be cut	State should buy recycled
PA		S	operator's option	5% PP on bids; Grants and low-interest loans
RI	$0.75/tire on new tires sales $5 deposit/tire	S P		Funding stockpile clean-up; Promotes use of recycled products
SC	$2/new tire sales	S P H	bans whole tires	7.5% PP; Grants to counties and local governments; State required to buy recycled
SD	$0.25/tire vehicle registration	S P	bans tires by 7/1/95 unless allowed by state rules	Grant fund
TN	$/tire retail sales		bans whole tires - 1/95	Grants
TX	$2/tire retail sales	S P G H D	bans whole tires	$0.85/tire processor credit; Tax credits; 15% PP on asphalt rubber; Low-interest loans
UT	graduate tax per tire size	S P H		$20/ton reimbursement to end-user
VT			bans whole tires	State required to buy recycled; 5% PP
VA	$0.50/tire disposal fee on new tire sales - sunsets 12/31/94	S P	bans whole tires	Contract services; 10% Tax credit for recycled equipment -Sunsets 12/31/94
WA	$1 fee on new tire sales	S P H		Grants to local governments
WV		S P H	bans whole tire (1988) bans all tires (6/1/93	State required to buy recycled
WI	$2/tire per new vehicle title transfer	S P H	bans tires - 1/1/95	$20/ton reimbursement to end-user; Grants
WY		S		State required to buy recycled

Also, many states have imposed taxes on scrap tires to be used to fund programs centered around solving the scrap tire problem.

Disposal of whole tires in scrap tire piles represents an environmental hazard in several ways. Scrap tire piles catch fire and are very difficult to extinguish - frequently burning for days. These tire fires generate significant air, land, and water pollution. Scrap tire piles, particularly whole tires, provide excellent refuge and breeding sites for disease-carrying rodents and mosquitoes. It has been shown that the Asian Tiger Mosquito, Aedes Albopictus, breeds well in scrap-tire piles and is a carrier of Dengue fever, Lacrosse encephalitis, and yellow fever in the United States.

Scrap tires move a lot because the landfilling/dumping costs less farther away from a city or affluent suburbs. Also, reused tires are processed far from their original point.

In the past, as landfill fees went up, the casing jockey paid farmers or land owners a fee to dump scrap tires on unused land. In the last few years, publicity about the tire pile fire/land owner liability has reduced this practice. And this contributes to "midnight dumping."

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B. Summary of Existing Approaches

Scrap tires, ranging from whole carcasses to finely ground rubber with steel and fabric removed, are reused in a number of relatively low-value applications. The most important uses include burning for fuel, and use in asphalt highways. These uses consumed approximately 11% and less than 1% respectively of the scrap tires generated in 1990. While there has been much publicity concerning pyrolysis which is a thermal process for generating gas, oil and carbon black, this approach has little commercial usage. In Table 2, the aspects of commercial viability (value), applications potential (volume), and energy savings (value) are compared qualitatively with those for this surface-modification technology.

Table 2
RELATIVE MERITS OF SCRAP TIRE REUSE TECHNOLOGIES

Reuse Technology	Commercial Viability (Value)	Applications (Volume)	Energy Savings (Value)
FUEL	L - M	M - H	M
CONVERSION (pyrolysis)	L	M- H	L
REUSE:			
In Asphalt	L	H	L
As Inert Filler	L	M	M
As Active Component	H	M - H	H

L=Low; M=Medium; H=High

The current major uses for scrap tire rubber are described in further detail below. It should be noted that technologies already exist for the shredding and grinding of scrap tires into finely-divided rubber, and for separating the steel and fabric. A number of firms are doing this on a commercial basis in the United States. The steel, derived from scrap tires, is currently being recycled back into new steel.

Fuel

Scrap tire rubber is a good fuel. Burning tire derived fuel (TDF) generates approximately 14,000 BTU per pound. This is somewhat more energy than is generated by the burning of coal. The sulfur content of tire rubber is between that of hard and soft coal.

Scrap tire rubber is used as a fuel in cement kilns and in the generation of electric power. Tires are particularly well suited for cement kiln use because the steel from the tires is also beneficial to the cement.

There are problems with the use of tires as a fuel. 1.) Whole tires and tire chips are difficult to feed into furnaces that were developed for burning coal. This is because as the rubber is moving towards the burning zone and gets hot, it becomes sticky and then "runny" as it decomposes. This makes it very difficult to use a significant proportion of rubber in a furnace designed to burn coal and/or oil. 2.) The economics of using tires as a fuel are marginal at best. In this application, the tires are competing with coal that costs $0.02-0.03 per pound. If tire chips are required, shredding must be performed. This process costs at least $0.02-0.03 per pound of tires shredded. Hence, the use of tires as a fuel is only viable if whole tires can be burned, or if one includes the disposal cost (tipping fees). 3.) There is considerable public resistance to the burning of tires. 4.) Burning tire rubber precludes its further use as a material.

There is an industry that shreds and grinds scrap tires for specific markets. TDF is usually the whole tire shredded to 2-4 inch pieces with the steel bead removed. Most of the boilers that use TDF are coal fired, displacing up to 10 to 20% of the coal. Some TDF is smaller and is processed to be "90% steel free" referring to the removal of the fine tread wire. There are some boiler operators that are concerned about the fine steel fusing during the burning of the rubber and then interrupting the removal of ash from boilers with grates. This could cause additional maintenance costs.

Asphalt Highways

The use of ground tire rubber in the construction of asphalt highways holds promise to improve the performance and durability. However mixed results indicate that several variables must be controlled in order to optimize this technology.

Federal legislation, Intermodal Surface Transportation Efficiency Act of 1991, Public Law 102-240 -- Section 1038, requires the use of scrap rubber or certain other scrap materials in construction of all federally-financed highways. It appears that the purpose of this legislation is to consume scrap materials, not to improve the highways. This law has been partially responsible for a large number of companies being formed to grind scrap tires. Crumb rubber (nominally 3 to 40 mesh) is produced by some 48 companies in the U.S.; 38 which have been in business less than 3 years.

The use of scrap tire rubber in asphalt highways has some problems. It increases the material costs for a highway. It also requires the addition of new equipment for mixing and "reacting" the rubber into the asphalt. In addition, it requires a change in the way roads are made--and change is not welcomed by the highway construction industry. Another way to view this application is that the ground rubber is replacing aggregate, not a high value use.

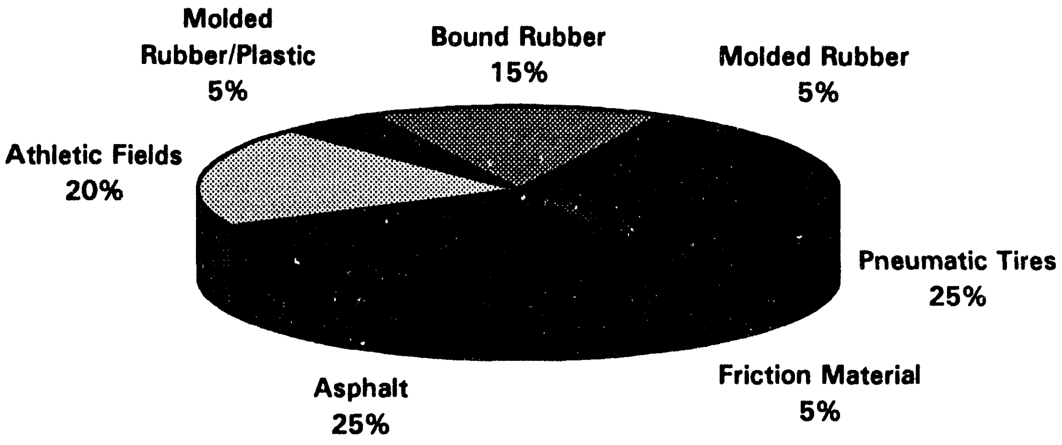
Materials

The highest-value applications for scrap tire rubber is where it is used as a material. Polymeric materials have prices from about $0.35 per pound to over $5.00 per pound; far higher than the costs for coal or aggregate.

Scrap tire rubber cannot be simply "remelted" back into new elastomeric products because it is a thermoset. Heating above a certain temperature simply results in the rubber decomposing (pyrolysis). Hence, to use scrap rubber as a material it has to be combined with other "moldable" materials. These other materials can be thermosets or thermoplastics. There are a number of such combinations in commercial use. Examples include running tracks and playground surfaces (polyurethane binder) molded rubber goods, pneumatic tires, and a variety of molded plastic products. A breakdown of the material uses of scrap tire rubber is summarized in Figure 2.

FIGURE 2

USES FOR GROUND RUBBER
(1992 Numbers)



In essentially all of these applications, the physical properties of the matrix material is reduced by the incorporation of the rubber. There are a few examples where the use of rubber improves some properties. The major incentive for using scrap rubber in these products is cost reduction. However, the reduced physical properties relegate these materials to low-end, low cost applications.

The problem of property reduction with the use of rubber in these polymer applications is caused by poor compatibility and bonding between the rubber particles and the matrix polymer. With poor bonding, stresses exerted on a part are not transmitted uniformly throughout the part and localized stress concentrations cause early failure.

Other Applications

There are numerous other, relatively minor uses for scrap tire rubber. Some of these include cutting out sections of tires to form loading dock bumpers, boat fenders, and soles for sandals; connecting together bunches of scrap tires and sinking them in the ocean to form fishing reefs; and ground rubber as a soil modifier for landscaping and for spreading around children's play areas.

C. Surface Treatment - A New Approach

Surface modification of rubber particles involves reacting the rubber particles with chlorine gas. This treatment changes the surface of the rubber particles such that they are now more amenable to combining with polymers.

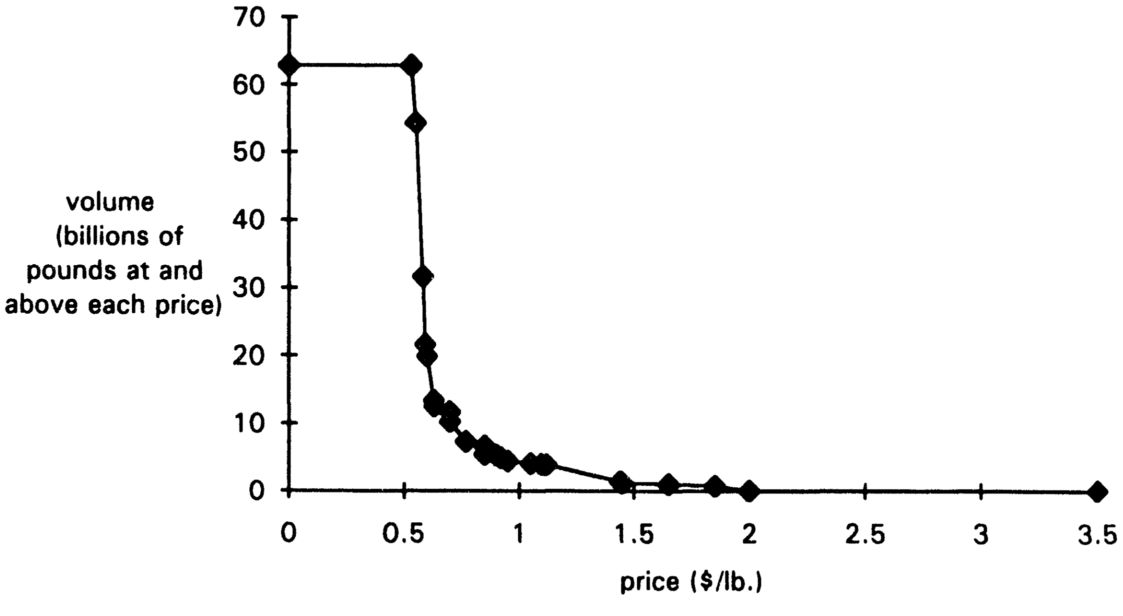
Without surface activation (or expensive copolymers) there is no bonding or limited bonding of the rubber particles. Therefore, the uses are confined mostly to "filler" (the rubber particles are adding volume, but do little or nothing in the way of contributing to the physical properties), competing with calcium carbonate, which is low priced. This is because of poor compatibility and bonding between the rubber particles and the continuous phase materials. Examples of materials "filled" with rubber particles include polyethylene, uncured rubber, and polyurethane.

The uses are all below $0.30 per pound and bonding is limited by surface properties. The manufactured end products with reduced physical properties are generally used in lower-performance applications, which are very price sensitive.

After surface modification, the cost of the rubber may be $0.35-0.65 per pound. In this price range, surface treated rubber potentially competes with the 65 billion pound per year polymer market. Figure 3 shows the cumulative amount of polymers sold at a certain price or higher.

Figure 3

Polymer Price Versus Cumulative Volume Production



These prices may be as much as $0.15 too high depending on market fluctuations. Figure 3 is a very important picture of the potential market for surface treated rubber.

Modification of the surface of scrap rubber particles can significantly improve their compatibility and adhesion properties. This enables fabrication of end-products, containing rubber particles, which have superior properties and can be used in higher performance, higher value applications. Inorganic fillers are surface-modified by the application of coatings and coupling agents. These "surface-modified" fillers have broad commercial usage. Attempts to use similar coatings approaches to modify the surface of rubber particles have had little success. In these approaches coatings (termed treatments) were used that targeted improved compatibility with large-volume thermoplastics and rubber. These thermoplastics and rubber are low cost materials to begin with, and incorporation of coated rubber particles has a minimal effect in lowering the overall raw material costs. Furthermore, since reductions in physical properties still occur, the performance/price ratios do not significantly improve the competitive position of these materials versus unfilled.

Since 1989, the U.S. Department of Energy has been funding the development of a superior approach for the surface-modification of scrap tire rubber particles. In this approach, the rubber is reacted with chlorine to impart greater compatibility and adhesion and modify the bulk physical properties. This treatment is simple and inexpensive; it involves brief exposure to a reactive gas atmosphere and since the surface molecules are chemically modified, and not just coated, the treatment is permanent.

