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ARMSTRONG LABORATORY

RECYCLING PROCESS FOR AIRCRAFT PLASTICS ASND COMPOSITES

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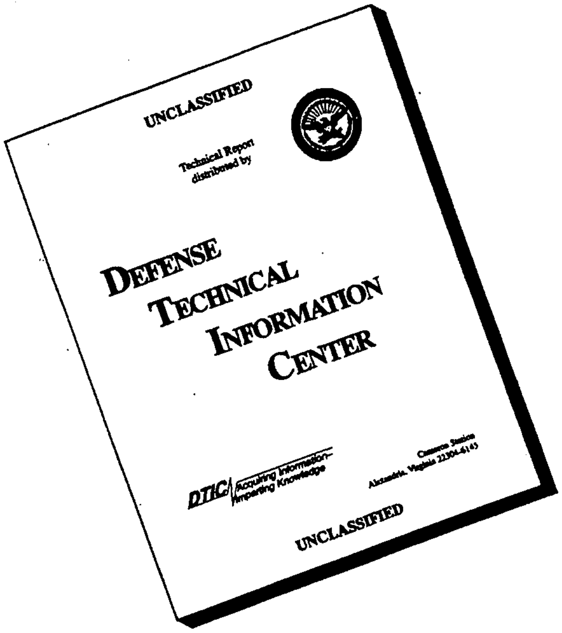

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A novel low-temperature catalytic tertiary recycling process has been investigated for use in reclaiming plastics and composite materials. The plastics and composites were selected to be representative of those used in Air Force aircraft and munitions. Results show that all types of plastics, thermosets as well as thermoplastics, can be converted in high yields to valuable hydrocarbon products with this novel catalytic conversion process. Conversion times are rapid and the process is closed and, thus, nonpolluting. Additional tests on used plastic blast media, a hazardous waste stream, and composite materials demonstrate the utility of the low-temperature catalytic conversion process. Catalytic conversion of used plastic blast media removed the organic components and reduced the volume of hazardous material by a factor of 5. In that form, the remaining heavy metal oxides can be resmelted, eliminating the hazardous waste stream. Epoxy, polyester, imide, and engineering thermoplastic composite matrices are converted into low molecular weight hydrocarbons leaving valuable fibers behind that can be reused to fabricate additional composite materials. Economic projections show that a recycling plant based on this process will pay for itself in one to two years. A related technology has been demonstrated on a large scale (100 tons/day) for recycling used tires, which shows that there is a high probability for success with large-scale tertiary recycling of plastics and composites.

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EXECUTIVE SUMMARY

Plastics are the least recycled material in municipal solid waste and are the fastest growing component of landfills. The poor economics of current plastics recycling technologies dictates that new approaches be developed to reclaim these valuable resources. Chemical or tertiary recycling, conversion of plastics into low molecular weight hydrocarbons for reuse as chemicals or fuels, is the most desirable means for reconciling waste plastics and the environment. Adherent Technologies in conjunction with Tire Recycling Technologies Corp. (TRTC) is exploring an innovative low-temperature, catalytic conversion process for recycling plastics. The Phase I program consisted of initial feasibility studies on recycling a variety of aircraft plastics and composites. Results show that all types of plastics, thermosets as well as thermoplastics, can be converted in high yields to valuable hydrocarbon products with this novel catalytic conversion process. Conversion times are rapid and the process is closed and, thus, nonpolluting. The resultant hydrocarbon products vary with the plastic feedstock, but a surprisingly small number of compounds form the majority of product from a given plastic. This economically sound process gives virtually infinite life to plastic materials. Optimization of the process will likely increase yields.

Plastic blast media (PBM) used to strip aircraft paints are classified as hazardous wastes because of their heavy metal content unless they can be reclaimed. There is currently no reclamation process for Type II PBM material (urea/formaldehyde), and it is landfilled or stockpiled as hazardous waste. Catalytic conversion of the Type II PBM in the Phase I program removed the organic components and reduced the volume of hazardous material by more than a factor of 5. The conversion products did not contain any extremely toxic species. The residue contained 18% of metallic elements by weight in a carbon matrix. The carbon may be separated by a flotation or burning process to further concentrate the metallic compounds. In that form, the residue may be sent to a specialty smelter to reclaim the metallic elements and eliminate any hazardous waste.

Additional tests on reclamation of composite materials showed that epoxy, imide, and engineering thermoplastic matrices can be converted to low molecular weight hydrocarbons leaving behind valuable fibers. The fibers may be reused in molding compounds, which adds substantially to the economics of the process. Economic projections show that a plastic or composite recycling plant should be highly profitable and will pay for itself in one year after operating expenses.

TRTC has demonstrated a related chemical recycling process on a large scale with a prototype 100-ton/day plant that converts tires to their starting materials: oil, gas, carbon black, and steel. Each of those products has ready resale markets. The success of the tire recycling process shows that there is a high probability for success with large-scale chemical recycling of plastics and composites. Plastics recycling should have improved economics over the tire process because plastics have a higher hydrocarbon content and form more valuable products, which would further improve the economics of this innovative recycling technology.

PREFACE

This report was prepared by Adherent Technologies, 9621 Camino del Sol NE, Albuquerque, New Mexico 87111 under Contract Number F08635-93-C-0109 for the Armstrong Laboratory Environics Directorate (AL/EQ), Suite 2, 139 Barnes Drive, Tyndall Air Force Base, Florida 32403-5319.

This final report describes a novel low-temperature catalytic tertiary recycling process that has been investigated for use in reclaiming plastics and composite materials. The plastics and composites tested were representative of those used in US Air Force aircraft and munitions. Results show that all types of plastics can be converted in high yields into valuable petroleum resources. Conversion occurs rapidly and because the process is closed, it is nonpolluting.

The authors wish to acknowledge the technical support provided by Lieutenant Phillip Brown of the Environics Directorate.

This is a SBIR Phase I report. The contractor has given permission for public release. This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service, where it will be available to the general public, including foreign nations.

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INTRODUCTION

Plastics Recycling Background

Recycling is becoming a necessity for most of the world's population as ever-increasing volumes of municipal solid waste (MSW) are generated. In 1990, almost 200 million tons of MSW were generated in the US (Figure 1). A national policy was formulated in 1970 to encourage states, cities, and counties to join in a recycling effort [1]; however, no corresponding federal effort is being made to develop markets for recyclable materials and supply has not created its own demand. Prices for recyclables vary widely depending upon the region of the country and the recyclable material.

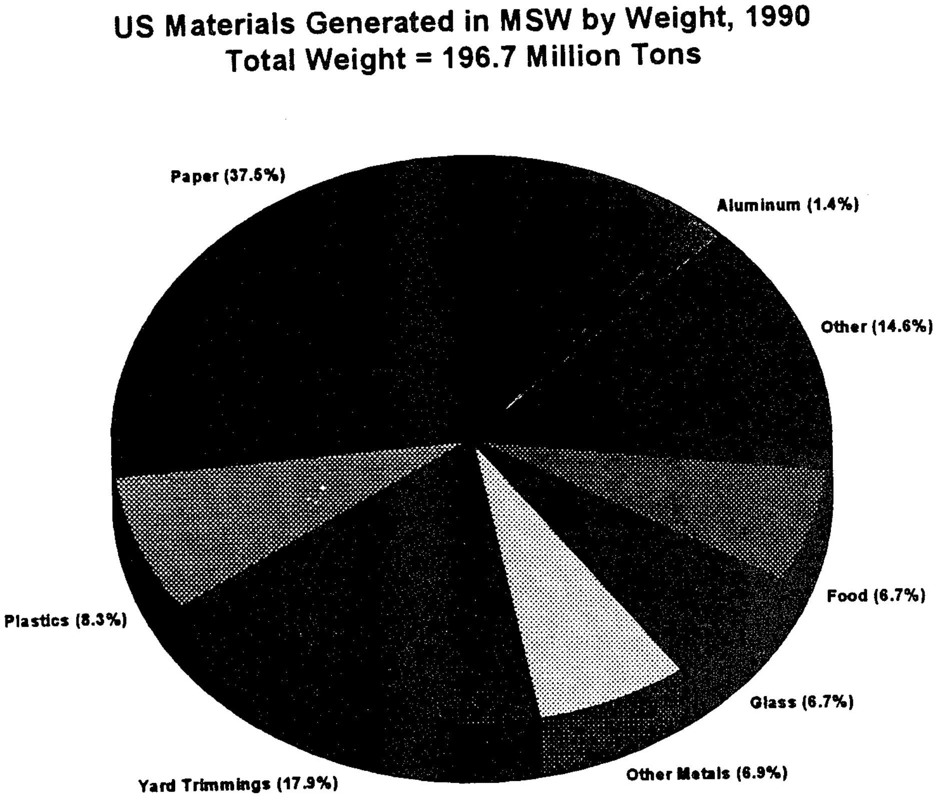


Figure 1. Materials Generated in Municipal Solid Waste by Weight

Plastics represent one of the greatest challenges to effective recycling programs. While plastics constitute roughly 8% of MSW by weight (Figure 1), they represent 20% by volume [2]. Costs for virgin plastic materials derived from petroleum are low. Currently, the cost of shipping, flaking, washing, and pelletizing a bale of recycled plastic often exceeds the cost of producing virgin plastic pellets. Given this, the market dictates the preference for landfilling over recovery for the majority of plastics waste. The result is that plastics have the dubious distinction of being the "least recycled material" with a recycling rate of only 2.2% (Figure 2).

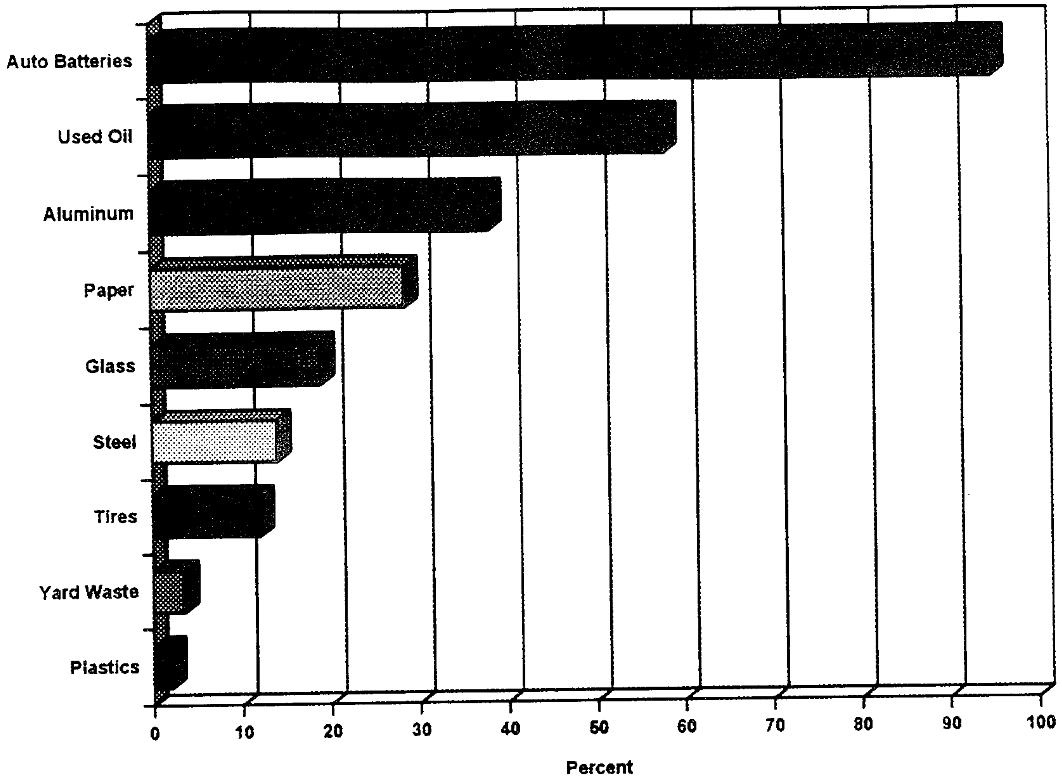


Figure 2. US Recovery Rates for Major Components of MSW (1990) [3]

There are also numerous technical barriers to traditional plastics recycling besides poor economics. These barriers include concerns about contamination, reduced physical properties of recycled materials, unwanted colors and odors, poor processability, high equipment conversion costs to handle regrind, and uncertain laws regarding the use of recycled plastics [4]. In the rush to recycle, adequate development of collection, processing, and reclamation systems has lagged, leading to uncompetitive prices for, and difficulty in marketing, the collected plastic [5-7]. As such, waste plastics constitute a growing share of the waste stream (Figure 3) [3,8]. Additional problems occur when waste plastics are contaminated with significant amounts of hazardous material and must be placed in a special hazardous waste landfill. Challenges facing the plastics recycling industry are detailed in two recent books [9,10].

