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Los Alamos
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A White Paper for

Catalytic Depolymerization of Rubber

To be Performed by:

Los Alamos National Laboratory
Los Alamos, NM 87545
(under DOE contract W-7405-ENG-36)

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I. Title

Catalytic Depolymerization of Rubber

II. Type Effort

S&T

III. Proposed by:

Los Alamos National Laboratory

IV. Capability Sought and Possible Uses

The goal of this program is to develop technology capable of depolymerizing rubber either for waste minimization or operational military purposes. Necessary features of this technology are that it be both sufficiently robust to accommodate a wide range of operational scenarios and environmental conditions (that is, weather, chemical or trace contaminants) and that—for waste minimization/recycling purposes—it provide a substantial level of degradation and a relatively clean suite of organic products.

V. Technical Description

Olefin metathesis is an emerging chemical technique now being used to catalyze the polymerization and rearrangement of olefins for commercial purposes; it has recently proven capable of depolymerizing polymers such as rubber and other polydienes. As is the case for many developing chemical technologies, the major industrial and academic emphasis has been on the preparation of new polymers for commercial application, not on the degradation of existing polymers; thus the development of depolymerization catalysts has not kept pace with that of polymerization catalysts. Although the technology was originally applied only to the degradation of butadiene polymers (such as those found in solid rocket propellant), recent efforts indicate that the degradation of more complex materials (such as carbon-black butadiene rubbers, butadiene rubbers, natural rubber, styrene-butadiene rubber) is possible. We believe that olefin metathesis depolymerization technology has matured to the point where it can be applied to cleanup and pollution prevention activities within the DOE and DoD complexes. We anticipate that this new area of applied and basic research will lead to technology transfer opportunities in depolymerization and recycling.

Transition metal catalyzed olefin metathesis reactions represent a broad class of commercially useful chemical reactions. The mechanism is generally (though not completely) understood and involves transition metal complexes binding to the polymer. These reactions are reversible, and even with small amounts of catalyst (starting material:catalyst ratios of 10,000:1), equilibration may be more rapid than can be measured.

It is crucial to the optimization of depolymerization that a robust catalyst be available, since contaminants or trace additives in the polymer may poison the catalyst. In simple experiments, a simple catalyst system employing tungsten hexachloride, tetramethyltin, and chlorobenzene (a solvent for the catalyst) depolymerizes natural rubber from an initial molecular weight of greater than 1 million to a final molecular weight of 5800 (a low-molecular-weight *liquid* oligomer) in 3 hours at 80°C. The raw materials used in such

catalyst systems are relatively inexpensive and offer a possible alternative to the costly processes currently employed for disposing of waste rubber products at federal facilities.

Of the commercial elastomers in use today, polyolefinic materials (such as polyisoprene, neoprene, nitrile rubbers, SBR rubbers, ethylene-propylene rubbers, etc.) constitute the largest group in use, although specialty products are manufactured from a variety of different feedstocks and include such well-known polymers as Viton-A™, Hypalon™, butyl and silicone rubber. Therefore, initial work will involve a detailed analysis of the olefinic materials and other constituents present in rubber gloves that are to be depolymerized. Once these analyses are complete, we will examine the catalyst systems noted above and test simple depolymerization systems on a baseline rubber formulation to determine the degree of degradation and its effect on mechanical properties. An important component of this phase of the effort will be to conduct a simple matrix of tests (for example, the amount of agent, location of application, duration, and temperature) on standard heavy truck tires at an independent tire-testing agency. Testing these catalysts in pilot-scale experiments (that is, modeling of process reactions) will allow us to evaluate their viability for depolymerization in waste minimization/recycling of rubber feeds. A final goal of this investigation would be to aid the integration of depolymerization technology into standard cleanup procedures for both government and civilian facilities and to examine deployment strategies for military applications.

VI. Risks and Limitations

Although olefin metathesis is a chemical process well studied in academia and development of this technology in industry is proceeding towards economic viability in several instances, degradative metathesis has never been used except as an analytical technique to determine functionality in complex polymers such as styrene. Although it is certain that this technique can degrade a variety of polymers including olefinic dienes, what this program must determine is the optimum level of degradation achievable with a catalyst system (for waste minimization purposes), the interaction of the catalyst with trace levels of entrained processing and mechanical additives, the level of degradation of intact heavy truck tires required to cause failure under step-load dynamometer testing, and further, whether or not such a level of degradation is achievable in a militarily significant time with the limited amounts of catalyst that are likely to be available in a military situation.

VII. Project Plan

Milestones	Date
Complete literature survey of catalytic olefin metathesis	8/94
Characterization and screening of target rubber compositions	11/94
Parametric testing of baseline catalyst/rubber composition (Subcontractor)	10/94
Complete laboratory screening of metathesis reactions and polymer testing;	
Final catalyst selection	12/95
Pilot-scale evaluation of reaction for waste rubber recycling	6/96
Full scale performance testing on tires/target rubber components (with Subcontractor)	6/96
Final report	9/96

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VIII. Project Cost by Fiscal Year

We are requesting a level of effort (2.0 FTE staff and 2.0 consultant) commensurate with the aggressive approach outlined above.

Fiscal Year	FY94	FY95	FY96	Total
	$325K	$650K	$650K	$1625K

IX. Organization Point of Contact

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