The process has been further developed to enable the rubber particles to be used in high performance, high cost polymer systems. In these systems, the performance/price ratios for "filled" systems have distinct advantages over unfilled systems. This provides a sufficient driving force for commercial implementation.

III. THE PROGRAM

As a result of a DOE competitive procurement, a cost-share R&D contract was awarded to Air Products and Chemicals, Inc. for the utilization of scrap tire rubber in surface-modification technology. This project would not have been undertaken by Air Products without DOE funding because of the large risk involved.

A. Phase I Results [Jan. 1989 - Oct. 1991]

In this contract, a feasibility study was performed on the surface-modification technology for scrap tire rubber reuse. Noteworthy accomplishments and conclusions from the feasibility study are summarized below:

- **Effective surface treatment chemistries were developed.** Enhanced adhesion was confirmed by T-peel tests using polyurethane which was cast onto treated and untreated slabs of rubber. It was observed that with the untreated rubber slabs, only 3 pounds per inch is required to tear the laminate apart. With the treated rubber slab samples, the rubber slab itself tore at 150 pounds per inch -- before the adhesive bond failed.

- **Permanent surface treatment chemistries were developed.** The important discovery was made that the addition of chlorine to the treatment atmosphere imparted permanent enhanced adhesion to the rubber particles.

- **Favorable process requirements evaluated.** It was determined that the surface treatment does not depend upon the type of grinding used to prepare the particles, that pre-treatment and post-treatment processing is not required, and that relatively low concentrations of the reactive gases are effective in achieving an acceptable level of surface modification.

- **Polyurethane/scrap rubber composites successfully prepared.** Use of up to 40% (by weight) of the modified rubber in a polyurethane formulation maintains essentially all of the important physical properties.

- **Products molded in treated-filled and unfilled polyurethanes exhibit the same stiffness and will perform essentially identically.** The significance of these data is that the elastic moduli of the surface-modified rubber filled composite and unfilled polyurethane are virtually identical over the range of 0-100% elongation, which brackets the working range of nearly all cast polyurethanes.

- **Polyurethane market applications identified.** Many potential end-use applications for surface-treated rubber in polyurethane matrices were identified and four target applications were selected for in-depth evaluations.

- **Favorable process economics evaluated.** Phase I economics for the surface-modification approach to reuse of scrap tires were very attractive. The variable treatment costs were estimated to be $0.15 - 0.17 per pound. This would allow a very attractive selling price for applications substituting expensive raw materials (i.e., polyurethane intermediates) , which are in the $1-4 per pound range.

- **Favorable capital costs.** The projected capital requirements for a surface-modification facility are quite modest. In the Phase I Feasibility Study, it was estimated that a 20 million pound per year pilot plant would cost $3 - 4 million. It is interesting to note that this estimated capital cost is only 1/2 - 1/3 the cost of a tire rubber-to-energy incineration plant, on a per tire basis.

- **Strong Industry Interest.** There is much interest and support in several industrial segments where there are potentially large markets for surface-modified scrap rubber particles. For example, the Rubber Manufacturers Association (RMA) has strongly endorsed the surface-modification approach, and has offered their support.

- **Strong Interest of State and Local Governments.** Substantial interest in this surface-modification process has been found within various state and local government agencies.

B. Phase II

Phase II accomplished two major goals:

- Applications development was supported in order to assess market potential. This would confirm the widespread usage of surface modification technology and justify continued support of this program.

- A commercially viable process was developed. At the end of Phase I, rubber treatment was only being done on a one pound per batch scale and in order to be attractive economically the process needs to be scaled up to the commercial level.

Also, the energy, economic, and environmental impact of surface-modification technology was confirmed.

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1. Market/Applications Development

Applications Development Target Selection

Base polymer selection. The base polymers selected for demonstration with polar surface treated tire rubber, produced by gas-phase chlorination, were polyurethanes, polysulfide elastomers, and epoxy resins. Compatibility, cost, performance and processing parameters would need to be considered. Applications development in other polymers may require different surface modifications.

Selection of target polymers in which to demonstrate the utility of surface treated rubber required taking into consideration a number of factors. Phase I of the program resulted in positive indications of compatibility of polar surface treated tire rubber particles with polar polymers[1] such as polyurethanes, epoxies, and polysulfide elastomers. The results obtained were consistent with the known relationships between surface energy, wetting, and solubility parameter to adhesion and polymer miscibility[2]. Put simply, the idea of "like dissolves like" extends to the interaction between treated rubber surfaces and the continuous polymer phase in which they are mixed. In Phase II of the project, the utility of treated tire rubber with a polar surface was explored, so the selection of polyurethanes, epoxies and polysulfide rubbers for demonstrations is not novel, but rather an extension of the discoveries in Phase I. Exploration of other chemical surface treatment types, such as non-polar unsaturated surfaces is left for the future. The inescapable consequences of the chemical composition and resulting properties strongly suggests that a classical chemical-structure/property approach to polymer compatibility be employed in the future. Experimental results in polyether-based polyurethanes, epoxy resins and polysulfide elastomers have borne out this expectation.

The treated tire rubber particles can be described as cross-linked elastomeric particles with a range of available sizes. They have a polar surface and are black in color. Market utility is then dependent on these properties, the overall properties of each composite and the economic effect of replacing virgin polymer with treated tire rubber.

Volume cost. Polymer compatiblity alone cannot predict the market utility of treated tire rubber. Once the technical utility of treated tire rubber in a polymer is established, the actual employment will depend on the relative cost of the materials, the improvement or reduction in properties, and the effect on processing. This will all affect the cost/performance characteristics of the final product. Table 3 shows

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[1] Utilization of Waste Tires Employing Novel Surface Modification Technology: Final Report, Bernard D. Bauman, U. S. Department of Energy, October 1991

[2] Adhesion and Bonding, Reprint from Encyclopedia of Polymer Science and Technology, Norbert M. Bikales, ed., Wiley-Interscience, 1971.

the volume cost and cost per pound of various thermoset and thermoplastic materials and additives in decreasing order. A favorable scenario for the use of treated tire rubber is the replacement of higher volume cost materials with an acceptable change in properties or property improvement at an acceptable cost. Volume cost is used for this comparison since it takes into account the differences in density of the materials

Table 3
Approximate Volume Cost of Various Materials

Base Material	Volume Cost[3] ($/cubic inch)	Approximate Cost[4] ($/pound)
polysulfide rubber	0.1178	2.60
polycarbonate	0.1083	2.50
polyamide (Nylon 6)	0.1020	2.65
poly(chloroprene)	0.0765	1.71
epoxy resins (with curative)	0.0701	1.75
polyurethane(mid-range)	0.0596	1.50
acrylonitrile butadiene styrene	0.0557	1.47
poly(methylmethacrylate)	0.0516	1.21
nitrile rubber	0.0452	1.27
poly(ethyleneterephthalate)	0.0359	0.77
ethylene-propylene-diene rubber	0.0358	1.15
polybutadiene	0.0266	0.76
Surface Treated 80-mesh tire rubber	0.0263	0.65
styrene-butadiene rubber	0.0248	0.74
Surface Treated 20-mesh tire rubber	0.0159	0.40
rubber dust	0.0151	0.038
polystyrene (high impact)	0.0151	0.40
carbon black	0.0149	0.23
natural rubber	0.0146	0.50
low-density polyethylene	0.0127	0.38
high density polyethylene	0.0126	0.34
reprocessed synthetic rubber	0.0078	0.18
tire buffings	0.0072	0.18
calcium carbonate, 3-micron coated	0.0058	0.06

⇑
Substitution
Favored by
Cost
Reduction

Substitution
Favored by
Property
Improvement
⇓

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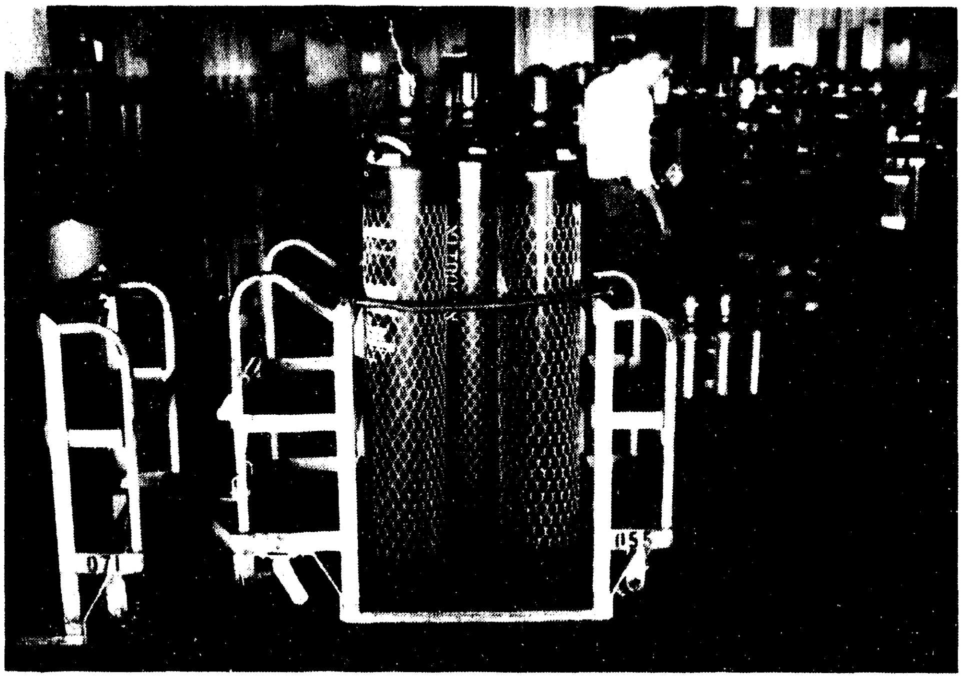
[3] Specific gravity data from:
Modern Plastics Encyclopedia, McGraw-Hill, New York NY, October 1991
The Vanderbilt Rubber Handbook, Robert O. Babbit ed., R. T. Vanderbilt Co., Inc., Norwalk CT, 1978

[4] Polymer cost data from :
Modern Plastics, Robert J. Martino ed., McGraw-Hill, New York NY, July 1992, p. 68, polyethylenes, polypropylene, polystyrene, ABS, PVC,
Modern Plastics Encyclopedia, McGraw-Hill, New York NY, October 1991, various polymers
Morton International, Chicago IL, polysulfides
Pacific Anchor div. Air Products and Chemicals, Inc., Allentown PA, epoxy resins
Miles Polymers, Pittsburgh PA, polyurethanes
Air Products and Chemicals, Allentown PA, polyurethanes
Rubber World, Don R. Smith ed., March 1992, pp. 37-46, elastomers, carbon black, pigments and fillers
Rohm & Haas Inc., Philadelphia PA, acrylic resins
Eastman Chemicals and Palstics, Kingsport TN, PET

Application demonstration selection. Application demonstration selection needed to be based on the expectation of technical success of incorporation of treated rubber into target polymers while preserving or enhancing pyhsical attributes of the polymer for various end-uses. It was also desirable to select individual demonstrations based on the similarity of materials and processing to other applications for the same polymer so that each demonstration could represent a larger portion of the total use of the particular base polymer. For example, a successful substitution in a fast-gelling polyurethane cast elastomer, or in a fast reacting polyurethane/polyurea reaction injection molded product effectively demonstrates efficacy in a broad range of polyurethane products with simpler processing.

Polyurethane Solid Cast Industrial Wheels. Solid cast polyurethane wheels, shown in Figure 4, were produced with substitution levels of 16.7% and 26.5% polar surface treated tire rubber. Eight standard 8" diameter by 2" wide wheels cast in a 60 Shore D polyether/diphenyl methane diisocyanate based polyurethane with a steel hub insert for fitting a sealed roller bearing were placed in service at Air Products and Chemicals, Inc. specialty gas cylinder filling plant in Hometown, PA.

Figure 4 - Solid Cast Polyurethane Wheels With Surface-Treated Ground Tire Rubber in Service at a Specialty Gas Filling and Distribution Center.



Four wheeled carts are used to transport cylinders to various parts of the plant in a continuous automated system operating on a 24-hour schedule with 102 carts in service. Two wheels on each cart are fixed and two are swivel mounted. Four wheels with 16.7% treated tire rubber were placed on one cart while four wheels containing 26.5% treated tire rubber placed on another cart. The standard polyurethane wheels in service on the other carts have replaced a steel wheel with a thin polyurethane tread. The polyurethane wheels with their sealed bearings and very small steel hub effectively damp vibration resulting in a smoother ride and exceptional wheel installation service life. The polyurethane wheels have a service life in excess of 30 months(a failure has yet to occur) compared to the polyurethane treaded steel wheel service life of less than six months. Similar service life at lower polymer volume cost is expected from the wheels under test.

Production of these wheels with surface treated tire rubber for the demonstration required innovations in processing. Also, modifications of the surface treatment chemistry were required since the earlier process resulted in small voids due to foaming and longer gel times due to inhibition of the isocyanate reactivity.

The proprietary polyether/diphenyl methane diisocyanate prepolymer and curative system used in the standard wheel has a short gel or solidification time, of approximately 20 seconds. When treated tire rubber, or other solids, are added to such systems, the viscosity of the mixture increases, making it difficult to fill molds. No attempt was made to use more than 26.5% treated tire rubber since the viscosity of the reaction mixture had increased to the point that mold filling became critical. Laboratory trials with slower setting systems have incorporated up to 50% treated tire rubber in polyurethanes[5]. Adjustment of the viscosity of the polyurethane prepolymer and an increase in gel time would allow adequate mold filling with 50% treated tire rubber, where performance is less critical. The solid polyurethane wheels are used for carrying heavy loads with low rolling resistance. Since the addition of the current version of treated tire rubber reduces the hardness of the wheel, wheel deflection and rolling resistance increase with the percentage of treated tire rubber. This can be mitigated by treating the rubber to obtain a higher hardness or reformulating with a higher hardness polyurethane. In this phase, time constraints precluded developing a formulation based on a different polyurethane.