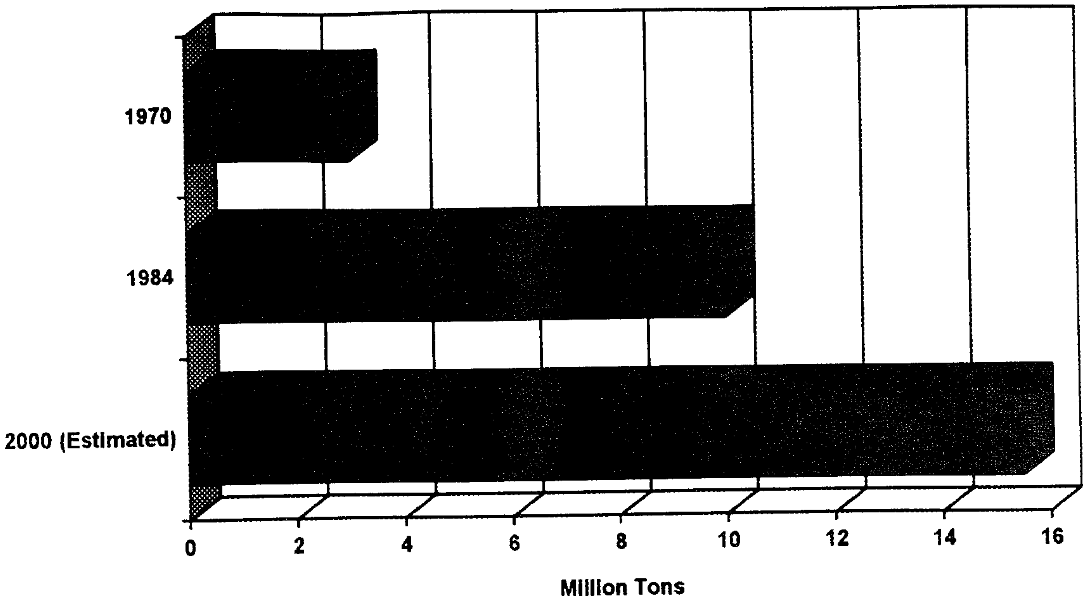


Figure 3. Rate of Plastics Introduction into Landfills [4]

Economic benefits associated with diverting material from landfills have increased recently and will continue to increase as tipping fees rise to pay for mandated environmental protection under the new federal regulations promulgated in the 1991 amendments to the Resource Conservation and Recovery Act (RCRA). Nationally, landfills are increasingly difficult to site, as suitable geology is required in order for them to be cost effective, and the public increasingly rejects landfills near home or work. Siting problems are significantly compounded for hazardous waste landfills. These factors should lead policymakers to choose to conserve landfill space by promoting recycling when economically feasible.

A new approach to plastics reclamation is needed to improve the economics of and overcome the technical barriers associated with the current plastics recycling methods. The most promising approach is chemical or tertiary recycling [11]. This process breaks polymeric waste into reusable fractions for reincarnation as polymers, monomers, fuels, or chemicals, thus promoting conservation of scarce petroleum products.

An effective low-temperature, catalytic chemical recycling process has been developed by Tire Recycling Technologies Corporation (TRTC, Albuquerque, NM) for reclaiming used tires. That process has been demonstrated with a large-scale (100 ton/day) prototype machine, which is described in Appendix A. Because of the similarity in chemical structure between many plastics and the rubber used in tires, a similar process should prove effective for tertiary recycling of plastics.

Adherent Technologies has exclusive research and development rights to explore additional applications for the tire recycling process under contract to TRTC.

Initial feasibility studies on tertiary recycling of a variety of common consumer plastics including polyethylene, polyethylene terephthalate, polystyrene, and polyvinyl chloride show that a modified version of the tire recycling process has the potential to solve many of the economic problems associated with current plastics recycling efforts. As seen in Figure 4, these chemistries represent the bulk of plastics types currently being produced.

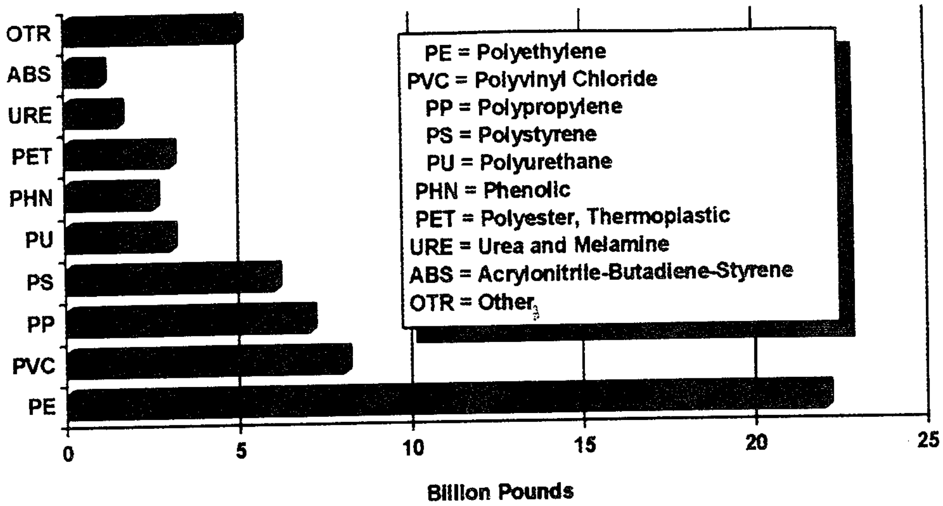


Figure 4. Plastics Production by Volume in 1993

Air Force Plastics Recycling

In general, the Air Force represents a microcosm of the country and its recycling needs. It is expected that the Air Force generates an equivalent share of waste plastic from food and consumer goods packaging to that of the country on the whole on a *pro rata* basis. High-performance plastics and composites are used extensively by the Air Force in aircraft, weapon, and missile systems to save weight and increase performance. Those plastics and plastics used in supporting those systems represent an increase in plastics use and scrap generated over the general population.

Because of the increased performance attainable with composite material construction, the polymeric content of military and commercial aircraft is increasing dramatically as each new generation is introduced. Recent additions to the Air Force inventory, the B-2, F117A, and F-22 (under development), are approaching the definition of "all composite aircraft" [12]. Increasing composites use in military and space systems is expected to continue far into the next century [13,14]. The vast majority of composites currently in use are thermoset-based epoxies and bismaleimides. Once a thermoset part is cured, it cannot be changed. Production parts with delaminations, high void content, or lack of dimensional control must be scrapped. Manufacturers currently scrap more composite materials by weight than are used in final US Department of Defense (DoD) parts [15]. DoD/aerospace composites use totaled $644.3 million in 1990 or nearly 40 million pounds [16]. There is currently no process available for recycling these materials, so they are landfilled. The same is true for other plastic parts on aircraft including thermoplastic composites, circuit boards, insulation, cable coatings, rubber boots, potting materials, and hoses. Together, these materials represent a valuable resource that is being buried in landfills.

There are numerous reasons for the Air Force to encourage recycling and to develop recycling processes for its needs. Because aircraft materials represent the high-cost/high-performance end of the plastics and composites markets, reclaiming those materials should provide an economic benefit. A successful chemical recycling process would allow recovery of the valuable and often exotic hydrocarbons from aircraft composite and plastic materials and would also provide a means to recover fibers and metal powders contained in those materials. Carbon fibers vary in price from $20 to $1,000 per pound and would have significant value for use as composite reinforcements in secondary, lower-performance applications. Often, exotic metals are used in specialty coating materials that could be recovered from a chemical recycling process and reused. Chemical recycling is also a means to dispose of sensitive or classified organic materials without incineration and provides a means to eliminate or reduce mixed hazardous wastes containing organic materials.

Recycling also preserves limited and scarce resources that, in turn, will increase US readiness by reducing dependence upon foreign oil sources. Each 100-ton/day tire recycling plant reclaims over 250 barrels of oil per day. Because of their much higher hydrocarbon content, waste plastics represent an even more valuable resource that is being landfilled. Finally, in this age of environmental awareness and activism, it is important that the Air Force project and maintain an image consistent with conservation.

Phase I Program

As stated in the Phase I proposal, the primary objective of the Phase I program was to determine the applicability of the Wallace low-temperature, catalytic conversion process for tertiary recycling of aircraft plastics and composites. Secondary objectives include identifying the types of plastics and composites for which the process is applicable, determining products and yields as a function of operating parameters, estimating the economics of the process on a commercial scale, and identifying handling and operating requirements for a large-scale tertiary plastics recycling system.

The Phase I program consisted of an in-depth study of the low-temperature, catalytic recycling process on a variety of aircraft plastic and composite chemistries. Materials selected for use in Phase I represent common plastics and composites being used in Air Force systems today as well as materials being investigated for use on future systems. In addition, a material currently treated as hazardous waste, used plastic blast media (PBM) Type II, was studied extensively. Results show that this chemical recycling technology is applicable to all the plastics examined including intractable epoxies, high-temperature polyimide, and the Type II PBM (urea-formaldehyde) systems.

In addition to hydrocarbon gases and liquids, valuable carbon and boron fibers were recovered from composite materials that can be reused in fabricating composite parts. The hazardous waste Type II PBM was reduced in volume by greater than a factor of 5 into a residue composed of carbon ash and metal oxides. The ash residue may be processed in a specialty smelter to reclaim the valuable barium, chromium, cadmium, zinc, titanium, and strontium metals in it. An economic analysis of the conversion products from each material recycled shows that all may be recycled profitably. A bench-scale continuous-feed reactor was also built and operated during the Phase I program to identify scale-up design issues for the follow-on Phase II program.

EXPERIMENTAL

Materials

Substrate materials used in Phase I feasibility studies were obtained from a variety of sources representing materials in use within the DoD, experimental aerospace materials, and generic plastic materials. PBM Types II and V, new (per MIL-P-85891[AS]) and used, were obtained from Mr. J.D. Christenson at Hill AFB. Lt. Phillip Brown, the program monitor, provided an F-15 tail rudder (Figure 5), and Capt. C. Culvert, US Navy, provided an acrylonitrile butadiene styrene (ABS) sonobouy launch tube and polycarbonate end cap.

Hexcel Corp. (Dublin, CA) provided a number of glass-, Kevlar-, and carbon-reinforced composite materials left from DoD qualification tests. Fiberite Corp. (Phoenix, AZ) provided carbon/thermoplastic and polyimide composite samples. FM-123 epoxy adhesive was obtained from American Cyanamid (Stanford, CN). Auto shredder residue ("auto fluff") was provided by TRTC (Albuquerque, NM) and used oil filters were gladly donated by a local garage. Samples of polyurethane were prepared by casting films of a flexible system based on toluene diisocyanate, aromatic diamine, and polyol (TU-89, Conap, Inc., Olean, NY).

A listing of materials studied in the Phase I program is given in Table I.

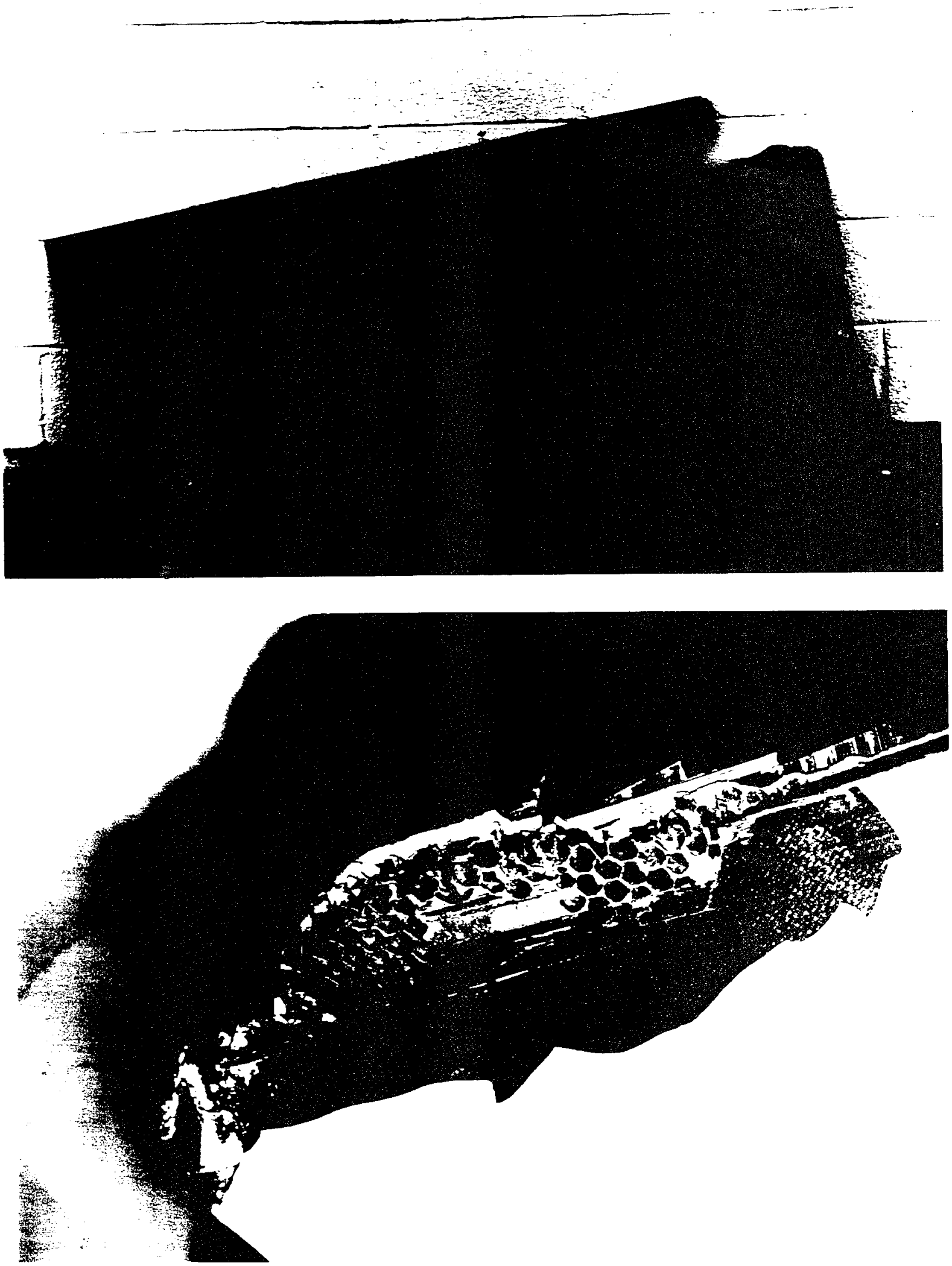


Figure 5. Top: F-15 Tail Rudder (≈4 feet long); Bottom: Sample Area Showing the Honeycomb Core, Adhesive, Boron/Epoxy Skin, and Paint

Table I

Materials Subjected to the Tertiary Recycling Process

I. Plastic Blast Media	Type V New and Used Type II New and Used
II. Thermoset Composites	Carbon/Epoxy Boron/Epoxy (F-15 rudder) Kevlar/Epoxy Glass/Epoxy Carbon/Polyimide Glass/Bismaleimide
III. Thermoplastic Composites	Carbon/Polyetheretherketone (PEEK) Carbon/Polyetherimide (PEI)
IV. Other Plastics and Organics	Epoxy Adhesive Polyurethane Polycarbonate Acrylonitrile Butadiene Styrene (ABS) Used Oil Filters Auto Shredder Residue

Apparatus

The plastic conversion studies were conducted in an apparatus constructed from laboratory glassware (Figure 6). The actual glassware setup is shown in Figure 7. Catalyst composition and process parameters are proprietary to TRTC and are not covered in this document. Each plastic feedstock was converted using an identical set-up and amount of catalyst. Sample size was approximately 15 g for each type of plastic. The catalysts were mixed throughout the plastic feedstock to simulate a multipass continuous reactor of the type used in the large-scale tire recycling process (Appendix A). Gas samples were collected in gas sampling tubes.

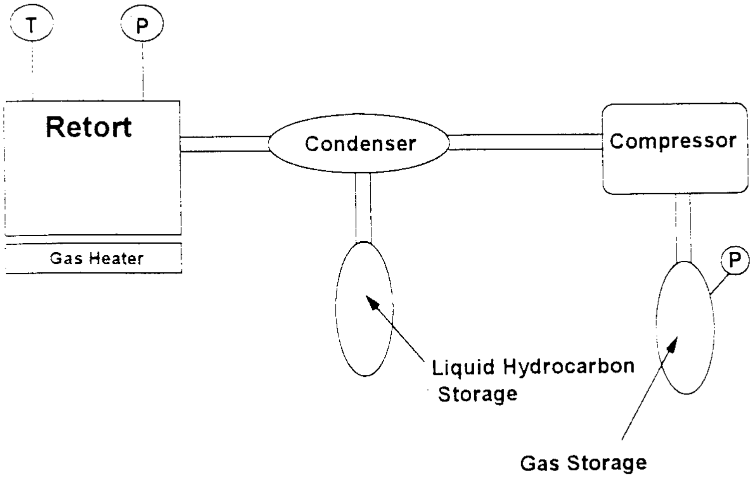


Figure 6. Schematic of the Chemical Recycling System

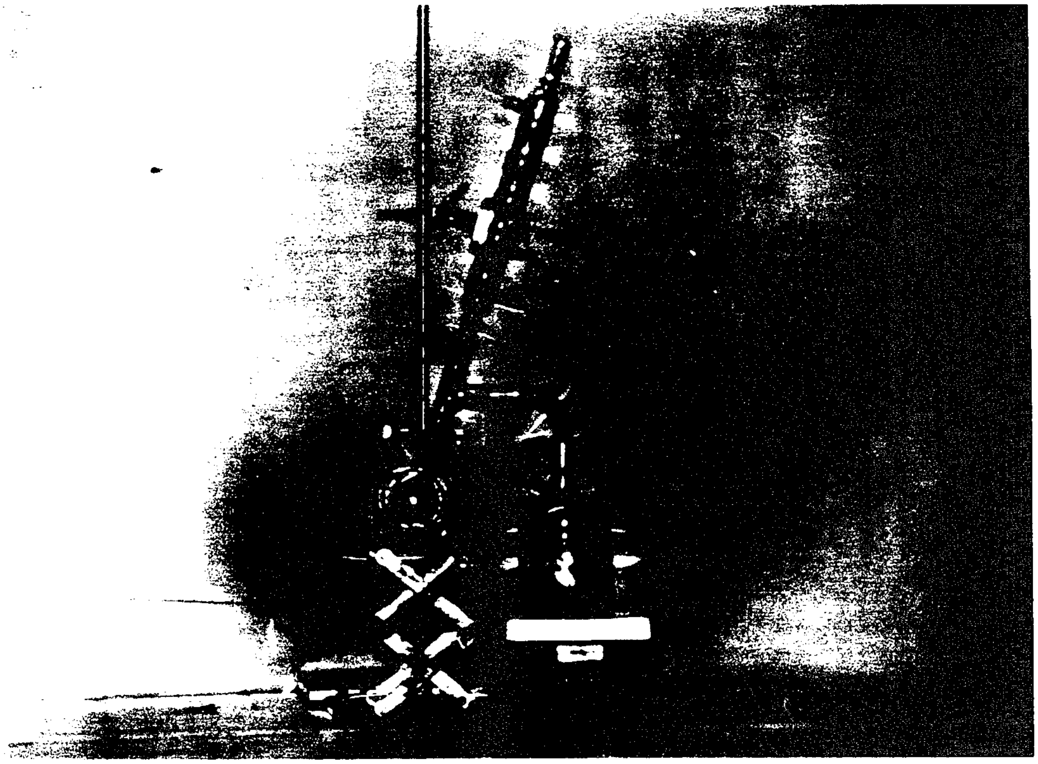


Figure 7. Laboratory Tertiary Plastics Recycling Setup

Analysis

Off gases and conversion products were analyzed using gas chromatography and mass spectroscopy techniques under contract to Assaigai Analytical Laboratories (Albuquerque, NM). The gas separations were conducted on a light hydrocarbon column for C1-C6.

Conversion products were analyzed using the procedure specified in EPA Method 8270 for semivolatile analysis. The residues were dissolved in methylene chloride before introduction into the column. All the residues were completely miscible in the methylene chloride except for the polyetheretherketone (PEEK) product, which had to be run in methanol. A J&W capillary column, DB5-MS, with a 0.25-mm inside diameter, 0.25-µm film thickness, and 30-m length was used for the semivolatile separations. The separation procedure consisted of introduction of the mixture onto the column at 40°C followed by a 4-minute hold before ramping to 270°C at 10°C/min and finally ramping to 300°C at 15°C/min. A sample chromatograph for converted polystyrene is shown in Figure 8. Elution peaks were analyzed by mass spectroscopy with a scan range between 35 and 500 amu. Peak components were identified by matching with a library of 50,000 compounds. Only compounds with a >70% confidence match are reported unless otherwise noted. Because absolute identification of complex organic compounds is difficult with this technique, components listed throughout this report are tentative identifications that would require additional investigation to verify their structures.

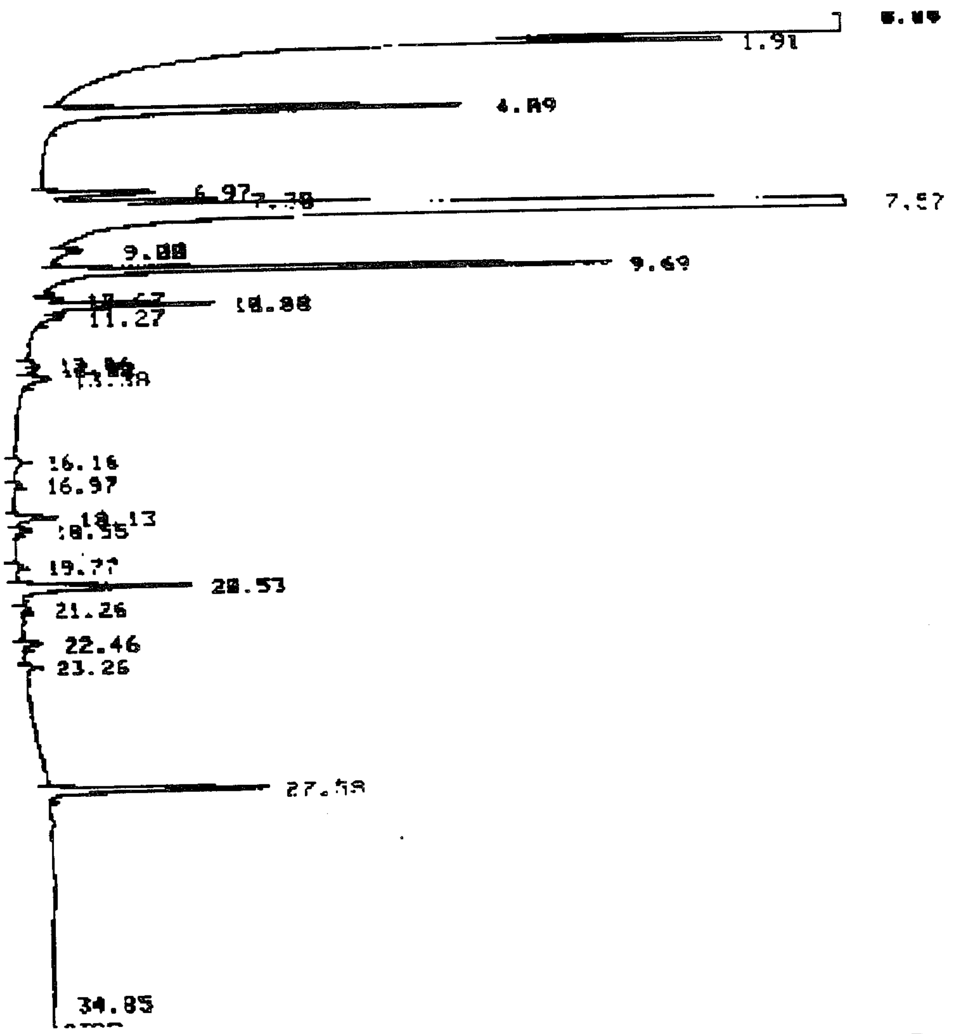


Figure 8. Gas Chromatogram of Polystyrene Liquid Conversion Product

Ash residues were analyzed for atomic composition using inductively coupled plasma spectroscopy (ICPS) and x-ray fluorescence spectroscopy under contract to Analytical Technologies, Inc. (Albuquerque, NM). ICPS measurements were made on samples digested in nitric acid. Fluorescence measurements were made directly on the residue powder.