Special equipment for mixing the treated tire rubber, urethane prepolymer and curative were rented from Edge-Sweets Company since the manufacturer of these wheels did not have suitable equipment. This particular equipment takes the metered component streams and introduces the solid additives directly in the dynamic mixhead on the way to the mold. Residence time of the materials in the mixhead is less than two seconds, making casting of fast gelling systems with treated tire rubber possible. In producing polyurethane cast elastomers, it is

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[5] Utilization of Waste Tires Employing Novel Surface Modification Technology: Final Report, Bernard D. Bauman, U. S. Department of Energy, October 1991

necessary that the components be metered precisely and mixed thoroughly in order for the right chemistry to take place in the mold. Metering is most frequently accomplished with positive displacemant pumps. Many of the metering devices in service throughout the cast elastomer industry could be damaged by handling of fine solids. Production of high quality parts without porosity also require that any gases trapped in the mixture by mixing operations be removed prior to filling the molds or at least before the polymer mixture solidifies. Dispersion of solid additives in prepolymer, polyol, or curative streams, with subsequent vacuum degassing is precluded by the potential for damage to the pumps in certain equipment.

The formation of polar chemical groups on the surface of treated tire rubber can result in generation of sites which will react with isocyanates and isocyanate functional prepolymers. This can result in a slowdown of the reaction, premature crosslinking of the prepolymer and formation of carbon dioxide, as illustrated in Figures 5 and 6. The reaction which forms carbon dioxde is much slower than the reactions which result in solidification of the prepolymer, making it impossible to remove gases from fast-gelling systems or to store dispersions of treated tire rubber in isocyanate functional components

Figure 5 - Surface Treated Ground Tire Rubber in Polyurethane Prepolymer Showing Foam Rise in a Test Sample.

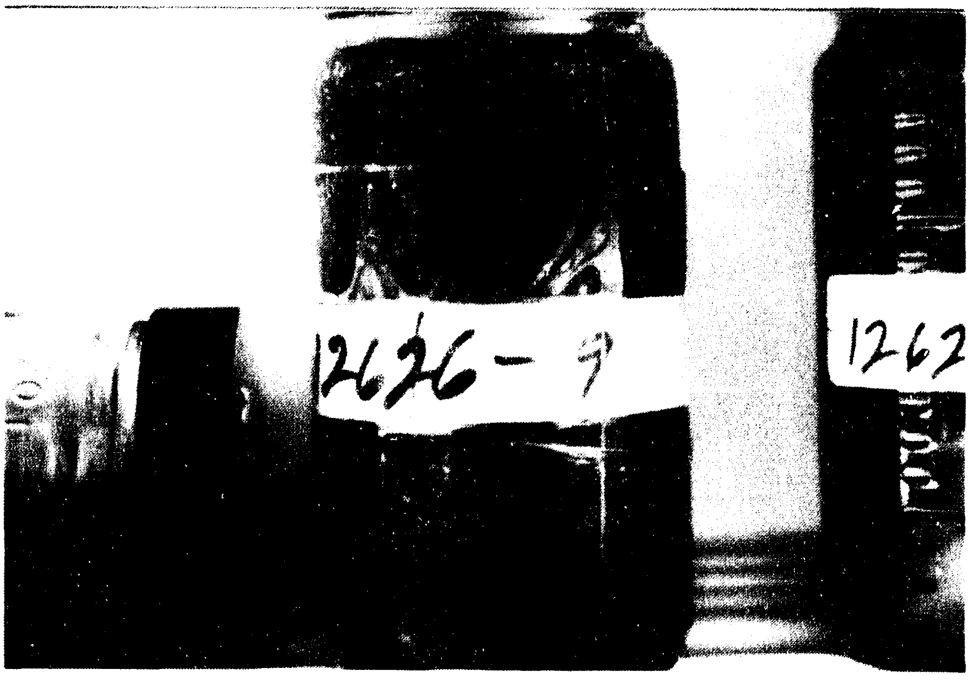


Figure 6 - Surface Treated Ground Tire Rubber in Polyurethane Prepolymer. Altered Treatment Chemistry has Eliminated Foam Rise and Mixture Remains Fully Fluid.

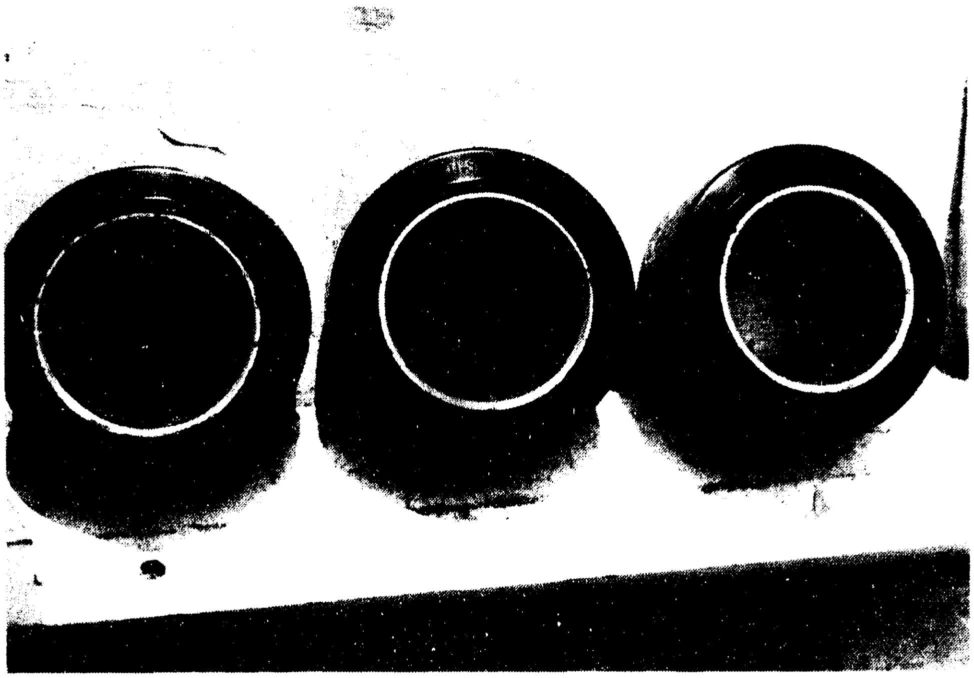
Production of void free polyurethanes with fast gel times requires that the tire rubber treatment be carefully controlled and that it be handled like any other additive for polyurethanes by keeping it in a sealed container with a dessicant to assure dryness. High temperature drying techniques for treated tire rubber have not been found effective in assuring void free castings.

With the successful production of fast-gelling, void free polyurethane wheels using 16.7% and 26.5%treated tire rubber, efficacy has been demonstrated in one of the most critical polyurethane processes. Process equipment, surface treatment chemistry, materials handling, and polymer formulation require careful consideration. This is not, however, an unusual requirement in the manufacture of polyurethanes.

Based on the ease with which the treated tire rubber was incorporated in this critical application, once the treatment chemistry and processing issues are resolved, it can be concluded that a 25% incorporation in polyurethanes which can accept particles and are not aesthetically hindered by the color of the treated tire rubber is commercially feasible, and that higher levels of substitution are certainly possible.

Polyurethane solid cast forklift tires. Solid cast polyurethane forklift tires, shown in Figure 7, were produced on two occasions by two different processors. Both processors found it necessary to utilize the model FFH particle handling mixhead from Edge-Sweets company due to the fast gel times of the prepolymers.

Figure 7 - Solid Cast Polyurethane Forklift Tires Incorporating Surface Treated Tire Rubber.

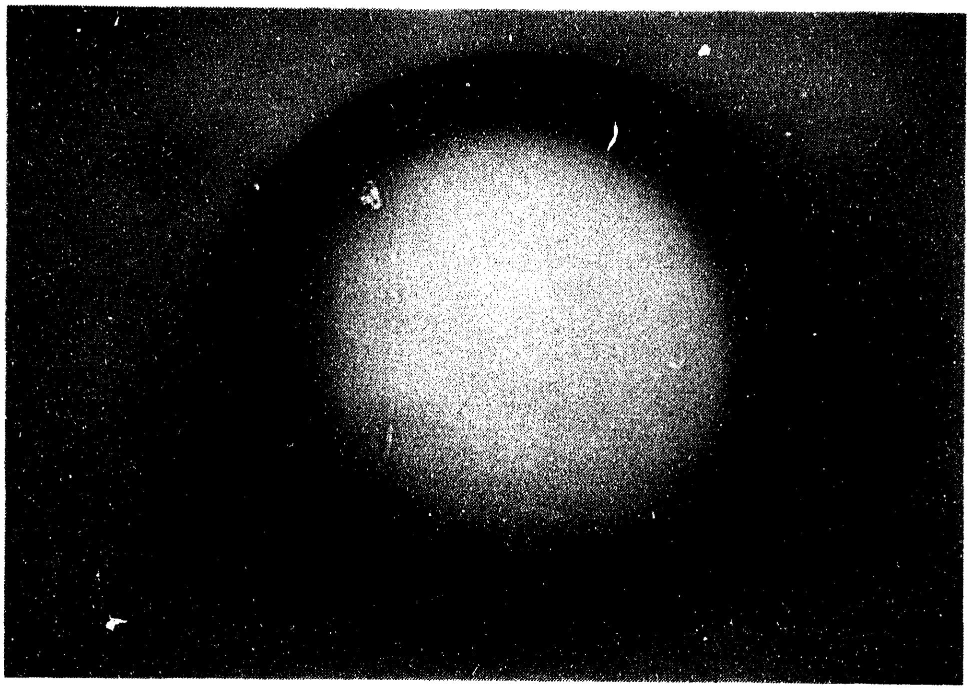


In the first instance, 10" x 6" forklift tires were cast onto steel hub inserts using the earlier chemistry surface treatment at levels of 15% and 30%. This resulted in formation of small voids due to carbon dioxide generation.

When the later version of the surface treatment chemistry was employed production of 10" x 6" forklift tires was acomplished without difficulty by the manufacturer of the solid wheels.

Polyurethane Microcellular Bicycle Tires. Microcellular polyurethane bicycle tires incorporating up to 30% by weight treated tire rubber were prepared during April 1993, and are shown in Figure 8.

Figure 8 - Surface Treated Ground Tire Rubber in a Polyurethane Microcellular Bicycle Tire.



A microcellular polyurethane is a foam with very small gas cells, primarily closed, i.e., not interconnected. The target density of the microcellular polyurethane was 19.0 pounds per cubic foot. The specific gravity of the microcellular polymer is usually carefully controlled by the quantitative addition of hydrochlorofluorocarbon blowing agent . Gas, apparently carbon dioxide, was generated during the reaction with the treated tire rubber and caused a reduction in density to 14.7 pounds per cubic foot. The chemistry of carbon dioxide generation by adsorbed moisture and carboxylic acid groups[6] is well known. The same acid-functional groups believed to account for a portion of the gas generation also caused inhibition of the gelling reaction despite the presence of a tin-based catalyst in the reaction mixture. This information was utilized to produce treated tire rubber with modified chemsitry that generated little or no gas nor inhibited gelling in subsequent trials. Commercialization of treated tire rubber in microcellular bicycle tires will be easier if the improved treatment chemistry is applied and moisture is excluded. Other properties of the finished tire, such as tear resistance, were unaffected.

The dispersion of the treated tire rubber in the polyol side of the system was found to be improved by the surface treatment. Treated tire rubber wetted out and dispersed in the polyol quickly and without leaving any unwettted agglomerates.

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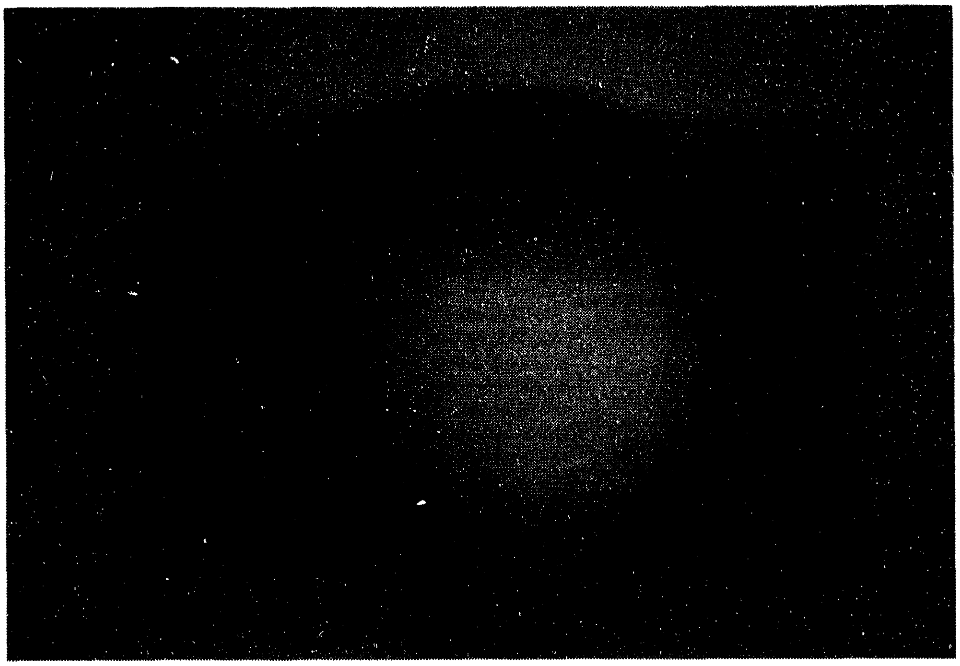
[6] Polyurethane Handbook, Gunter Oertel ed., Hanser Publishers/Macmillan Publishing Co., New YorkNY, 1985, p. 63

The surface produced was good, and there was no evidence of treated rubber particles breaking free when the microcellular material was torn or abraded, indicating the excellent adhesion of the particles to the polyurethane. The black color from the treated rubber was a positive attribute, since black pigments are preblended with the polyol in order to produce a bicycle tire that looks like rubber. Incorporation of ground tire rubber with adhesive surface treatments to prevent tearing out of the particles has been previously demonstrated to improve wet traction, which is notoriously poor for pure polyurethane tires.