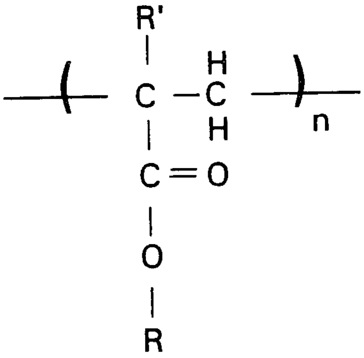
RESULTS

Plastic Blast Media

PBM was obtained from Hill AFB in new and used condition. PBM is used to strip paint, grime, corrosion products, *etc.*, from aircraft surfaces. The Type V (acrylic) is used primarily for paint stripping, while the Type II (urea/formaldehyde) is used for landing gear and similar applications.

Type V

Acrylic polymers are formed from the free radical polymerization of acrylic/acid esters. Acrylic polymers such as the Type V PBM have the general structure shown in Figure 9.



where

R = allyl
butyl
ethyl
2-ethylhexyl
hexyl
isobutyl
isopropyl
methyl
propyl

and R' = H
methyl

Figure 9. Chemical Structure of Acrylic Polymers

The Type V new PBM converted to liquid and gaseous hydrocarbons with virtually no residue in a matter of five minutes with a 60% liquid yield. The used Type V also converted to liquid and gas products rapidly, but left a 3% by weight dark powder residue as well. The appearance of the Type V materials before and after conversion is shown in Figure 10.

Type V Plastic Blast Media (New)

Type V Plastic Blast Media (Used)

Figure 10. Type V (acrylic) PBM Materials and Conversion Residues

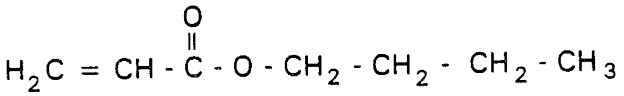
Liquid yield dropped to 40% with the used Type V PBM. The higher gas yield with the used material may be due to a high gas conversion product of the paint in the sample or to an interaction between the paint and Type V conversion process. The residue is a mixture of carbon black and pigments and compounds from the paint and primer system(s) that were stripped. A comparison of the liquid conversion compounds identified by matching library mass spectra from the Type V new and used samples is given in Table II. Only compounds exhibiting concentrations >4% in either sample are listed individually in Table II. Available toxicity data is also given in Table II [17,18]. Chemical structures for the compounds given in Table II are shown in Figure 11.

Table II

Comparison of Type V PBM New and Used Conversion Products

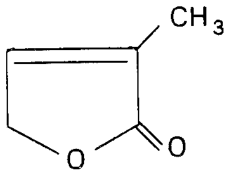
	Concentration (percent)			
Major Identified Component (> 4%)	**New**	**Used**	**Retention Time (minutes)**	**Toxicity**
cyclopentanone	not detected	4.7	6.83	1950 kg/mg[a]
butyl ester 2-propenoic acid	61.8[b]	42.7[b]	9.43	3730 kg/mg[c]
3-methyl-2(5H)-furanone	2.1	4.3	11.17	3000 kg/mg[a]
butyl ester 2-butenoic acid	2.6[b]	16.7[b]	11.24	d
dimethyl methylene butanedioic acid	3.3	5.4	13.47	2440 kg/mg[c]
naphthalene	5.8	not detected	15.35	10 ppm[e]
bis(2-ethyl hexyl) phthalate	6.4	5.4	32.00	31 g/kg[c]
other	18.0	20.8	various	n/a

a. intraperitoneal mouse LD:50.
b. poor spectral match.
c. oral rat LD:50.
d. not found, expect similar to butyl ester 2-propenoic acid.
e. threshold limit value.

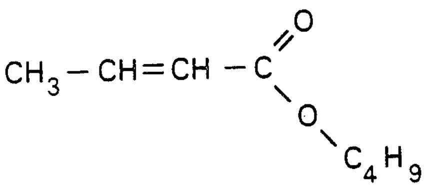


$H_2C = CH - \overset{O}{\overset{\|}{C}} - O - CH_2 - CH_2 - CH_2 - CH_3$

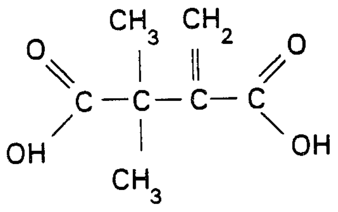
butyl ester 2-propenoic acid
(butyl acrylate)



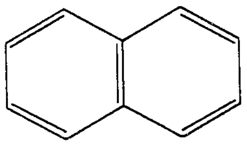
3-methyl-2(5H)-furanone



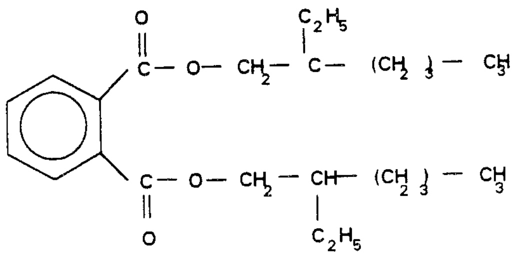
butyl ester 2-butenoic acid



dimethyl methylene butane dioic acid



naphthalene



bis(2-ethyl hexyl) phthalate

Figure 11. Conversion Products of Type V PBM

Results given in Table II show that the major conversion compounds for new and used samples are very similar. The similarity in results between the new and used samples indicates that the PBM constitutes the majority of each sample and that impurities from the stripped paint in the used sample do not significantly interfere with the decomposition reactions of the Type V PBM. As such, the higher gas yield with the used material must be due to formation of volatile conversion products from the paint. As would be expected, there are a much larger number of compounds in the other (< 4%) category for the used material that come from the stripped paint. Fourteen peaks or individual compounds were found in the new Type V liquid and 20 were observed for the used Type V liquid. Gas analysis results, given in Table III, show only the expected low molecular weight compounds (methane, propane, propylene, and isobutene) with traces of higher molecular weight species largely containing oxygen groups.

Examination of the data given in Table II shows that the butyl ester of 2-propenoic acid is the largest constituent of either sample. We can hypothesize that the majority of the Type V polymer is poly(butyl acrylate) and that the conversion process is breaking the polymer down largely into its starting monomer, butyl ester of acrylic acid (= butyl ester 2-propenoic acid). This conversion to monomer in high yields has only been observed for one other polymer examined with this process--polystyrene. These two polymers have bulky side groups with electron withdrawing capability that can stabilize free radicals formed upon the breaking of main chain bonds, which allows formation of the original monomer in high yields.

Further examination of conversion products from the new Type V PBM shows that the majority of identified compounds are rearrangements of the butyl ester of acrylic acid. Many of those compounds show an extra methyl group attached to the unsaturation. There is also a small amount of bis(2-ethylhexyl)phthalate present in both samples. This probably indicates that two monomer units of 2-ethylhexyl ester of methacrylic acid have rearranged into the aromatic diester. Thus, we can infer that a small percentage of poly(2-ethylhexyl ester) methacrylate is present in the Type V blend.

The toxicity data given in Tables II and III show that none of the conversion products identified are extremely toxic. Naphthalene and traces of benzene are the most toxic compounds identified.

Type II

Urea-formaldehyde polymerization chemistry is shown in Figure 12. The second reaction is favored under the low formaldehyde/urea ratios used in laminating resins. It is expected that the network structure (1) in Figure 12 is what is used in the Type II PBM because the military specification for Type II (MIL-P-85891[AS]) is for a thermosetting system. As seen in Figure 12, the final urea-formaldehyde structure is a network of heterocyclic trimer rings connected through carbonyl linking groups. This type of cross-linked structure is more thermally stable than linear polymers like the Type V acrylic and should be more difficult to convert to low molecular weight hydrocarbons.

Table III

Gaseous Conversion Products for Type V PBM

Major Identified Components	**Concentration (percent)**		
	New	**Used**	**Toxicity**
methane	28.0	51.2	1000 ppm[a]
propane	12.0	--	1000 ppm
propene	25.5	10.2	none est.
i-butene	34.5	35.9	not found
cis-2-pentene	--	2.7	100 ppm[a]

Trace Components	**New**	**Used**	**Toxicity**
2-methyl-1-propen-1-one		X	not found
i-butane		X	660 ppm[a]
2-butyne	X	X	100 mg/kg[c]
2-butene		X	not found
1,1-dimethylcyclopropane	X	X	not found
2-methyl-1,3-butadiene	X	X	1000 ppm[a]
trimethyl ester boric acid/ trimethoxy boroxin/ethyl ester carbonic acid		X	1700 mg/kg[b]
3-hexyne	X		1040 mg/kg[d]
benzene	X		10 ppm[a]
methyl ester 2-butenoic acid	X	X	not found

a. threshold limit value.
b. intraperitoneal mouse LD:50 (ethyl ester carbonic acid).
c. intravenous mouse LD:50.
d. subcutaneous mouse TDL.

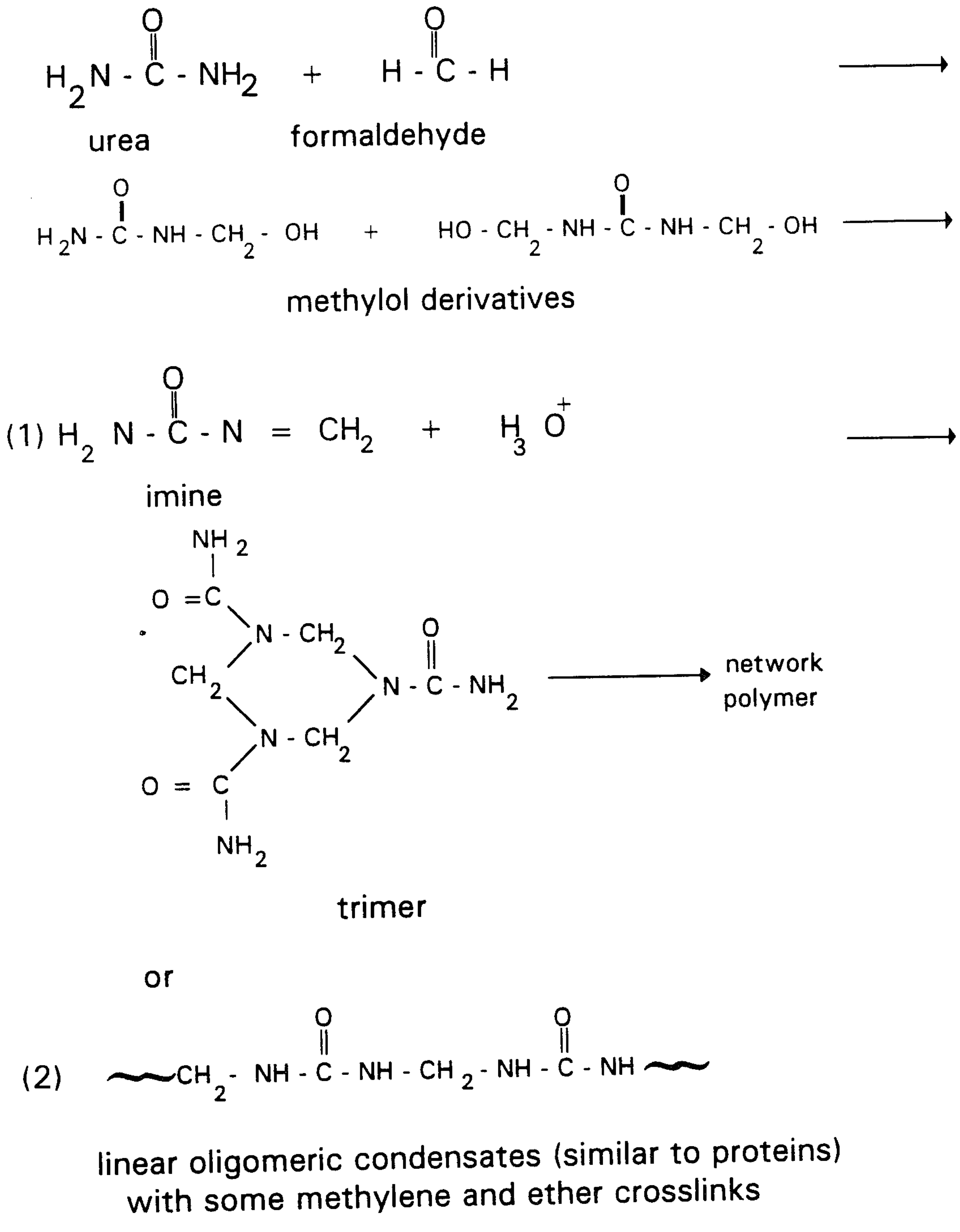
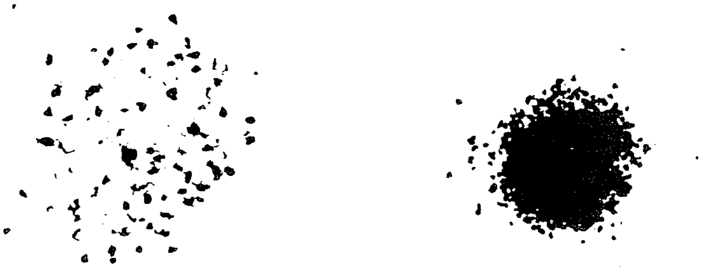


Figure 12. Urea-Formaldehyde Polymerization Reactions [19]

The Type II (urea-formaldehyde) new PBM converted in nine minutes leaving a 6% by weight residue that looks like carbon black. The hydrocarbon conversion products were gas and a yellow-brown tar that coated the reaction vessel and condenser system. A liquid yield cannot be accurately calculated for the tar, but it appeared visually that the Type II PBM produced much more gas than the Type V material. The used Type II PBM produced 11% liquid in the trap and left a 25% dark powder residue (Figure 13).



Type II Plastic Blast Media (New)

Type II Plastic Blast Media (Used)

Figure 13. Appearance of Type II (urea-formaldehyde) Materials and Conversion Residues

As with the Type V material, the presence of the paint impurities significantly affected the conversion yield of the Type II PBM. Major conversion components of the Type II new and used PBM material are given in Table IV.

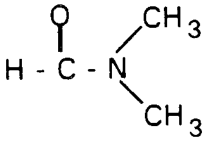
Table IV

Liquid Conversion Products from Type II PBM

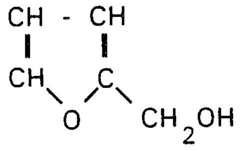
Identified Component (> 4%)	Concentration (percent)		Retention Time (minutes)	Toxicity
	New	Used		
dimethyl aminoacetonitrile	--	35.0[a]	6.21	3800 ppm[b]
N,N-dimethyl formamide	7.9	24.8	6.55	10 ppm[c]
2-furanmethanol	8.6	20.9	8.44	5 ppm[c]
5-methylpyrimidine	--	16.4	8.66	not found
2-pyridinamine	7.1	--	8.90	not found
3-methyl (1H) pyrazole	--	1.3[a]	10.07	not found
N,N-dimethyl urea	5.9	--	12.27	not found
2,6-dimethylpyrazine	13.7[a]	--	13.08	not found
(1H)-1,2,4-triazole	30.7[a]	--	17.43	not found
3-methyl-2-butenoic acid (methyl ester)	6.6[a]	--	17.84	not found
Other	19.5	1.6	various	n/a

a. Poor spectral match.
b. LD:50 oral rat (acetonitrile).
c. Threshold limit value.

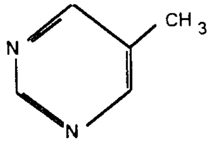
The chemical structures of the conversion products from Type II PBM (Table IV) are shown in Figure 14. Examination of the structures shown in Figure 14 and the urea-formaldehyde polymerization chemistry (Figure 12) reveals several important points. A 1:1 mixture of urea and formaldehyde has a 1:1 ratio of nitrogen and carbon atoms. The conversion products from the Type II PBM are rich in carbon compared to nitrogen (Figure 14). The minor conversion products identified (not shown) are also carbon-rich. This indicates a high formaldehyde/urea ratio that would favor Reaction (1) in Figure 12. The conversion compounds shown in Figure 14 are, in general, chemicals commonly used in industrial processes and, as such, should have ready resale markets when separated and purified.



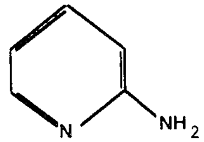
N,N-dimethyl formamide



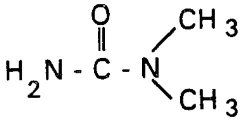
2 furnmethanol
(furfuryl alcohol)



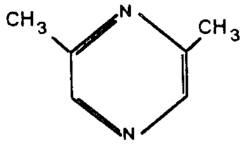
5-methylpyrimidine



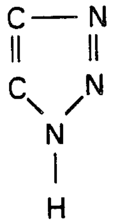
2 pyridinamine
(2-aminopyridine)



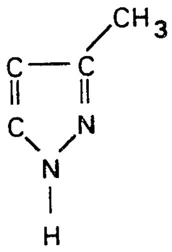
N,N-dimethyl urea



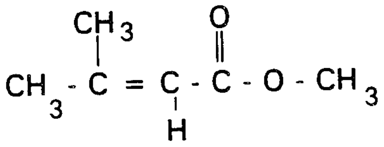
2,6-dimethyl pyrazine



1-H-1,2,4 triazole



3-methyl-(1H)pyrazole



$CH_3 - \overset{CH_3}{\overset{|}{C}} = \underset{H}{\underset{|}{C}} - \overset{O}{\overset{\|}{C}} - O - CH_3$

methyl ester 3-methyl-2-butenoic acid

Figure 14. Conversion Compounds from Type II PBM (see Table IV)

Toxicity data were not found for the majority of the components identified in Table IV. Most of these are complex heterocycles that may not have established toxicity limits. A thorough computer search of toxicity data will be required before a commercial recycling operation of PBM can be designed and operated.

Unlike the Type V results, the Type II new and used conversion products are generally not the same. This is likely a result of the complex network formed by urea-formaldehyde polymerization and the interaction of the conversion products with breakdown products from the paint chips in the used material. Surprisingly, fewer compounds comprise the used Type II conversion products (9) than the new material (19). Ninety-seven percent of the conversion products from the Type II used PBM is concentrated in only four compounds. As such, purification of those compounds can be accomplished relatively easily by distillation, which will produce valuable chemicals from what would otherwise be waste material to be landfilled.

Offgas analysis results for Type II PBM, new and used, are given in Table V. The more complex urea-formaldehyde system shows many more gaseous components than the Type V PBM (Table III) except for the major products of the new Type II, which shows only methane and propane. None of the identified gaseous components are extremely toxic. Only a few nitrogen-containing compounds are present as trace components of the Type II gas. The nitrogen is either evolved as ammonia, which would not be detected by the test method used, or remains in the liquid products. Since the liquid components generally constitute a much larger amount of the conversion products and the majority of the liquid products contain nitrogen (Table IV), it appears that most of the nitrogen remains with the liquid and tar products. A production system using the Type II PBM as feedstock may have to be scrubbed for ammonia, however.

Table V

Gaseous Conversion Products from Type II PBM

Major Identified Components	Concentration		
	New	Used	Toxicity
Methane	73.2	93.7	1000 ppm[a]
Propane	26.8	trace	1000 ppm[a]
Propene	--	1.0	none est.
i-butane	--	3.0	660 ppm[a]
i-butylene	--	0.2	100 ppm[a]
trans-butene	--	0.4	100 ppm[a]

Table V

Gaseous Conversion Products from Type II PBM (concluded)

Trace Components	New	Used	Toxicity
1-pentene	--	0.2	none est.
2-methyl-2-butene	--	0.2	100 ppm[a]
hexane	--	1.3	500 ppm
3-butenoic acid		X	500 mg/kg[b]
ethenyl oxirane	X		40 ppm[a]
3-methyl pyridizine	X		not found
1,3-butadiene/1 or 2-butyne	X	X	1000 ppm[a]
1-buten-3-yne	X	X	not found
1,3-pentadiene		X	18 mg/kg[c]
furan	X		5.2 mg/kg[d]
N-acetylpropanamide		X	not found
1,3-cyclopentadiene/ 3-penten-1-yne		X	75 ppm[a]
trimethyl boroxin/trimethyl ester boric acid	X	X	none est.
methylcyclopentane	X	X	1000 ppm[e]
methyl ester carbonic acid		X	1700 mg/kg
methyl ester 2-methyl-2-propenoic acid		X	3000 mg/kg

a. threshold limit value.
b. oral mouse LD:50.
c. intravenous mouse LD:50.
d. intraperitoneal rat LD:50.
e. aquatic toxicity rating TLM 96.

Composition of the ash residue once the hydrocarbons have been removed determines its value or liability as hazardous waste. ICPS analytical results of the residues from conversion of used Types II and V PBM for the eight metals classified by RCRA as hazardous waste are given in Table VI.

Metals listed as "less than" in Table VI are present in concentrations below the detection limit of ICPS for the sample size provided. Only barium, chromium, and lead are present in significant amounts in the Type II residue, while barium, cadmium, and chromium are present in the Type V. Semiquantitative x-ray fluorescence results are given in Table VII for the Type II residue. X-ray fluorescence is sensitive to all elements above oxygen.

Table VI

Concentration of RCRA-Controlled Metals in PBM Ash

	Concentration (ppm)	
Metal	**Type II Used**	**Type V Used**
Silver	4.4	<4.0
Arsenic	<40	<40
Barium	9,620	3,090
Cadmium	1.7	110
Chromium	1,970	306
Mercury	<0.2	<0.2
Lead	641	<40
Selenium	<40	<40

Results given in Table VII show significant quantities of titanium, iron, and zinc in addition to the ICPS results given in Table VI. The presence of barium is somewhat surprising and probably indicates the use of barium titanate pigments in some of the aircraft coatings. Strontium in the Type II residue may also indicate the use of strontium titanates as well. The observed elements are consistent with aircraft corrosion-resistant primers and coatings.

At present, Type V PBM is recycled under contract by Hill AFB and not treated as generated hazardous waste [15,20]. There is currently no recycling process for the Type II PBM [15,20].

Results from converting PBM with the low-temperature, catalytic process under development show that valuable hydrocarbon chemicals are produced from each type of PBM in high yields. Application of this process for recycling PBM may improve the economics of recycling for Type V PBM and will provide a means for recycling Type II PBM that does not currently exist and remove it from being a hazardous waste stream. Sixty percent of the Type V liquid products are acrylic monomers that may be repolymerized into new Type V material.