Microcellular Polyurethane Wheelchair Tires. Microcellular polyurethane wheelchair tires, shown in Figure 9, were produced using treated tire rubber at 12% with no difficulty encountered in manufacture.

Figure 9 - Polyurethane Microcellular Wheelchair Tire.



These tires were under evaluation for use on powered wheelchairs. As soon as the rubber became exposed, it was found that black scuff marks were left on tile floors. One primary benefit that was expected, and demonstrated, is the improvement in wet traction. The deposition of the black scuff marks indicates that exposure of the rubber particles is the mechanism for wet traction improvement, but it could not be taken advantage of in this instance. The use of a surface treated industrial rubber scrap with low scuff characteristics would allow use in this application.

Polyurethane Microcellular Hand Truck Tires. Microcellular hand truck tires were prepared with treated tire rubber at 12% of the total composition. The tires were placed in service on hand trucks used for carrying cases of beverages, such as beer and soft drinks. The resulting tires were half the weight of a solid tire and comparable in weight to a pneumatic tire without the risk of going flat due to foreign object damage. No difficulty in manufacture was encountered. Flat-spotting occurred when the carts were left loaded overnight with both straight polyurethane foamed tires and with foamed polyurethane tires containing treated tire rubber. Flat-spotting is a form of compression set in which the tire flattens where it contacts the floor below and holds the flat shape for an extended period of time. The observable effect is to experience a bump every time the flat spot contacts the floor when rolling. The flat-spotting was reduced for the neat polyurethane tires by increasing the density of the foamed tire, but tires with treated tire rubber at the higher density had not yet been produced at the time of publication.

Polyurethane Industrial Enclosures. One application demonstrated under the program is a family of proprietary commercial enclosures, molded with approximately 40% rubber particles in a thermoset polyurethane. In this case, the rubber particles improve undisclosed properties of the end products as well as reduce the raw material costs. The total demand for treated rubber in this application has been estimated by the manufacturer at 100 million pounds per year. In this particular product, the polyurethane used is a "low end" material costing approximately $1.25 per pound. This product is not currently produced in modified polyurethane, so the demand for treated rubber would be in addition to that caused by substitution in products now made with polyurethane.

Polysulfide Elastomer Solvent-Impermeable Membranes for Tank Farms. With the continuing growth of the philosophy of responsible care on environmental issues, the chemical processing and oil industries have been seeking new methods to assure containment of chemicals and petroleum derivatives. A membrane based on liquid polysulfide rubber containing 40% treated tire rubber was developed and demonstrated at a chemicals manufacturing site. The membrane installation is shown in Figure 10 and the completed membrane is shown in Figure 11.

Figure 10 - Installing The Treated Rubber Bearing Polysulfide Barrier Membrane at a Chemical Plant.

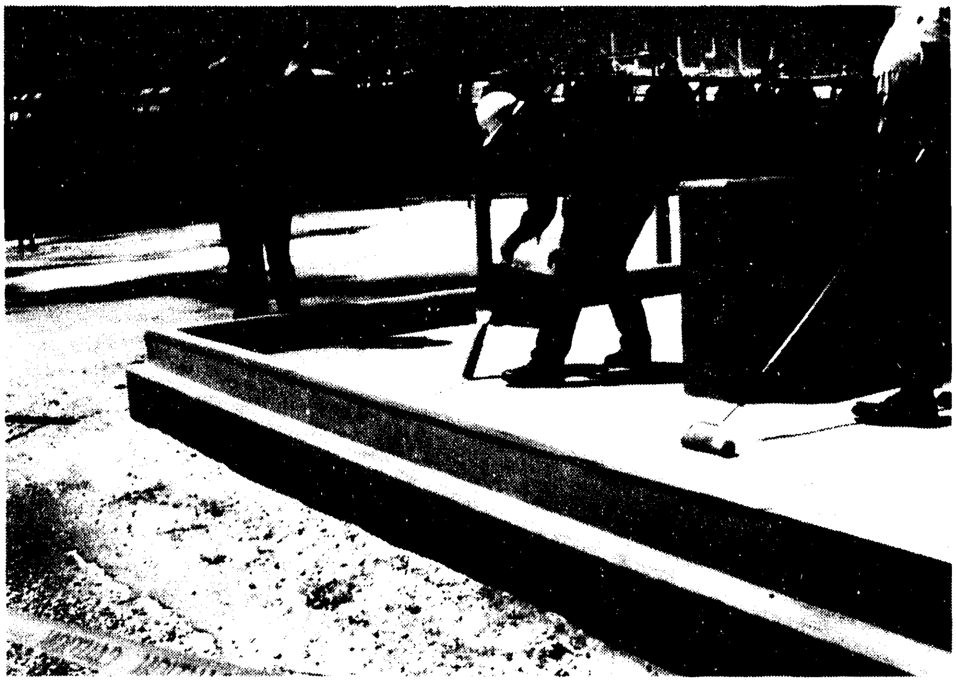
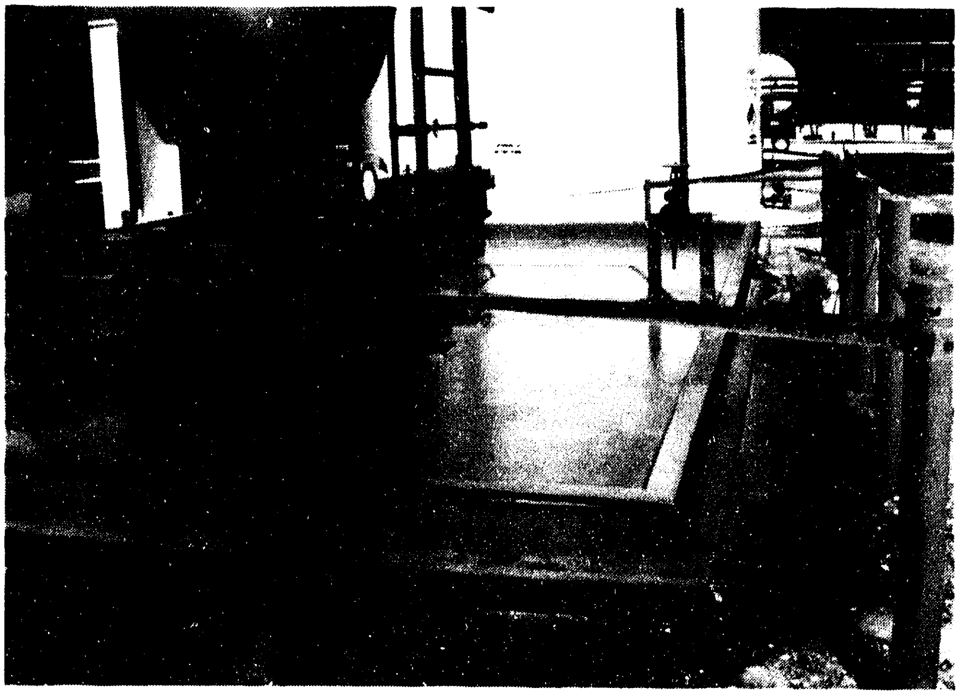


Figure 11 - The Completed Polysulfide Barrier Membrane Incorporating Treated Tire Rubber Closely Resembles The Concrete Pad That it Protects.



The purpose of such a membrane is to prevent spilled gasoline, oil, etc. from seeping into the ground water during the time it takes(up to 36 hours) to empty the containment dyke into another vessel.

Conventional metal oxide curing systems were adversely affected by the acidity of early surface treatment chemistries which prevented the solidification of the membrane. A proprietary curing system which was not affected by the acidity of the earlier surface treatment chemistry was developed for this application by an independent party.

This specific membrane, based on a liquid polysulfide with 40% treated tire rubber is sprayed, brushed, or rolled in place. The treated rubber is important because it increases the toughness of the system and lowers the raw material cost. The reinforcing effect of the treated rubber allows the membrane to bear forklift and foot traffic. Typically, each tank has a one acre dyke which would require about 2000 pounds of treated rubber particles.

Polysulfide Roof Sealant. A roof sealant based on polysulfide liquid rubber with 40% treated tire rubber was developed to meet specific performance and cost constraints. This product is applied as a liquid and cures in less than one minute. Again, the reinforcing nature of the treated tire rubber in polysulfide rubber is important for this application. The exceptional adhesion, elongation and weatherability of the polysulfide liquid rubber are advantageous. A proprietary cure system which was not affected by the acidity of in the earlier treatment chemistry was formulated, as in the tank farm membrane.

Architectural, glazing and other polysulfide sealants. A polysulfide formulator with a large market share evaluated treated tire rubber with the earlier surface treatment in a polysulfide formulation based on a conventional activated manganese dioxide cure system using a simple plug-in experiment. The acidity of the earlier surface treatment inhibited the cure. Carboxylic acids are known to act as cure retarders in manganese dioxide cured polysulfides. Use of the modified surface treatment with low acidity is expected to remedy this problem, but had not been tested as of the writing of this report.

Fracture toughening in epoxy resins. A laboratory study was conducted at Lehigh University by Reza Bagheri under the direction of Dr. Ray Pearson. This study showed that fracture toughness of epoxy resins is enhanced by both treated and untreated tire rubber when combined with conventional carboxyl terminated nitrile rubbers. Professor Pearson has published numerous research papers dealing with fracture toughness of modified epoxy resins and is considered a leading authority in this field. Toughening was measured as the increased force required to cause crack propagation through the sample. The tire rubber was not as effective as the modifiers on a part for part basis, but the treated tire rubber is less than half the cost of the carboxyl terminated nitrile rubber materials. The treated tire rubber was tested at levels between 2.5% and 10%. Previous work under Phase I of the program at 10% and 20% showed increased elongation but also an excessive decrease in flexural modulus, indicating that, for structural applications, 10% was the probable upper use limit for treated tire rubber in epoxy resins. What has not been measured is the work to break the specimen which is higher with the treated rubber. Cracks, once initiated in the treated rubber sample were stopped short of complete fracture of the specimen, indicating a difference in the toughening mechanism. Optimum use of both carboxyl terminated nitrile rubber modifiers and treated tire rubber could lead to composites with properties which cannot be obtained with either modifier alone.

Scanning electron micrographs of the fracture surfaces as seen in Figures 12 and 13, show that the treated tire rubber particles were torn in half, indicating strong adhesion of the treated tire rubber to the surrounding epoxy matrix while the untreated tire rubber did not adhere to the epoxy resin, leaving voids at the fracture surface.

Figure 12 - Scanning Electron Micrograph of Epoxy Resin Fracture Surface Shows No Adhesion Between Untreated Tire Rubber and the Surrounding Epoxy Resin.

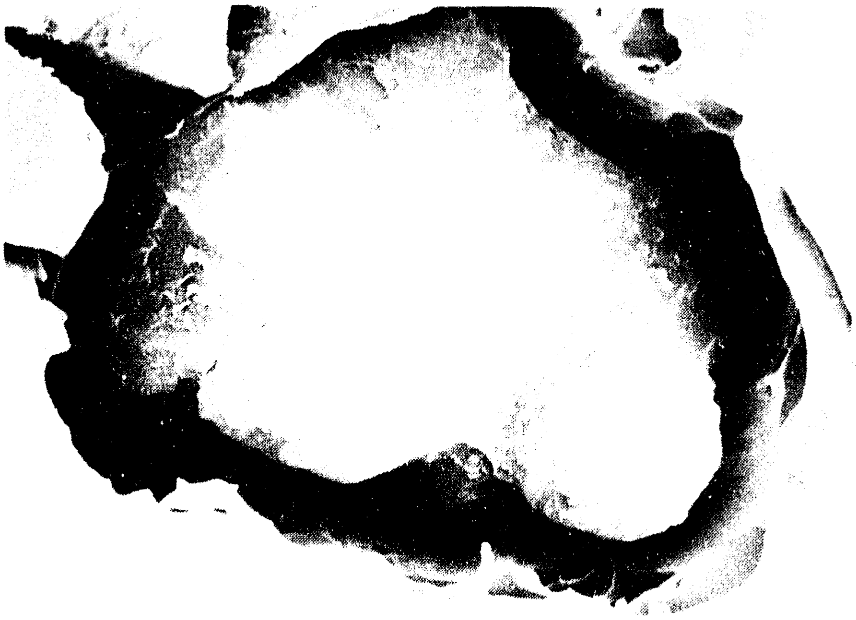
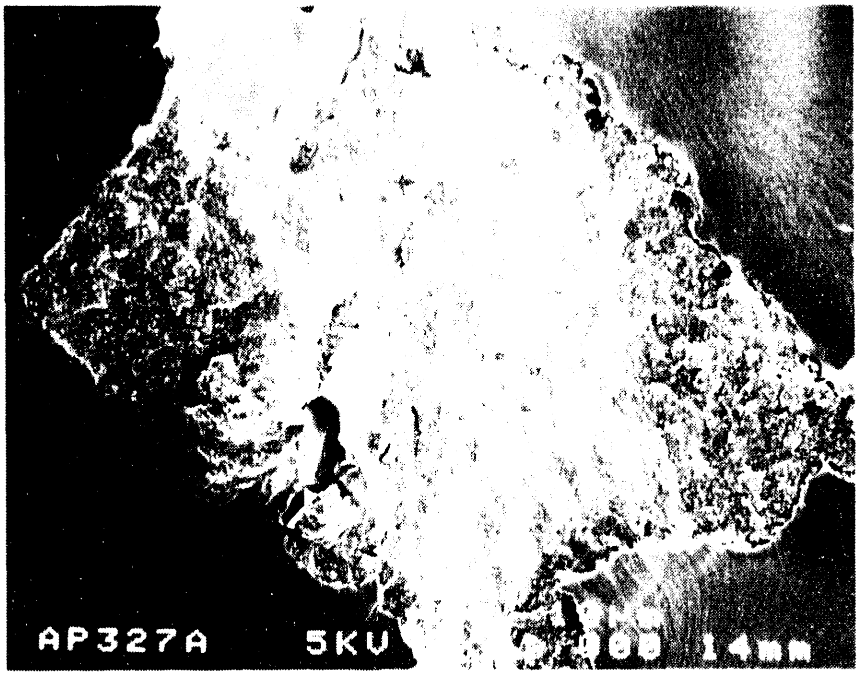


Figure 13 - Surface Treated Ground Tire Rubber Adheres to Epoxy Resin. The Rubber Particles are Torn at the Fracture Surface as Shown in This Scanning Electron Micrograph.