Table VII

X-ray Fluorescence Analysis of Type II PBM Ash

Element	Weight Percent*
Sodium	0.03
Magnesium	0.04
Aluminum	0.18
Silicon	0.40
Phosphorus	0.14
Sulfur	0.40
Chlorine	0.29
Calcium	0.47
Titanium	8.80
Chromium	0.31
Manganese	0.30
Iron	1.50
Zinc	3.30
Strontium	0.40
Zirconium	0.03
Barium	2.40
Total	18.99**

*For the oxide.
**Balance carbon and traces of light elements.

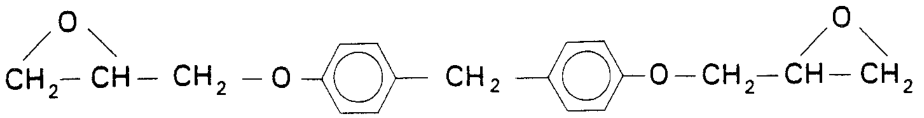
There are several means for disposition of the residues from the conversion process. The preferred method will depend upon economics. Since the conversion process greatly reduces the volume of the used PBM, it may be desirable to landfill the residue as is after burning off or using a flotation process for the carbon to further reduce volume. Note that 80% of the residue is carbon. The residue may also be smelted to reclaim the metals in it, or they may be acid digested for reclamation. The preferred means of final disposition of the residues will require further study and will depend on volume produced, lot-to-lot variability, transportation costs, landfill fees, and value of the residue components. Because of the high titanium, zinc, and barium content of the residue, it is expected that the concentrated residue constitutes a valuable ore for these and other metals.

Thermoset Composite Materials

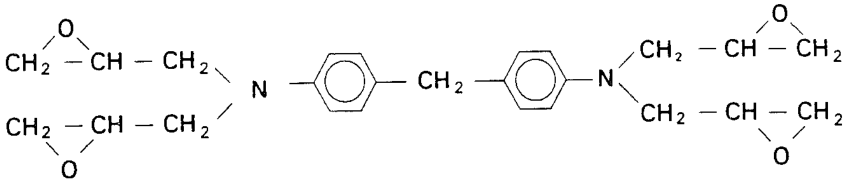
Epoxy Matrix

Common epoxy resin system components used in DoD applications are shown in Figure 15. The curing agents are typically amines although some anhydrides are also used. Figure 16 shows resultant cure reaction structures with an amine curing agent. Initial reaction occurs between the epoxide groups and primary amines to form linear polymer chains that increase the molecular weight. The initial reaction forms secondary amines and hydroxyl groups that react with epoxide groups later in the cure to form cross-links between chains. At final cure, the system is fused into one giant molecule. Often, complicated mixtures of different epoxides, toughening materials, such as nylon and rubber, and cure accelerators are used in aircraft composite matrix applications. Cured epoxies are insoluble glasses that are highly chemical resistant. They can generally only be broken down in hot concentrated inorganic acids.

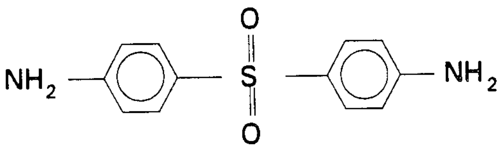
Two types of epoxy matrix laminates were studied with the low-temperature catalytic conversion process: a unidirectional 24-ply carbon fiber-reinforced system from Hexcel Corporation (F584) and a sample of boron-reinforced epoxy from an F-15 tail rudder (Figure 5). Samples from the tail rudder skin were pried from the honeycomb core and most of the paint removed before the conversion process. Both epoxy matrix samples readily broke down in a matter of minutes producing a hydrocarbon tar that coated the retort, trap, and condenser. The carbon/F584 conversion reaction was stopped after 4.5 minutes and appeared to be complete. The remaining carbon fibers represented 69 weight percent of the original composite. No other residues were observed. On a volume basis, 69 weight percent carbon fibers corresponds to 61 volume percent, which is the normal fiber volume range for this type of composite.



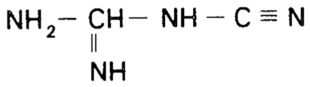
Diglycidyl Ether of Bisphenol A (DGEBA)



Tetraglycidyl Methylene Dianiline (TGMDA)

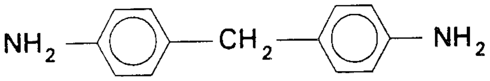


Diamino Diphenyl Sulfone (DDS)



$NH_2-\underset{\underset{NH}{\|}}{C}H-NH-C\equiv N$

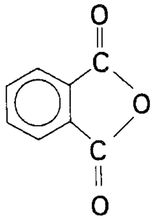
Dicyandiamide (DICY)



Methylene Dianiline (MDA)

$BF_3\cdot NH_2-CH_2-CH_3$

Boron Trifluoride Monomethyl Amine Complex ($BF_3\cdot$ MEA)



Phthalic Anhydride

Figure 15. Representative Components of Aircraft Epoxy Resins

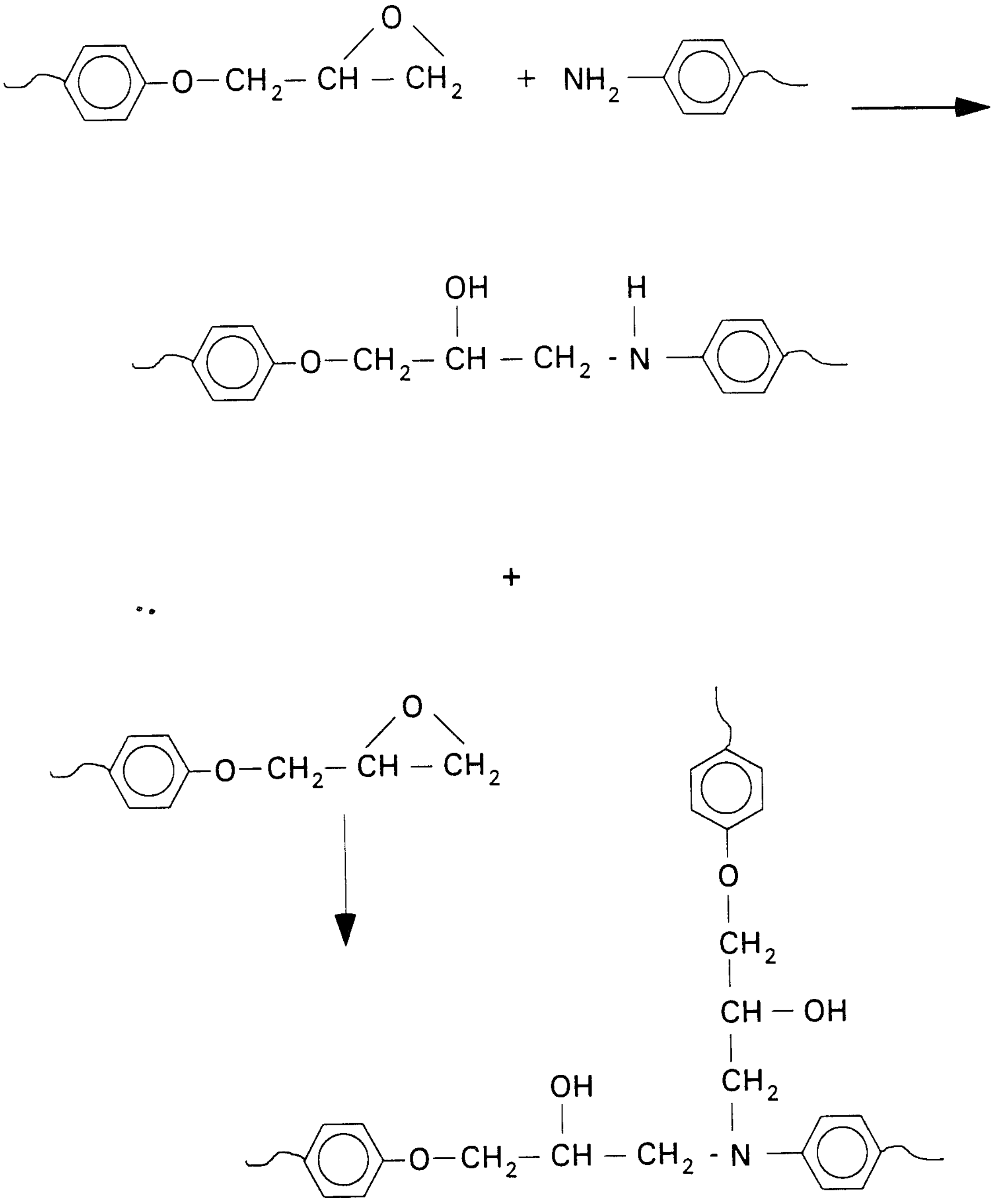


Figure 16. Epoxy-Amine Curing Reaction

The F-15 boron/epoxy was converted in four minutes leaving 56 weight percent of fiber and glass scrim cloth residue. Separate weights were not obtained for the boron and glass. The epoxy appeared to be completely removed from the composite laminates leaving behind only fibers. The carbon fibers remained as single ply sheets that could easily be spread apart. The boron fibers were a loose unorganized mass. The appearance of the epoxy matrix composites before and after conversion are shown in Figures 17 and 18. No evidence of epoxy could be found upon microscopic examination of the fibers. Both epoxy conversion tars were readily soluble in acetone.

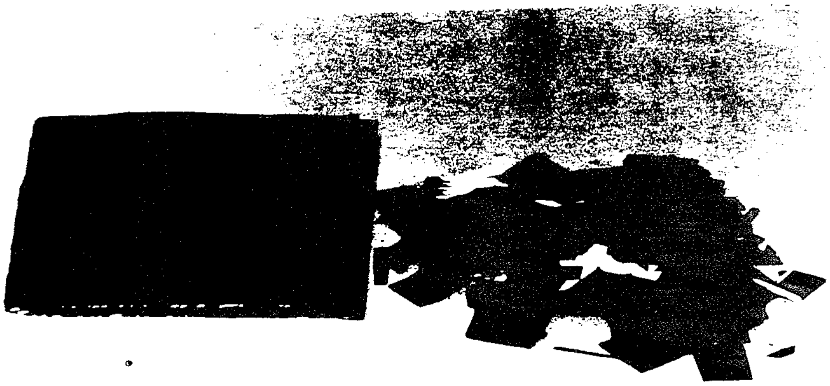
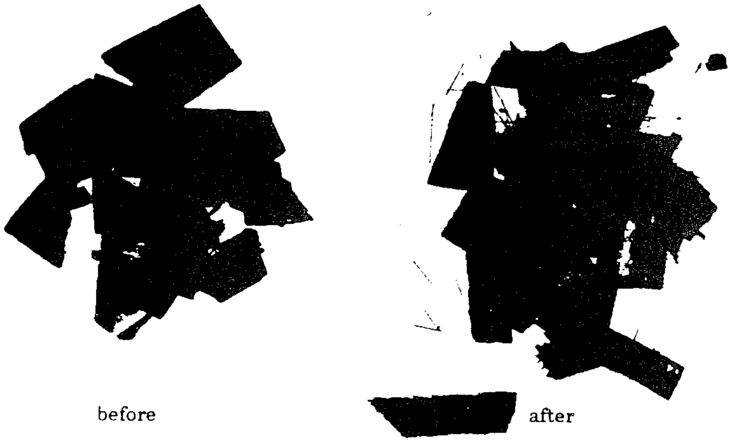


Figure 17. Carbon/F584 Epoxy Laminate and Loose Plies of Fibers



before

after

F15 Rudder Material (Boron/Epoxy)

Figure 18. F-15 Boron/Epoxy Skin Material before and after Removal of Epoxy

As might be expected from their complex structures (Figure 16), chemical analysis of both epoxy tars yielded a complex mixture of components. The F584 epoxy tar contained 21 compounds and the F-15 epoxy contained 23. Most of those compounds were present in concentrations less than 4%. Major components (>4%) of the F584 epoxy system are given in Table VIII.