This could be significant in applications where toughening by rubber particles bridging of the two crack faces is desired. Such applications may exist in rubber toughened interlaminar areas of composite construction made by press curing of epoxy/fiber prepregs, or compression molded chopped fiber composites. This would also benefit floor coatings subject to vehicle traffic.

Conventional carboxyl terminated nitrile rubber modifiers used are fine dispersions of less than ten microns in diameter within the resin and will flow through the reinforcing fibers with the resin. The treated tire rubber has a particle size near 180 microns which will not allow it to flow through the fiber matrix. This will result in enrichment of the interlaminar area but at the expense of some fiber kinking. The effect would be to improve interlaminar toughness through a crack bridging mechanism at the expense of stiffness.

This study has demonstrated the potential for use of treated tire rubber in epoxy resins for compression molded composites and lining and coating applications, and quantified the level at which benefits may be realized.

Rubber modified epoxy coatings and lining applications. Epoxy resins are used for coating and lining concrete and masonry materials where an impervious barrier is desired. Treated tire rubber in both 20 and 80 mesh sizes is under evaluation for high-build epoxy base coats under hard epoxy top coats. The top coats tend to be brittle and the use of either a flexibilized epoxy base coat or a polyurethane base coat has been under study by a manufacturer of these floor coatings. The fracture toughening and increased elongation effects shown in the Lehigh University study and in Phase I of the program combined with the potential to reduce the cost of these coatings is significant. Laboratory evaluation of treated tire rubber in a floor coating formulation had not been completed as of the composition of this report.

Applications Development by Environmental Technologies Alternatives, Inc.
Environmental Technologies Alternatives, Inc (ETA) under a separate contract with the DOE, supported these efforts to develop applications for treated rubber and to assess the market potential.

As of this report, ETA had selected two industry market applications from over 20 such test and evaluation prospects with substantial market potential for surface modified rubber particles. The first was the shoe industry, specifically, shoe sole components. Working with Deja Shoe, and through them several key suppliers of Deja Shoe soles, ETA conducted substantial tests and evaluations and determined that treated -80 mesh rubber can be incorporated in a thermo-set nitrile based shoe sole compound at levels between 10-20% (by volume) of incorporation to produce a molded sole fully acceptable to all production, technical and quality requirements of the industry for a top-of-the line product.

Based on extensive laboratory and factory trials, this newly developed thermo-set compound utilizing surface modified rubber particulate has been approved for production.

A companion effort, directed toward the softer "shoe sole" market application, is underway. This program is proceeding on a similar but expanded level of effort in a thermo-plastic compound development to incorporate up to 50% of surface modified -80 mesh rubber requiring both variations in surface treatment levels and sole compounds which will include special modifiers and coupling agents, incorporating plastics and/or urethanes.

Testing for abrasion resistance, adhesion to shoe uppers, delamination within the sole, tensile, elongation tear strength, melt flow and hardness, plus consistency of processing and product appearance are all taking place to insure industry standards are being met or exceeded.

Early results have been quite encouraging and successful results are expected with actual completion now targeted for the fourth quarter of 1993. The goal is to produce a thermo-plastic sole compound containing approximately 50% of surface modified particles which meets or exceeds industry standards while achieving the desired cost benefit objectives targeted for this new shoe sole material.

While the final scope of this ongoing effort is still being defined, it has already been clearly demonstrated that the shoe industry is anxious to achieve a greater U.S. market share through technical innovation and quality performance at acceptable costs. This is expected to result in a significant use of surface treated rubber particles in a U.S. market of 1.2 billion pairs of shoes, in which the shoe sole typically weighs between 0.6 to 1 pound per shoe.

The second market application development on which there is excellent progress is within the wide market spectrum of foam products utilizing urethanes.

In this broad category of foam products, now under test and evaluation by ETA, Inc. and various client companies, each client application has unique requirements. Generally the testing phase is focused first on the selection of the surface treatment particles, both in particle size and surface treatment intensity. Then the percent of incorporation is studied. At each stage of testing, while the resulting affect on physical properties such as tensile, elongation, tear and stiffness is measured, appearance is observed, and likely processing problems prior to a full factory trial evaluation are noted.

In one such evaluation, the results were very positive. After extensive lab tests, surface-treated 30 mesh rubber was selected, since it had met or exceeded all client industry expectations in the laboratory.

A pilot plant trial using several hundred pounds of surface-treated 30 mesh rubber at the selected incorporation level resulted in very acceptable product processing and a reduction in material loss versus standard. Overall testing of the properties exceeded the quality and technical requirements of the product.

At this point, a very desirable side benefit became apparent due to the chlorine surface treatment of the rubber particles: the normal rubber odor is removed or, masked by the chlorine surface treatment. In this client/end user application, this noticeable lack of any rubber odor was a strong marketing plus.

With these positive results, the company has now scheduled a scaled up factory trial which will incorporate several thousands of pounds of surface-treated 30 mesh rubber in a final processing and quality evaluation test, along with a confirmation of the cost benefits of incorporating the surface modified particles. Currently the client is very confident that this factory trial will duplicate the pilot line trials. If the factory trial continues as successfully as predicted then the client company is prepared to proceed to manufacture in 1994.

Neither the company nor the application can be revealed by mutual agreement based on the client's heavy in-house test and evaluation efforts at his own expense. This foam application program represents a very high volume market application for surface modified rubber particles - likely to equal or exceed that of the shoe sole applications being developed.

As these two market applications, shoe soles and foam products, go forward and others under similar evaluation proceed, it is believed the acceptance of surface modified rubber particulate will gain credibility and wider acceptance. Much will be learned from the failures and successes of the trials.

Market Potential - Implication

Exact numbers cannot be placed on the potential market for treated rubber. The applications development thus far in this program is just the tip of the iceberg for the potential applications for treated rubber. Treated rubber is really a new material with a unique combination of physical properties and potential uses. Development of uses for treated rubber stimulates acceptance of the myriad ideas for potential treated rubber applications. These ideas for uses are not only simple displacement of polymers, but of wood, glass, and metal. Treated rubber opens up new opportunities in applications where displacement of wood, glass, and metal with synthetic materials is not feasible.

A good example of this is the stream of applications that followed the polysulfide dike liner (liners for gasoline and oil storage tanks) membrane application. As people considered this successful application, they recognized opportunities for similar polymer systems for completely different applications. Many of these subsequently identified applications have an even larger potential market than the dike liner application. Some specific applications for polysulfide treated rubber are as follows:

- Coating material for dikes under numerous chemical tanks/operations.
- Coating material for inside tanks.
- Landfill linings.
- Swimming pool sealant.
- Mastic material for sealing concrete drainage pipes.
- Solvent barrier coating for plastic containers.
- Sealant for asphalt roadways and pads.
- Ground cover to prevent dust blowing.
- Membrane covers for earthen dams and levees.

2. Process Development

At the end of Phase I, rubber was treated with chlorine in a mechanically fluidized bed reactor at a capacity of 1 pound per batch. This was a bench scale operation and there was a desire to scale this up so that more could be learned about the process requirements to make this process commercially feasible, to optimize specific applications, and to understand the economics. Also, larger amounts of material had to be made for applications development.

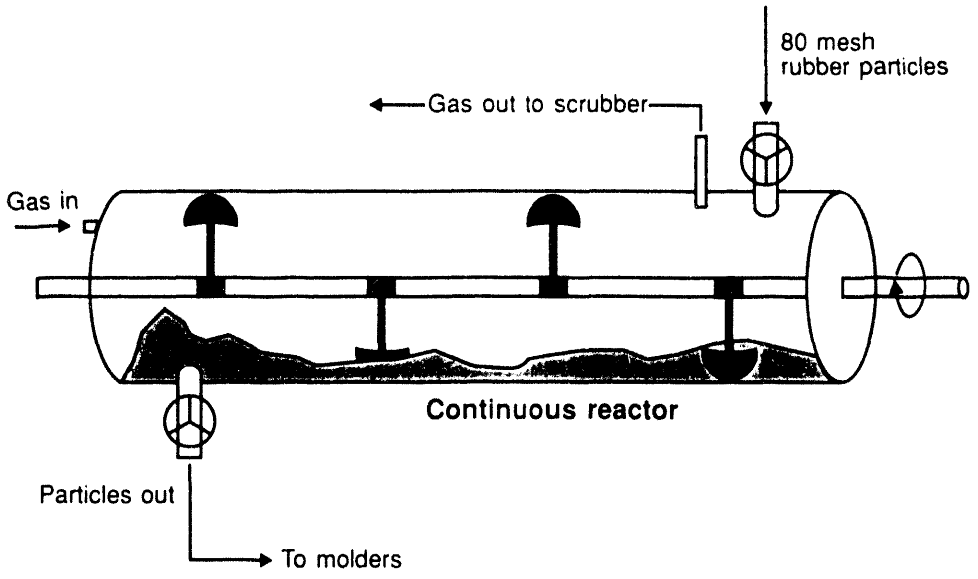
The key to choosing a reactor for this process was the similarity between particle drying and the surface modification process. This similarity includes residence time, heat transfer, and mass flow. Much time was devoted to evaluating commercially available mixers and dryers through discussions with vendors. The pros and cons of various pieces of equipment were weighed in light of corrosion and explosion considerations, which at the time were considered to be important design criteria. The Littleford reactor was chosen for a number of reasons:

- It is relatively inexpensive.
- Both batch and continuous types are available so lab tests could be done batchwise and moving to a continuous reactor would be possible.
- There is plenty of flexibility in adjusting process parameters.
- The design is amenable to safety pressure relief devices, such as rupture disks.
- It has the ability to handle various particle sizes.

Installation of Littleford Reactor

An industrial blender/mixer made by the Littleford Bros., Inc. (Florence, KY) was modified for the surface-modification process, and was installed. This unit shown in Figure 14 facilitated further definition of process requirements, optimization of the treatment process for specific applications, and production of larger quantities of treated rubber for product development. Very encouraging results have been obtained concerning the treatment process.

Figure 14
Schematic of the Littleford Reactor



Results

1. **Kinetics.** The rate of reaction is at least four times faster than indicated in the Phase I study. This is significant for several reasons. Lower treatment cycle time means that a smaller (and less expensive) reactor can be used to achieve a given production capacity. Secondly, the treatment chemistry is so fast and efficient that little or no purge is required to remove non-reacted treatment gas prior to discharge of treated rubber - further reducing cycle time. Thirdly, the efficiency of chlorine (reactive gas) utilization is essentially 100%, which is higher than projected from the Phase I work. The significance of this is reduced process costs for chlorine, and reduced scrubbing (neutralization) costs for non-reacted chlorine.

2. **Thermodynamics.** In the Phase I study, it was impossible to obtain thermodynamic data on the treatment process. From work in the Littleford reactor, it was determined that the heat of reaction produced from the surface treatment is very modest, and may not require heat removal via a cooling jacket. The significance of this is that the rate of processing the rubber may not be limited by the rate that heat can be removed from the reactor. The capital requirements for a reactor without a cooling jacket is reduced. In addition, costs associated with providing cooling water are eliminated.

The predominant reaction is understood to be chlorine addition across carbon carbon double bonds, not free radical addition. If free radical addition were occurring, hydrogen chloride would form and none was detected. In addition, this treatment is performed in the presence of molecular oxygen and it is well known that free radical processes do not occur in the presence of molecular oxygen. The predicted standard heat of reaction for the chlorination of rubber is approximately 1000 Btu per pound of chlorine reacted based on the analogous chlorination of butane to dichlorobutane as follows:

$$C_4H_8(g) + Cl_2(g) \rightarrow C_4H_8Cl_2(g).$$[7]

Calculations show that with a 3% chlorine incorporation the heat of reaction would raise the temperature of the rubber by 67 ^oF . Heat balance calculations were completed for trial runs performed in the Littleford reactor system to confirm the theoretical prediction. The experimental data are consistent with the prediction. Consider the heat balance around the reactor as follows:

$$Q_{reaction} + Q_{agitator} = Q_{H2O} + Q_{gas} + Q_{bed} + Q_{reactor} + Q_{air}$$

where:

$Q_{reaction}$ = heat released by reaction, Btu

$Q_{agitator}$ = mechanical energy from agitation, Btu

Q_{H2O} = heat absorbed by the cooling water in the jacket, Btu

Q_{gas} = heat absorbed by the gas flow, Btu

Q_{bed} = heat absorbed by the rubber, Btu

$Q_{reactor}$ = heat absorbed by the metal, Btu

Q_{air} = heat lost through natural convection, Btu.