Table VIII

Major Conversion Components of F584 Carbon/Epoxy Composite

Identified Compound	Concentrations (percent)	Retention Time (minutes)
aniline	5.4	10.9
ethylester 3-ethoxypropanoic acid	34.8	11.05
4-methylbenzenamine	5.1	12.86
3-phenoxy benzaldehyde	17.4*	27.08
4,4'-diamino-1,1'-biphenyl	8.3	28.00
other	19.0	various
*Poor spectral match.		

The starting epoxy components in the Hexcel F584 matrix system are proprietary and unknown to the authors. Chemical structures of the compounds given in Table VIII are shown in Figure 19. Examination of the major products for the F584 epoxy (Table VIII, Figure 19) shows that there are several aromatic amine compounds (aniline, methyl aniline, diamino biphenyl), which likely indicates that this epoxy is an aromatic amine-cured system. Common epoxy resins used in the manufacture of aircraft composites have the glycidyl group attached to a phenyl group through either an ether linkage or a nitrogen linkage (Figure 15).

The only prevalent compound containing oxygen from the F584 is the ethylester of 3-ethoxy propanoic acid (Table VIII, Figure 19). That compound appears to be due to a rearrangement reaction of two split-off cross-links (Figure 15). Thus, it appears that the base epoxy in the F584 system has the nitrogen linkage to the glycidyl groups. Tetraglycidyl methylene dianiline is the most common epoxy resin of this type (Figure 15). The presence of sulfur may also indicate diamino diphenyl sulfone (DDS) as a curing agent.

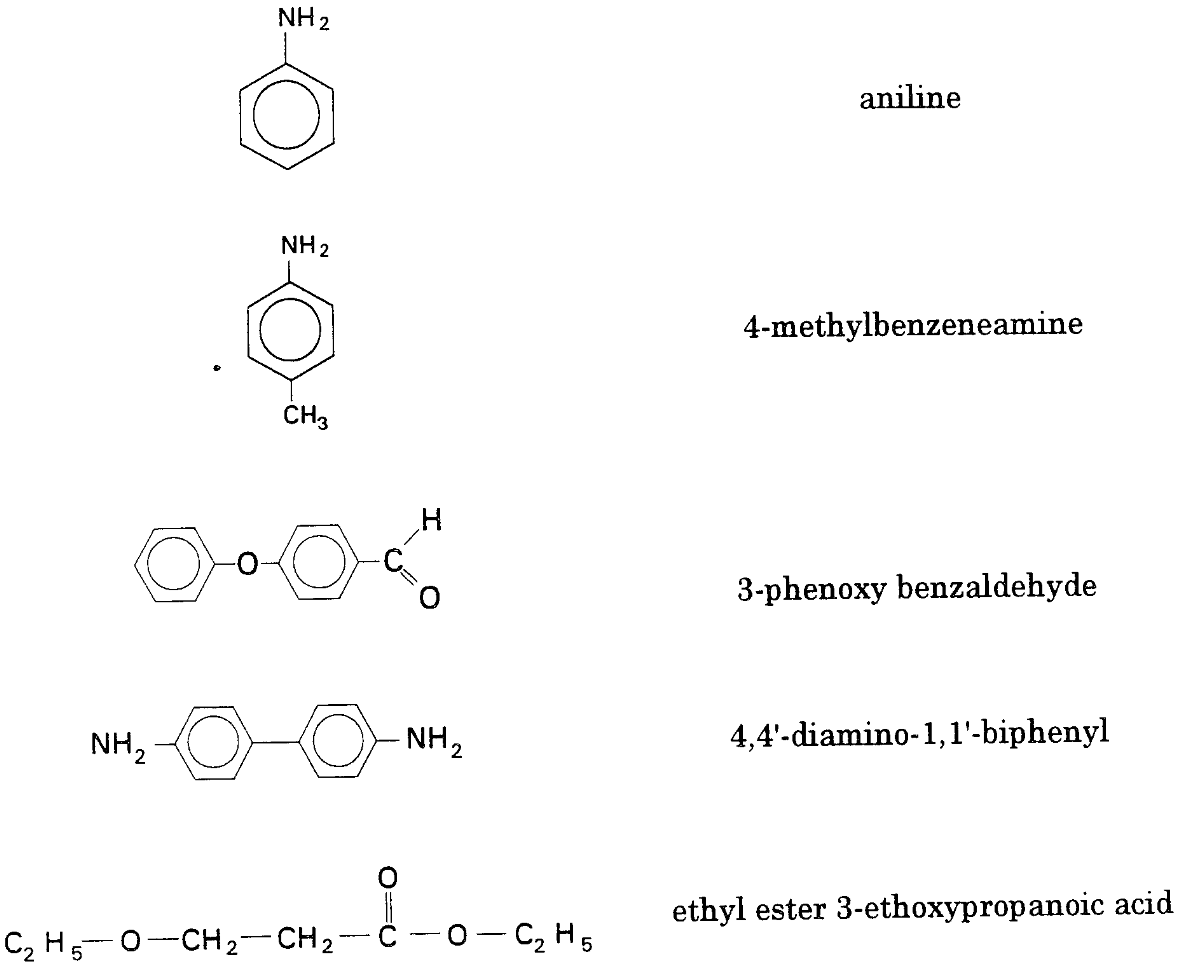


Figure 19. Conversion Products from F584 Epoxy

Analysis of the gas fraction given off from carbon/F584 epoxy conversion is given in Table IX. As seen in Table IX, propylene constitutes the vast majority of the gas fraction. Propylene likely comes from the glycidyl groups that have been scissioned from the ether linkages during conversion.

Table IX

Gas Analysis from Epoxy Conversion

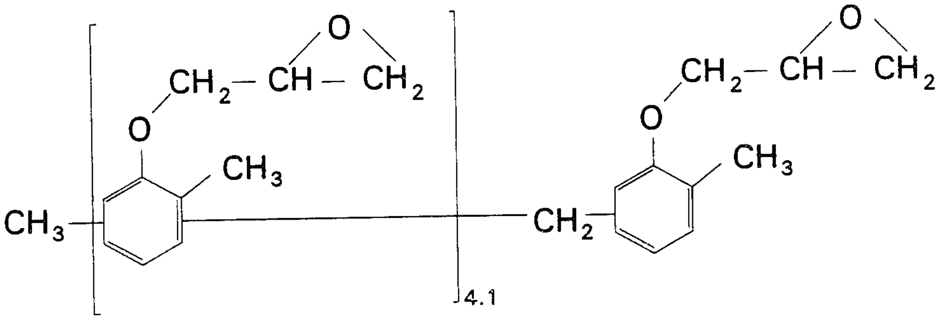
Identified Compound	Concentration (percent)
Methane	1.5
Propylene	98.4
Carbon Disulfide	traces
2-Butanone	traces
Benzene	0.1
Toluene	0.04
Styrene	traces
o-Xylene	traces
P/M-Xylene	traces

The chemical composition of the composite used in the F-15 empennage structure has been published by the Air Force [21]. The composition and chemical structures in the Boron/Avco 5505 (now Textron) are given in Figure 20. Major conversion products from the F-15 boron/epoxy sample are given in Table X. Chemical structures of the products given in Table X are shown in Figure 21.

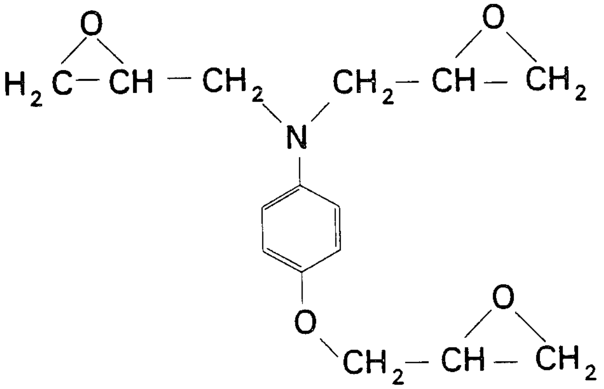
In contrast to the F584 system, the major conversion products from the boron/epoxy F-15 rudder contain a large amount of oxygen and no nitrogen. A small number of nitrogen-containing compounds are present in the minor components of the F-15 epoxy. Examination of the F-15 conversion products shown in Figure 21 and the starting epoxide structure shown in Figure 20 provides interesting insight into the conversion reaction mechanism. A high concentration of ethyl ester of 3-ethoxy-propenoic acid is seen (Table VIII) as was seen in the F584 system (Table VII). That compound appears to be due to a rearrangement of structures at cross-links

Analysis of Avco 5505

Composition		Weight Percent
Boron Fibers		60.1
Fiberglass Scrim Cloth		4.1
Resin Matrix	phr	35.8
Ciba ECN 1280	70.0	
Ciba 0510	30.0	
Diglycidyl Ether Bisphenol A (Figure 15)	3.0	
Dicyandiamide (Figure 15)	5.4	
Crosslinked Elastomer	?	



glycidyl ether of a cresol formaldehyde novolac
(CIBA ECN 1280)



n, n-diglycidyl-p-aminophenylglycidyl ether
(ERL 0510, TGPAP)

Figure 20. Composition of Avco 5505 Boron/Epoxy Used in F-15 Tail Rudder [21]

Table X

Major Conversion Components of F-15 Boron/Epoxy Composite

Compound	Concentration (percent)	Retention Time (minutes)
ethyl ester 3-ethoxypropenoic acid	32.4	11.03
2,3 or 4-methylphenol	5.0	12.47-12.87
2,4 or 2,5 or 2,6-dimethylphenol	7.8	13.49-14.21
2-(4-methylphenoxy) benzoic acid	7.9*	26.8
2-hydroxy-1,4-naphthalenedione	12.4*	27.63
4-methylcrysene	5.4	28.16
other	29.1	various
*Poor spectral match.		

that scission at ether and amine groups (Figure 16). The large number of methyl phenol groups also show the preference for scission at the ether linkage to the glycidyl group as well as the methylene bridge between phenyl groups in the cresol-based epoxide. The electron withdrawing ability of the phenyl groups would stabilize radicals at those sites and thus promote the scission reaction. The balance of the compounds given in Table VIII appear to be due to recombination reactions in the gas phase during the conversion process.

Both of these epoxy resins converted readily to low molecular weight hydrocarbons leaving the fibers available for reuse in other applications such as molding compounds.