During one run, 155 pounds of rubber were chlorinated in the Littleford reactor and cooling water flowed through the jacket. The predicted heat release for this run ($Q_{reaction}$) was 4700 Btu based on the standard heat of reaction derived for the chlorination of butane to dichlorobutane. The maximum amount of heat input to the system by the agitator ($Q_{agitator}$) was 12,700 Btu based on a 5 horsepower agitator operating for 1 hour. There were not sufficient data to calculate the exact heat input by the agitator during this run. The calculated

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[7] Standard heat of reaction calculated from standard heat of formations found in Perry's Chemical Engineering Handbook and estimated using the Benson method and the Chetah program.

amount of heat absorbed by the rubber, cooling water, gas, and reactor metal and the heat lost to natural convection totaled 8200 Btu.

During another run, 150 pounds of rubber were chlorinated with no cooling water flowing through the jacket, but there was some water sitting in the jacket and this absorbed some heat. The predicted heat release for this run was 4400 Btu. In this experiment, data was taken for the agitator heat input and it corresponded to 8600 Btu. Subtracting the calculated heat absorbed by the gas, rubber, metal, and air due to natural convection from the agitator's heat input, gives a heat of reaction equal to 4900 Btu's, which is 11% greater than the theoretical value.

Allowing for the error surrounding the raw data measurement (amount of chlorine added, cooling water flow rate, and temperature readings throughout the system), the numbers noted above are reasonable. The cost, both in time and money, of gathering more accurate data was not justified based on the small heat of reaction predicted by theory.

Conclusion

Proposed process for scale-up. Upon reviewing the new information on the treatment process requirements, it was determined that batch processing is more attractive than is continuous processing. Batch processing equipment is simpler and less expensive than analogous continuous process equipment. Table 4 compares the three general pilot plant concepts and demonstrates why a batch-wise processing scheme was pursued. Batch processing involves charging the reactor with rubber particles, treating the rubber, removing the treated rubber from the reactor, and then starting all over again. In a continuous dense phase system, the rubber is treated in a fluidized bed reactor. Raw rubber is continually fed to the reactor, treated, and removed. In the continuous dilute phase process, the reactor is a pipe with an abundance of gas flowing through it and very little rubber.

Table 4
Comparison of Pilot Plant Concepts

	Batch	Continuous Dense Phase	Continuous Dilute Phase
probability of success	*****	****	***
scaleable	*****	***	**
capital cost	*****	**	***
variable cost	****	****	****
process control	****	****	***
flexibility	***	*	**
air required	*****	**	**
uniform residence time	*****	**	****

***** favorable

* not favorable

The speed and efficiency of the treatment means that product will be made in a way that approaches continuous output. This batch-wise processing will have low labor requirements, and use relatively simple process equipment. The continuous process would require significant process studies and engineering design, and the required process equipment would be considerably more expensive. The reaction is so fast that developing a process control scheme to handle addition of a small amount of chlorine to a large amount of powder in a continuous operation would be challenging. A batch process may offer simpler control through load cells. Batch operation also offers the ability to change product grades easily.

Experience with the Littleford reactor pointed toward important design criteria. In the Littleford, the configuration of the vessel, and the action of the agitator plows cause rubber particles to accumulate in areas within the vessel. When these build-ups periodically release, they fall into the product and cause off-spec material. It is impossible to completely unload all treated rubber from a given batch so some material is returned and receives a second treatment with the next batch. Also, it takes several minutes to unload a Littleford reactor because of the small exit port, and this increases cycle time.

Forberg-Design Mixer

After learning these new process requirements, the available dryers and mixers were once again reviewed quickly and the Forberg-design mixer, shown in Figure 15, was chosen. It has the following characteristics:

- Best mixing action of all mixers.

- Relatively inexpensive (less than the Littleford).

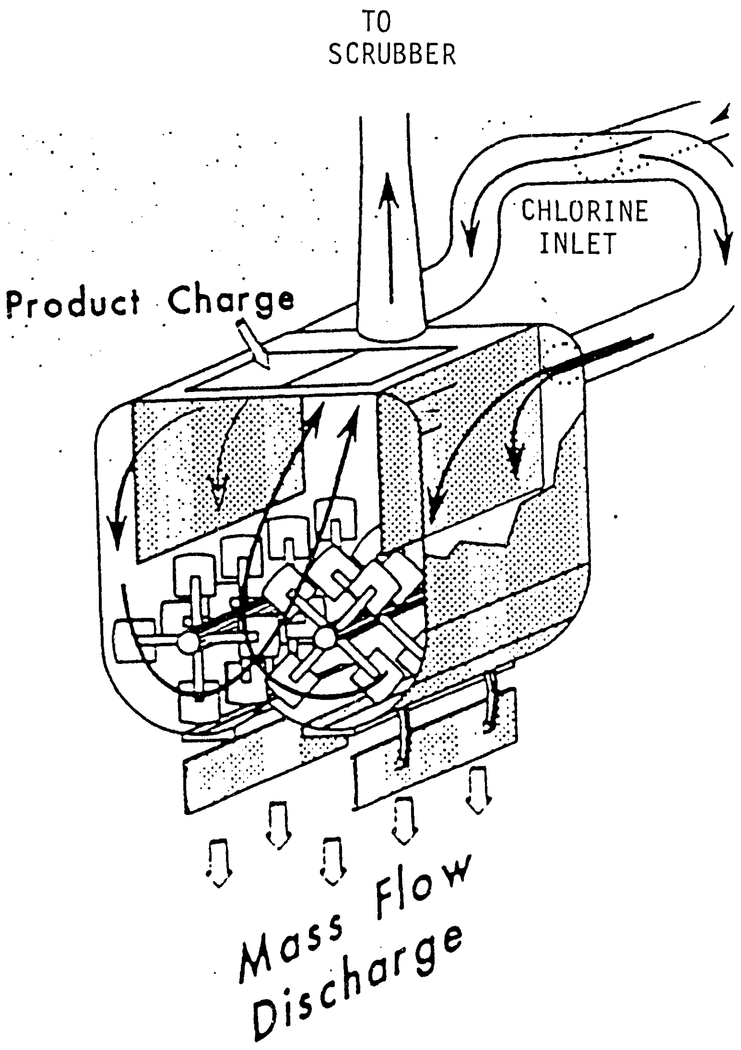
- Low horsepower agitator.

- A new design feature (inner wall partition), which enhances the use of the Forberg-design mixer as a dryer, would also enhance this design for this treatment process. This design feature allows the introduction of the gas (chlorine and air) gradually, without the possibility of burning the powder locally and would allow for more uniform treatments.

- Effective at fluidizing 80 mesh rubber (confirmed by tests).

- Ability to unload in a small fraction of the reaction time (3-4 seconds).

Figure 15
Schematic of Forberg-Design Reactor



Materials Handling

Materials handling is a crucial component of the rubber treatment process. Capacity, caking, and binding were among the factors considered in choosing the most appropriate materials handling system.

Both untreated and treated rubber particles have similar flow properties. Jenike and Johanson, Inc. determined the treated material's flow characteristics, compacted bulk density, and wall friction angle for four different construction materials. These properties were used in selecting the silo's geometry, interior coating, hopper slope, outlet size, and wall design (including the construction material and wall thickness). These properties are often affected by temperature, humidity, and other external variables. If the materials will be stored at other than ambient temperatures or if the surrounding atmosphere is humid, the laboratory should replicate these conditions when testing the materials' flow properties.

Pneumatic conveying permeability and cohesive strength were also evaluated to assess the amenability of various conveying systems. Both treated and untreated 80 mesh rubber from Rouse Rubber Industries, Inc., are non-free flowing; they require flow promotion action; they tend to flow as agglomerated particles.

If the materials are stored at higher temperature and allowed to cool in storage at rest, they cake. Cooling of these materials to about 80°F and adding a parting agent before bagging or storage may eliminate the formation of the lumps.

It is expected that the treated rubber will have to be bagged for some customers. There are numerous choices for bagging equipment. Two types of gross-weigher baggers tested with the treated and untreated ground rubber produced by Rouse Rubber Industries, Inc. were as follows:

- Velox Industrial Packaging Systems, Inc. and Bemis gross valve-bag air packers.
- Velox Industrial Packaging Systems, Inc. gross open-mouth-bag packer with a double screw feeder.

The test results show that the Velox open-mouth-bag packer can handle both products without any problems. The valve-bag air packer plugged during the dribble run if any larger agglomerates were present in the bulk product. The air packer worked well when all larger lumps had been broken before bagging. The bagging accuracy for both systems is ±4 ounces at 2 sigma. If the product caking and lumping can be eliminated then the valve-bag air packer is recommended; it is less expensive in construction and operation. There are also more potential suppliers for the air packer systems. The valve-bags, however, leak during flattening, and the product is exposed to air moisture (through the valve). Some vendors offer valve-bag sealers, but they are still in the development stage

Explosion Testing
As with all powder handling, there is the possibility of a dust explosion occurring during the handling and treatment of scrap tire rubber. The quantitative data characterizing dust explosion properties of solids are used for designing and constructing equipment used in processes involving powders. Fenwal Safety Systems, Inc. quantified the danger for this process.

First, Micron Powder Systems classified the rubber so that all the fines could be collected and tested at Fenwal for explosibility. Testing the fines established the worst possible case that could occur. Maximum explosion pressure (P_{max}) and maximum rate of pressure rise (R_{max}) were identified from tests carried out in a 190 liter spherical steel vessel. A dust cloud was forced into the vessel with compressed air and ignited with a 5000 joule pyrotechnic squib. Dust cloud explosions were carried out at various concentrations and monitored by a computerized system. The three highest values for R_{max} and P_{max} were averaged to give the final value. This is in accordance with ASTM Standard E1226-88. The K_{st}, which is the internationally recognized index used to classify the explosion severity of a material, was calculated according to the following formula:

$$K_{st} = R_{max} V^{1/3}, \quad \text{where: } V = \text{the vessel volume.}$$

The maximum safe oxygen concentration (MSOC) at which there is no combustion, was determined by tests carried out in 190 liter spherical steel vessel with a 5000 joule pyrotechnic squib as an ignition source. Dust cloud deflagrations were carried out at a fixed dust cloud concentration at the lower explosion limit with lower and lower oxygen concentrations. Combustion was considered to occur when the deflagration pressure rise did not abruptly stop after discharge of the igniter, and rose about 1 bar above the initial pressure at a rate of 2.5 bar per second. Three negative tests in a row at the highest oxygen concentration established a value for the MSOC. The results of the tests are in Table 5. Two other dusts, lycopodium spores and Pittsburgh seam coal dust, are also shown in the table for comparison.

Table 5
Explosion Characteristics of Scrap Tire Rubber Dust And Two Reference Materials

	scrap tire rubber dust	Pittsburgh Seam Coal Dust	Lycopodium Spores
P_{max} (Bar g.)	9	8.1	8.8
R_{max} (Bar/s)	224	214	349
K_{st} (Bar-m/s)	129	123	201
dust class	St-1	St-1	St-2
MSOC (%)	15	18	14

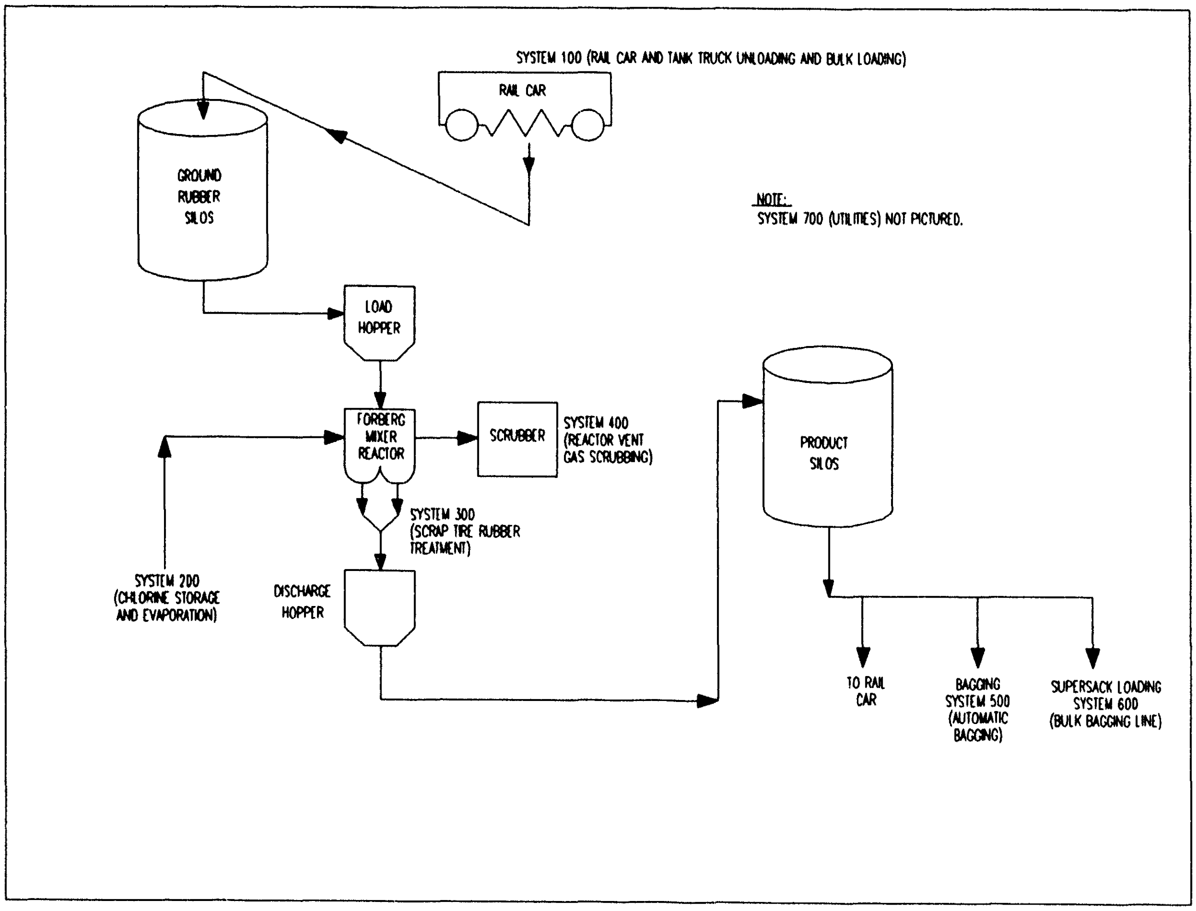
3. Plant Design

Engineering designs for a nominal 150 million pound per year treatment facility using batch processing were completed. The design criteria were based on the process requirements defined earlier in the Phase II work. Specific process equipment was evaluated at vendors' facilities, using treated and untreated rubber, to ensure that functional equipment was specified.

The design is based on ground rubber being transported to the plant and being treated in a Forberg-design mixer in a batch process. Each batch contains 5000 pounds of rubber and has a cycle time of 15 minutes. The product handling section is designed to be flexible in that the treated rubber can be bagged, bulk bagged (in Supersacks), or loaded into railcars.

The scrap tire rubber treatment pilot plant is depicted in the process flow diagram in Figure 16.

Figure 16
Process Flow Diagram for Scrap Tire Rubber Treatment Pilot Plant



The various sections of the process can be broken into seven systems and for quick identification they are labelled system 100, 200, 300, 400, 500, 600, and 700 and identified with a key piece of equipment. A concise description of each system and its key components follows.

<u>System 100</u>

- **Rail Car and Tank Truck Unloading and Bulk Loading**
  This system unloads bulk ground scrap-tire rubber from rail cars and transports it to any one of two storage silos, automatically via a model 16 GT-1000 Dynamic Air transporter at a rate of 30,000 to 40,000 pounds per hour.

  The finished product transfer system transports the treated scrap-tire rubber from the silo into a filter-receiver at a minimum rate of 20,000 pounds per hour. The settled product from the filter-receiver drops through an air-lock and an adjustable (length-wise) loading spout into a rail car or into a tank truck compartment.

- **Rail Car Mover and Track Scale**
  The rail car consists of 3 or 5 compartments, so repositioning of the rail car is required for a complete discharge. A track mobile is provided for this short rail car movement.

  A double "S" track scale, Fairbanks Scales Model No. 14-1308, is provided to weigh the rail cars with the raw material and the product.

- **Storage Silos (12,000 cubic foot working capacity each)**
  Two storage silos are provided for ground rubber (raw material) and one silo for finished product (surface-treated rubber). Each is equipped with a bin-vent filter to dedust the conveying air leaving the silo. Each silo discharges the product by gravity into a dual transporter system which operates alternately with respect to filling and conveying.

  All three silos have side explosion vents per the National Fire Protection Association Guide for Venting of Deflagrations (NFPA 68).

- **Transfer Tanks (Transporters)**
  The critical steady flow rates of the scrap tire rubber from a conical mass flow hopper are relatively low and they range from 9.3 to 23 tons per hour for a 1 foot diameter outlet. For this reason, a dual transfer tank conveying system is provided to convey the solids at a rate of 20,000 pounds per hour when the silo is full. Filling of the tank, not emptying, limits the transfer rate, particularly at high product level in the silo.

There is also an identical air dense phase conveying system for transferring the treated product from the silo into one of the two working bins or into the filter-receiver at the bulk loading station.

- **House Vacuum System**
  To collect any spills of solids, or to dedust process equipment, a central vacuuming system consisting of a Lamson Blower, a filter-receiver, a pneumatically operated dump gate, and a tote bin is provided.

System 200

- **Chlorine Storage and Evaporation**
  Chlorine is supplied in the liquid state, confined under pressure, in one ton containers holding a maximum of 2,000 pounds of liquid product. The storage capacity is for 12 full containers and 12 empty ones - always kept separately. The chlorine gas requirements of the process exceed the practicality of using a conventional multi-container gas withdrawal. The process, however, only accepts chlorine in a gas phase so one chlorine cylinder will be hooked up to an evaporator. Chlorine fed as a liquid will be evaporated and supplied to the process as a gas. The demand for chlorine gas is not uniform due to batch operation so a surge tank is provided.

System 300

- **Scrap-Tire-Rubber Treatment**
  The rubber powder is air conveyed from the storage silos into a reactor feed bin at a rate of 20,000 pounds per hour and drops batchwise (5000 pounds per batch) by gravity, into a reactor on load cells. The reactor is a mixer consisting of twin drums which have two counter-rotating agitators with angled paddles.

  The treatment gas, a mixture of chlorine gas and dry air, is injected in 10 minutes directly into the fluidized powder down the sides of the mixer. This brings the reacting gas into intimate contact with the rubber as it passes through the fluidizing mixing zone. Because all particles are continuously moving, product "burning" by chlorine is avoided. The gas flows in the same direction that the paddles move. The paddles overlap at the center of the reactor and completely sweep the entire bottom of both mixer drums. From 0.1 to 3 weight percent of chlorine is added to the rubber. After two minutes of air purging, the reactor is emptied completely through the bomb-bay discharge doors into a reactor discharge bin.

System 400

- **Reactor Vent Gas Scrubbing**

  Under normal operating conditions, all of the chlorine reacts and is bound to the rubber. A scrubbing system is provided for upset conditions, for example, if agitation stops or if the reactor is charged improperly. The vent gas is sent through the scrubber so that the chlorine is not released to the atmosphere.

System 500

- **Automatic Bagging and Palletizing**

  The treated product, stored temporarily in the silo, is transferred into the working bin at a rate of 20,000 pounds per hour. The conveying air and venting air from the bagger is exhausted into the atmosphere through a bag filter by a fan. The fan maintains a slight vacuum (-1 inch water) in the working bin.

  The product, which settles in the working bin, is withdrawn by a screw conveyor into a surge hopper. The surge hopper drops the product batch-wise into an automatic bagging and gross-weighing machine. Each bag filling cycle begins when the automatic bag placer places a paper bag on the bag holder spout; the bag holder clamps close, and the product is fed into the bag at the bulk rate. When the bag is filled to the correct weight the bag holder releases the filled bag. The filled bags are closed, flattened, checkweighed, palletized, and stretchwrapped.

System 600

- **Bulk Bagging Line**

  A Flexible Intermediate Bulk Container (FIBC), or bulk bag, system is designed to load 12 bags per hour on pallets. Final bag weights may range from 1,000 to 1,500 pounds per pallet.

  The bulk bagging system includes an automatic pallet and bottom slip-sheet dispenser. The pallet dispenser holds a minimum of ten empty pallets.

  Bags are manually hung on the machine prior to start of the filling operation and the product is withdrawn from the working bin into the bulk bag at bulk and dribble rates by the screw conveyor.

System 700

- **Utilities**

  This section includes the instrument and plant (compressed and dried) air systems, the fire protection systems, maintenance shop(s), and laboratory.

4. Capital Cost Estimate

The total capital cost for a 150 million pound per year treated scrap tire rubber facility is estimated to be $6.5 million. This corresponds to about $0.04 per pound per year of treated rubber. (Note: This is not the capital cost amoritized over the total life of the facility.) This cost is quite low compared to polymer production processes, such as emulsions, spray dried products, polyvinyl chloride, and polyvinyl alcohol, whose costs range from approximately $0.50 to $2.00 per pound per year of product. Also, it is noteworthy that the capital cost estimate for the treated rubber plant is very conservative and not all the items included in the estimate would be needed for the plant to be fully operational.

It is interesting to note that the rubber treatment section is only 11% of the total capital cost. Most of the expense (84%) is associated with material handling and storage. A summary capital cost estimate is found in Table 6. The costs are for the process part of the plant only. Site preparation, land costs, laboratories and office buildings are excluded. The following areas were estimated:

- Direct costs
  1. Process equipment - purchased equipment, spare parts, and transportation to the field.
  2. Equipment setting - labor associated with installation of the equipment, associated materials such as structural steel and foundations, and rental of machinery and tools needed to install the equipment.
  3. Process material - piping, insulation, conduit, wiring, valves, and instrumentation not already included with equipment.
  4. Process material labor - labor associated with installation of process material.
  5. Building (subcontract) - complete package including building, paint, electrical, heating ventilation, and air conditioning, and labor.

- Indirect costs
  1. Home office expense - overhead costs, such as purchasing and payroll.
  2. Field expense - includes travel, field supervision, and start-up costs.

Table 6
SCRAP TIRE RUBBER TREATMENT PLANT (150 MILLION POUNDS PER YEAR CAPACITY)
STUDY COST ESTIMATE, $1000 (1992)

(For the Process Part of the Plant Only)

System / Cost Description	100-Rubber Unloading, Loading & House Vacuuming	100-Storage Silos (3)	200-Chlorine Evaporation	300-Rubber Treatment	400-Vent Gas Scrubbing	500-Automatic Packaging	600-Bulk Bagging	700-Air Compressors & Dryers	Total All Systems
1	2	3	4	5	6	7	8	9	10
<u>DIRECT COSTS (D.C.)</u>									
Process Equipment	365	1,063	55	280	71	760	142	138	2,864
Equipment Setting	19	12	5	15	5	25	8	9	98
Process Material	86	200	11	230	27	60	28	8	650
Process Material Labor	58	158	6	85	21	80	20	8	426
Building (Subcontract)	160	--	170	--	--	1,280	--	20	1,630
Sub-Total (D.C.)	688	1,433	247	610	124	2,205	218	183	5,688
<u>INDIRECT COSTS (I.C.)</u>									
Home Office Expense	71	121	25	70	10	120	50	20	487
Field Expense	49	60	15	50	7	95	32	17	325
Sub-Total (I.C.)	120	181	40	120	17	215	82	37	812
TOTAL COSTS	**808**	**1,614**	**287**	**730**	**121**	**2,420**	**300**	**220**	**6,500**

REMARKS:

- **Column #2 also includes railroad truck scale, car mover, and building.**
- **Column #3: the three storage silos are shop fabricated and field welded.**
- **Column #4 shows cost of two chlorine evaporation units (10,000 lbs./day each), and building**
- **Column #5:, all equipment is carbon steel construction; it is not suitable for wet chlorine service.**
- **Column #7:, purchase of two fork lift trucks included.**

5. Economics

This surface-modification technology for reuse of scrap tire rubber is economically very attractive. Results from this Phase II work indicate that the overall economics are even better than indicated by projections in the Phase I final report. The reasons for this economic attractiveness are that the treatment process is very simple, the equipment needed is inexpensive, and because high-value applications for treated rubber are being identified. Aspects of these factors are discussed below.

Of all potential uses for scrap tires identified this far, this technology has by far the greatest economic incentives.

Treatment Economics

Results from this study reveal that the costs for performing surface treatments on rubber particles are very low; potentially less than $0.05 per pound. Recent findings that support this conclusion include:

1. Only low amounts of chlorine are needed to effect adequate treatment for most applications, resulting in low costs for chlorine.
2. The reaction of chlorine with rubber particles consumes all of the chlorine, almost eliminating the costs associated with neutralizing untreated chlorine in the process gas prior to release to the atmosphere.
3. There is essentially no hydrogen chloride by-product formed in the process, further reducing costs for neutralizing process gas prior to discharge to the atmosphere.
4. The capital costs for building a treatment facility are very low, such that amortizing that low cost over the volume of rubber treated in the depreciation period adds very little to the treatment costs.
5. Very simple process equipment is required, which results in low maintenance costs.

Economics of Scale and Grinding on Site

Five different scenarios were evaluated to probe the importance of economy of scale associated with large commercial process plants, and to assess the economic benefits of performing the rubber grinding at the same facility. The scenarios considered were treatment plants with capacities of 10, 50, and 150 million pounds per year, without grinding capabilities, and treatment plants with capacities of 50 and 150 million pounds per year located adjacent to a grinding operation. All of these analyses were based on treatment of -80 mesh rubber; the costs for processing coarser material will be lower since costs for larger particle size rubber is lower, and less chlorine will be required because of the reduce surface area per pound of material. The cost comparisons for these five scenarios are summarized in Table 7.

Table 7
Economics at Different Scale Production Facilities

Capacity (million lb/yr)	**10**	**50**	**150**	**50**	**150**
	ship rubber to site	ship rubber to site	ship rubber to site	grind rubber on site	grind rubber on site
Unit Cost Components					
rubber	0.270 a	0.270 a	0.270 a	0.250 k	0.250 k
chlorine	0.004 b	0.004 b	0.004 b	0.004 b	0.004 b
scrubbing	0.005 c	0.005 c	0.005 c	0.005 c	0.005 c
labor	0.039 d	0.016 i	0.008 m	0.016 i	0.008 m
packaging	0.010 e	0.010 e	0.010 e	0.010 e	0.010 e
maintenance	0.007 f	0.007 f	0.007 f	0.007 f	0.007 f
amort. equipment	0.024 g	0.018 j	0.013 n	0.016 l	0.012 o
utilities	0.006 h	0.006 h	0.006 h	0.006 h	0.006 h
	------------	------------	------------	------------	------------
Totals ($/lb.)	**0.365**	**0.336**	**0.323**	**0.314**	**0.302**

Notes:

a. Current price for -80 mesh rubber plus $0.02/lb for shipping 800 miles.
b. Assumes 5 lb. Cl_2 per 1000 lb. rubber, and $0.75/lb. Cl_2 price.
c. Estimate from Phase I Final Report.
d. Assumes 8 employees @ $49,000/yr.
e. Assumes packaging in 50 lb. bags.
f. Estimate based on experience to date.
g. $1.2 million amortized over 5 years (50 million lb).
h. Estimate from Phase I final Report.
i. Assumes 16 employees @ $49,000/yr.
j. $4.5 million amortized over 5 years (250 million lb.).
k. Current price for -80 mesh rubber, FOB.
l. $4.0 million amortized over 5 years (250 million lb.).
m. Assumes 24 employees @ $49,000/yr.
n. $10 million amortized over 5 years (750 million lb.).
o. $9 million amortized over 5 years (750 million lb.).

It should be noted that in this table a capital cost of $10 million has been used. The additional $3.5 million over the cost identified in the engineering study is to cover items such as site preparation, quality control, lab buildings, and office buildings.

Noteworthy conclusions from the economic analyses include:

- The largest cost component in the production of treated rubber particles is grinding the rubber. Typical market price for ground rubber ranges from about \$0.10 - 0.30 per pound. for material in the range of -40 mesh to -120 mesh respectively. This is higher than the variable treatment costs, projected to be \$0.05 - 0.10 per pound. Buying -80 mesh ground rubber represents 74-83% of the variable costs for making treated rubber particles. Tire grinding, via current technologies, is inherently costly because it requires much energy. The smaller the particle size, the more expensive the rubber particles.

- Performing the rubber grinding operation at the same site that the surface-treatment is performed will reduce the cost by approximately \$0.02 per pound, which is the shipping cost. Reduction in capital requirements by elimination of some duplication of material handling equipment is essentially insignificant.

- These analyses assume that the treated rubber will be packaged in 50 pound bags at a cost of \$0.01 per pound. If end users can use 1500-2000 pound super sacks of product, the packaging costs can be reduced to about \$0.001 per pound.

- Having the firm that does the surface-modification treatments also perform the rubber grinding in-house, instead of purchasing the ground rubber, has plusses and minuses. Benefits include the ability to get the ground rubber at lower costs, and to have greater control over quality of the ground rubber. Detriments include the need to invest more capital, hurdles associated with gaining technical competence in tire grinding, and exposure to potential interruption in rubber supply if the sole-source in-house grinding operation has a major problem - such as a fire.

- The optimal location for a rubber particle treatment operation will depend on several factors. Some of these include proximity to major end-user markets (minimize shipping costs), proximity to supply of ground rubber (minimize shipping costs), energy costs (primarily to minimize grinding costs), and local labor costs.

Economic Incentives to End Users

Raw Material Cost Reduction - In view of the projected manufacturing costs for making treated rubber particles, a selling price in the range of $0.35 - 0.75 per pound is reasonable. At these prices, there are substantial economic incentives for end-users to utilize surface-treated rubber. Raw material costs for the polymer systems used in applications development efforts in this Phase II study cost between $1.25 and 3.50 per pound. Hence, substituting 15-50% treated rubber, costing $0.65 per pound, for these other resins on a pound for pound basis will result in raw material cost savings of 7-41%.

Improved Performance - In addition, in many cases products made with treated rubber particles exhibit superior physical properties. This increases the value of the treated rubber even further since manufacturers can obtain higher prices for products having better performance.

Recycle Content Premiums - Pressure to favor products having post-consumer recycle content is causing additional incentives for use of treated rubber. For many applications, manufacturers can obtain premium pricing for products having recycle content. In some cases, manufacturers can charge up to 5% higher prices than for comparable products made with virgin resins.

6. Environmental/Safety/Health

Environmental Impact

It has been determined that treated rubber particles are in compliance with the Environmental Protection Agency (EPA) Toxic Substance Control Act (TOSCA). The chlorination process produces a layer of chlorinated rubber. Since chlorinated rubber is already on the TOSCA Inventory, nothing further is required for compliance with this law.

Even though this technology uses chlorine, no ozone-depleting materials are formed. Careful analysis of the head-space in the reactor after treatment failed to reveal the presence of any of the chlorinated organic compounds that have been associated with destroying the ozone layer. The analyses were conducted via Fourier transform infrared spectroscopy (FTIR) gas cell and Drager tube tests.

Essentially 100% of the treatment gas is incorporated in the product. This means that chlorine or hydrogen chloride by-product would have to be neutralized (scrubbed) only during upset conditions. The gases are very easy to neutralize, so they are totally prevented from becoming pollution. The neutralization process converts the chlorine-containing species to harmless salts, which can be disposed of easily and safely.

Safety

Finely ground rubber can create an explosive mixture with air at 200 mesh and finer. From tests conducted at Fenwal, the scrap tire rubber was found to have the characteristics of a class 1 dust. Therefore, equipment needs to be designed accordingly.

Health

Toxicology tests were performed on the treated rubber particles, including oral LD50, skin irritation, and eye irritation. The results indicate that this material is totally innocuous.

Analytical testing was performed on the treated rubber particles to determine whether any polychlorinated biphenyls (PCBs) are generated during the treatment process. No PCBs, down to the lower detection level of the analytical procedure used, could be found.

Experience in Phase II has continued to underscore the fact that this surface-modification technology has no negative impacts on safety, health, or the environment. Treatments are performed in a closed system such that no toxic gases are released. In fact, commercial implementation of this technology will help eliminate an environmental problem, scrap tire piles and the associated hazards.

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7. Energy Impact

The energy savings (recovery) from using surface-modified scrap tire rubber in place of other virgin polymers is substantial. It requires only 2,000 BTU to make one pound of surface-treated rubber particles. This includes the energy required for grinding the tires, manufacture and shipment of treatment chemicals, and for the treatment process. In contrast, it requires between 30,000 to 100,000 BTU to manufacture one pound of the various resins that could be substituted with treated rubber particles. Hence, energy savings (recovery) of 28,000 to 98,000 BTU are realized for each pound of rubber used in this way. For comparison, the burning of tires for energy recovers less than 14,000 BTU per pound. It is noteworthy that the rubber particle-filled materials can be recycled again or burned for energy at the end of the end-product's life.

The overall impact of the use of this technology on the national energy situation and on the scrap tire problem will be directly proportional to the volume of rubber used in this way. The market potential for surface-modified scrap rubber particles, though far from being well-defined, is thought to be substantial. Estimates range from 500 million to 5 billion pounds per year. Based on results and inferences from technical feasibility experiments, we believe that it is possible to use treated rubber particles in essentially all types of polymers.

It is reasonable to imagine that a substantial amount of treated rubber could be reused by replacing a portion of these other polymers. There are over 60 billion pounds per year of polymers made in the U. S. In 1991, the amount of scrap tire rubber disposed was 5.8 billion pounds. Hence, the amount of scrap rubber available is small in comparison to the amount of polymers available for replacement. It is also noteworthy that polymer resins filled with surfaced-treated rubber particles might be exported.

If all U.S. scrap tires were used, in a broad range of different systems, substituting for polymers having a weighted average embodied energy of 50,000 Btu per pound, the total energy saved would be 276 trillion Btu's. This is 0.3% of the total U. S. energy consumption, which totals 80 quadrillion Btu's.

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C. Conclusions

Significant commercial deployment of the surface-modification technology for scrap tire rubber reuse depends on the following important conclusions:

- In order for this treatment process to be commercially viable, it has to have the lowest possible cost. In examining the pounds of large volume polymers produced versus their price in Figure 3 on page 13, it is clear that in order to offer cost savings potential for the majority of these systems, the cost for treated rubber must be down in the range of $ 0.35 - 0.45 per pound. This can be achieved through the development of optimal process technology, and by the economies of scale associated with large-scale processing. In order for the lowest cost/highest volume potential to be fully realized, it will be necessary to identify/develop reliable process equipment that gives rapid and uniform treatment.

- The Forberg-design mixer reactor presents superior potential as the basis for process development studies.

- The treatment process utilizes a small amount of chlorine and almost all the chlorine is consumed.

- The capital costs for a rubber particle treatment facility are quite attractive. It is at least two orders of magnitude less expensive than are facilities to make new polymer materials.

- There are many diverse application possibilities for treated rubber.

- It will take much effort to support application engineers in end-product manufacturing companies. These application engineers will need support in solving technical problems that they will encounter, as is the case with all new products.

- Clearly, in order for this technology to have a meaningful impact on the scrap tire problem and energy conservation, large volume markets utilizing treated rubber must be established.

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D. Future Development Needs

Conceptual Design Development of Commercially Viable Process

A sufficient degree of confidence in the treatment process must exist to justify an investment to commercialize this process. Thus, a study is needed to address critical issues on a scale that will be meaningful for a large scale (150 million pound per year) operation.

While significant progress was made in Phase II concerning development of a commercially viable process for performing surface-modification, a number of items must still be addressed. The most important issue is how well a Forberg-design reactor will perform. In tests at vendors, it was demonstrated that a Forberg-design reactor is very effective in mechanically fluidizing rubber particles. However, actual treatment experiments must be performed in such a reactor to determine how fast chlorine can be charged to the process while getting uniform treatment on all particles. In a Forberg-design mixer reactor there is less heat transfer to the reactor walls than in a Littleford design. This raises concerns about whether excessive heat may accumulate in the rubber during very fast chlorine addition. Knowing the maximum possible rate of chlorine addition is necessary in order to accurately specify the size of reactor needed to achieve target production rates.

The chlorination of rubber process involves gases that are very corrosive towards metal, and it is critical that the materials of construction for the system be sufficiently corrosion resistant to provide durability and to not contaminate product. In the Phase II work, a study was performed to identify appropriate materials of construction, which is useful in ranking potential materials for use. However, in discussions with vendors of Forberg-design mixer reactors it was found that there are several alternatives to simply using different types of metal. These include liners made of more expensive materials, plasma arc spray coatings, and organic coatings.

Another area requiring further work is material handling. In the Phase II study, results were obtained that suggest that rubber is much easier to handle after treatment if it is cooled soon after treatment. It is indicated that applying pressure to hot rubber particles, such as when it is put into silos or bagged, causes the rubber particles to clump. Clumpy product is a problem in that it can clog material handling equipment, and it is difficult for end users to use and disperse. It is very difficult, if not impossible, to simulate conditions that cause clumping on a small scale and with a Littleford reactor.

In a future study, a Forberg-design reactor with a capacity of 1000 to 2000 pounds of rubber per batch needs to be installed and operated. This will provide an opportunity to determine how fast the chlorine addition can be performed, to evaluate a selected solution to the corrosion problem, and to identify any other operational problems inherent in the use of this type of reactor for this process, including clumping. The initial system should be very basic - a loading hopper, a reactor, and a discharge hopper.

Product/Market Applications Development

There are over 65 billion pounds of polymers made and used in the U.S. annually. Essentially all of these types of polymers can be used as the continuous-phase "glue" for binding rubber particles together in new composites - if the proper compatibility is effected. The opportunity for treated rubber particles can be viewed in two ways. It can be considered a cost-reducing filler, where its use results in lower raw material costs. Alternatively, new composites made with treated rubber and other polymers can be thought of as new materials, with unique combinations of physical properties, that can replace other materials - including metal, wood, and concrete, as well as rubber and plastics - in applications where the performance/price ratios are more favorable.

The first surface-modification developed (chlorination) produces a polar surface. This directly enhances the compatibility of rubber with polar polymers such as polyurethanes, polysulfides, and epoxies. This end of the polymer market is an excellent starting point since these polar polymers are relatively expensive and the incentives for using a cost-reducing "active component" are greatest.

To maximize the utilization of surface-treated rubber, applications must be developed in polymer systems beyond polar polymers. While approximately 9 billion pounds of polar polymers are used per year, the bulk of the greater than 65 billion pounds of rubber and plastics made each year are non-polar. Two approaches have been identified for enhancing the compatibility of scrap rubber with these non-polar polymers. The work needed for further development of these technologies is described next.

Surface Treatments - Further Developments

A number of surface-modification processes need to be further defined and developed in order to maximize scrap tire rubber particles' suitability for use with different polymer systems. Two fundamental surface modifications were developed as part of the Phase 1 Feasibility Study. These are chlorination to form a polar surface, and chlorination/dehydrohalogenation to form double bonds on the surface. It is expected that these two types of treatments will significantly increase the number of systems in which rubber particles can be used. It is expected that by using coupling agents in combination with these two families of surface treated rubber particles, a much larger potential for treated rubber will result.

Coupling agents are organometallic compounds that function by changing the interface between dissimilar phases. These are based on silicon, titanium, and zirconium. Coupling agents are widely used to enhance the compatibility of glass, alumina, mica, sand, and other minerals with rubber and plastics. In traditional applications, coupling agents compatibilize the polar surface of inorganic fillers with non-polar polymers. In the case of treated rubber particles, coupling agents will complex with the polar chlorinated surface of the rubber particles, and enhance compatibility with non-polar polymers. It is noteworthy that the three applications for treated rubber developed in the market place all employed coupling agents. Recent laboratory results from another group provides evidence for the strong interaction of coupling agents with the surface of treated rubber.

Properties to be Specified

It is imperative that technical specifications be established for treated rubber particles. It is expected that different specifications will be required for different applications. As samples of treated rubber particles are prepared for applications development studies, the starting rubber and the treated particles need to be characterized as thoroughly as possible. Properties to be quantified include particle size distribution, rubber composition (whole auto tires, truck and off-the-road tires, or tread buffings), grinding method, surface area, particle shape, bulk density, specific gravity, and percent chlorine incorporation. Other critical properties, such as surface energy, may also need to be identified.

Properties that are potentially important, for both raw materials and end products, have been identified, but many more tests still have to be done than have been done to quantify them.

Potential variables for raw material specifications are as follows:

- Volatiles.
- Acetone extract.
- Fiber content.
- Metal content.
- Particle size distribution.
- Ash content.
- Percent carbon black.
- Specific gravity.
- Mix of rubber types.
- Uncured rubber content.
- Grinding method used.
- Surface area.
- Moisture content.
- Bulk density.

Potential variables for product specifications are as follows:

- Volatiles.
- Particle size distribution.
- Chlorine content.
- Specific gravity.
- Mix of rubber types.
- Surface area.

It is becoming increasingly obvious that variables for product specifications are very end use dependent.

END

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