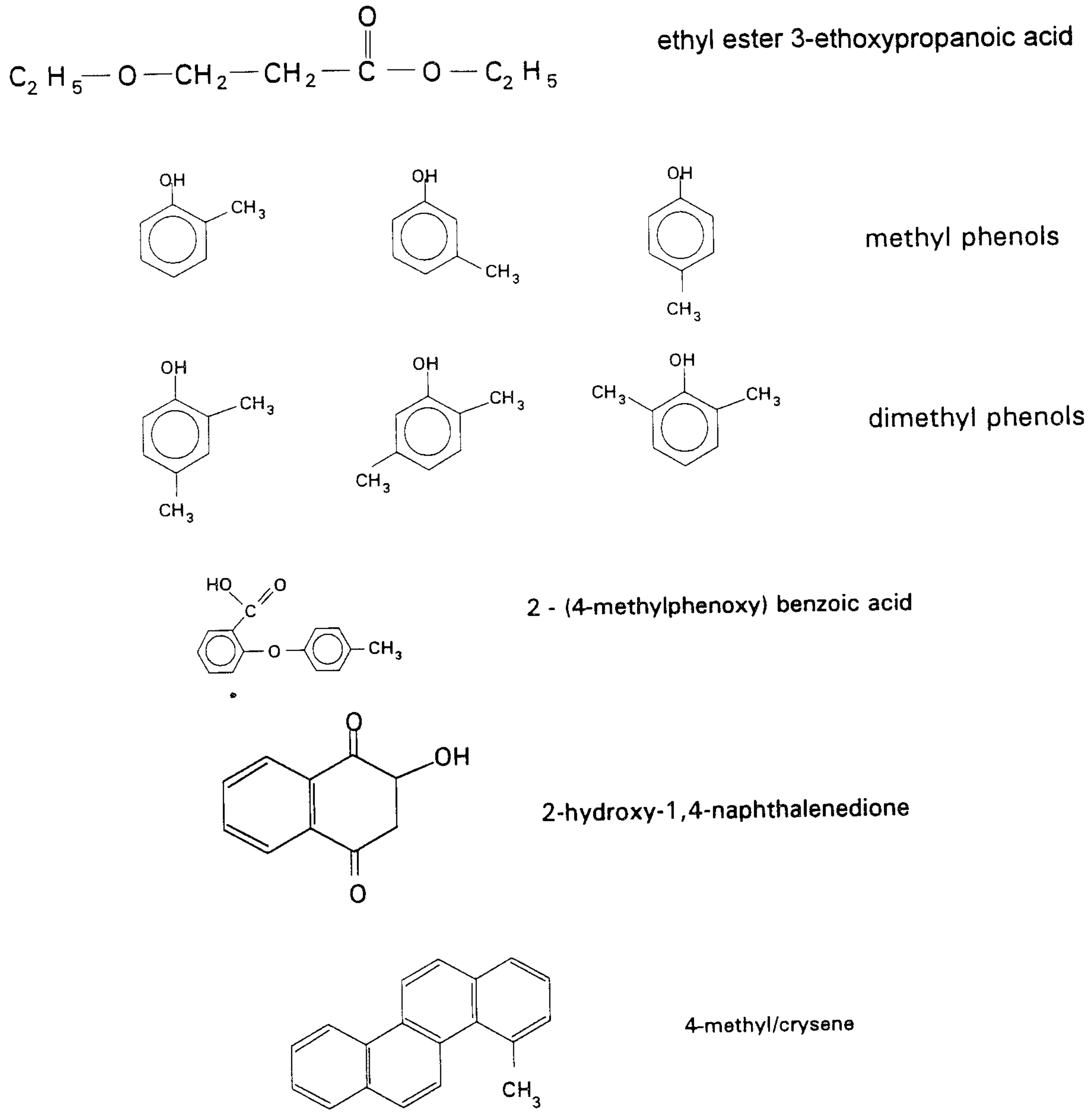


Figure 21. Chemical Structures of F-15 Boron/Epoxy Conversion Products

Imide Matrix

Polyimide and bismaleimide matrix composite materials are preferred for high-temperature applications near engine ducts and for future aircraft such as the high-speed civil transport. The most common polyimide matrix system is PMR-15, which is formed by a condensation reaction between the dimethyl ester of 3,3',4,4'-benzophenonetetracarboxylic acid, 4,4'-methylenedianiline, and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid [22]. The resultant structure is shown in Figure 22.

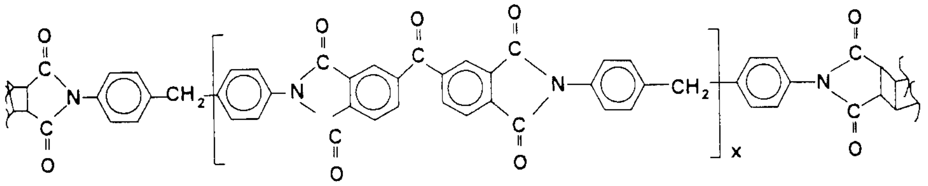


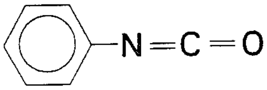
Figure 22. *Chemical Structure of Cured PMR-15 Polyimide*

The carbon/PMR-15 composite from Fiberite was converted only very slowly. A yellow gas evolved three minutes into the reaction. After 20 minutes, enough tar coated the reaction vessel to take an analysis sample, but the composite was not completely broken down. The persistence of the PMR-15 is a further demonstration of the high thermal stability of these materials. Analytical results for the PMR-15 conversion products obtained is given in Table XI. Structures of components given in Table XI are shown in Figure 23.

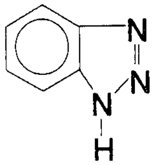
Table XI

Conversion Products of Carbon/PMR-15 Composite

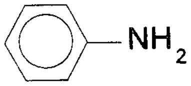
Identified Component	Concentration (percent)	Retention Time (minutes)
isocyanatobenzene/1H-benzotriazole	10.5	10.50
aniline	13.3	10.95
phenol	3.5	11.24
1-isocyanto-3- or 4-methylbenzene	5.8	12.78
2- or 4-methylbenzamine	11.9	12.88
2-methyl-1,1'-biphenyl	4.4	18.74
4-methyl-2,6-dihydroxyquinoline	5.7*	21.76
2,6-dimethyl-n-(3-methyl)benzeneamine/N-methyl benzeneamine	28.6*	23.17
other	16.3	various
*Poor spectral match.		



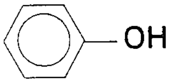
isocyanatobenzene



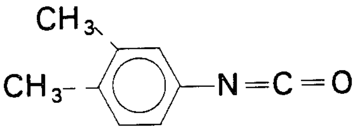
1H-benzotriazole



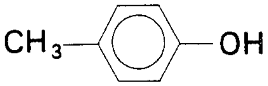
aniline



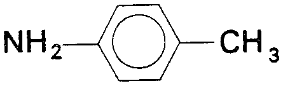
phenol



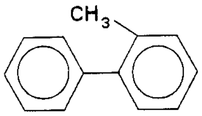
1-isocyanato-3 or 4-methylbenzene



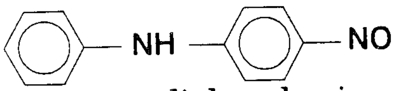
4-methylphenol



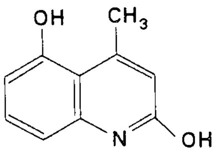
4-methylbenzamine



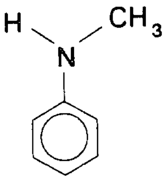
2-methyl-1,1'-biphenyl



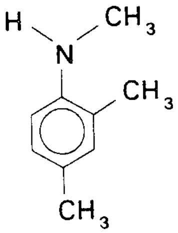
4-nitrosodiphenylamine



4-methyl-2,6-dihydroxyquinoline



N-methylbenzeneamine



2,6-dimethyl-n-(3-methyl) benzeneamine

Figure 23. Chemical Structures of PMR-15 Conversion Products

Comparison of the product structures shown in Figure 23 with the PMR-15 structure (Figure 22) reveals that the catalytic conversion reaction is scissioning the imide rings to make a variety of substituted phenyl compounds and recombination structures. This is an encouraging result and may indicate that even these very stable polymer structures can be broken down completely if the conversion process parameters are optimized.

Thermoplastic Composite Materials

Two engineering thermoplastic matrix composites were studied in the Phase I program: PEEK and polyetherimide (PEI). Both thermoplastics were reinforced with carbon fibers.

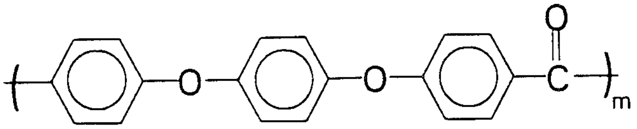
The PEEK matrix sample was run for 10 minutes. After 1 minute, a grey-colored gas evolved. Eventually, a small quantity of clear liquid formed in the condenser. The residue in the retort amounted to 82.8 weight percent of the original sample. That amount of carbon fiber corresponds to about 74 volume percent. Seventy plus volume percent fibers is more than commonly seen. Either the sample from Fiberite was high in fiber volume fraction or some carbonization of the PEEK occurred during the conversion reaction. Further study is needed to resolve this issue. Analysis of the clear liquid evolved from the carbon/PEEK sample is given in Table XII. The structure of PEEK and its conversion products are shown in Figure 24.

Table XII

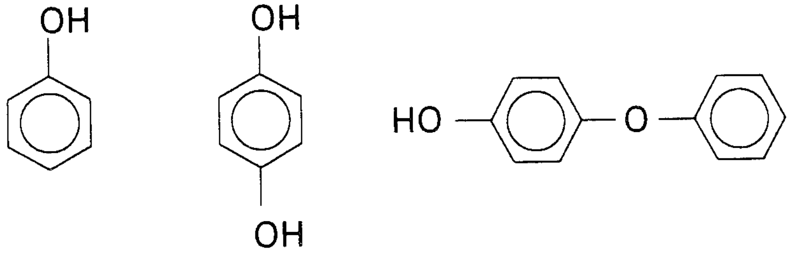
Conversion Products of Carbon/PEEK Composite

Identified Component	Concentration (percent)	Retention Time (minutes)
phenol	91.8	11.25
1,4-benzenediol	8.0	16.44
4-phenoxy-1-phenol	0.2	22.65

As seen in Table XII, 99% of the liquid conversion products from PEEK are phenol and hydroquinone. These are two common and valuable organic compounds. Producing these compounds in such high yields and purities will result in good economics for recycling of PEEK matrix waste components.



Polyetheretherketone (PEEK)



phenol

1,4-benzenediol (hydroquinone)

4-phenoxy-1-phenol

Figure 24. Chemical Structure of PEEK and its Conversion Products

The second thermoplastic composite examined in the Phase I program was a carbon-filled polyetherimide (Ultem, PEI) molding compound. The PEI matrix material is a high-temperature thermoplastic system used in packaging electronic components and for secondary aircraft structures.

The carbon/PEI converted to a very complex mixture with 29 identified components. Carbon/PEI also left a residue that looked like a carbon foam. A continuous system that augers the material through the retort would likely break up such a foam into carbon powder. Major components from PEI conversion are given in Table XIII. Chemical structures for PEI and its conversion products are given in Figure 25.

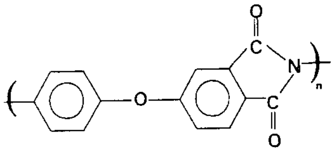
Examination of the products given in Table XIII shows that the majority are expected scission products from the PEI (Figure 25). Two of the products, ethyl ester 3-ethoxy propanoic acid and 3,3',4,4'-tetramethyl-1,1'-biphenyl, contain aliphatic hydrocarbon groups not expected from the PEI structure. This indicates that either the PEI sample contained a second polymer type or that some of the phenyl groups have opened up and fragmented. In all the catalytic conversion data reported here and previously generated, there is little evidence for the destruction of aromatic groups. As such, it is likely that the PEI sample contained a second copolymer containing aliphatic groups.

Table XIII

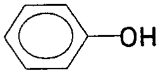
Major Conversion Products from Carbon/PEI

Identified Component	Concentration (percent)	Retention Time (minutes)
phenol	11.3	11.05
ethyl ester 3-ethoxy propanoic acid	37.2*	11.20
4-hydroxy benzonitrile	5.1	17.73
1-methyl-4-phenoxybenzene	4.2	19.82
3,3',4,4'-tetramethyl-1,1'-biphenyl	10.1*	22.75
5-methyl-1-p-5-benzimidazoleinone	6.4*	30.69
other	25.7	various

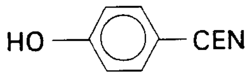
*Poor spectral match.



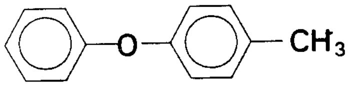
polyetherimide



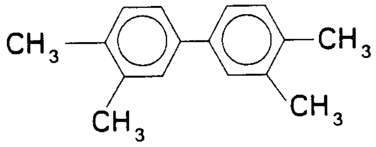
phenol



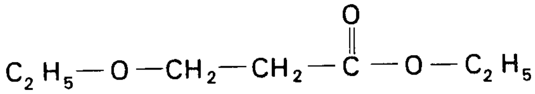
4-hydroxybenzonitrile



1-methyl-4-phenoxybenzene

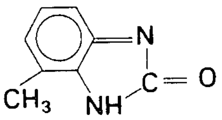


3,3',4,4'-tetramethyl-1,1'-biphenyl



$C_2H_5-O-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5$

ethylester of 3-ethoxypropanoic acid



5 methyl 1-p-5 benzimidazolinone

Figure 25. Chemical Structure of PEI and its Conversion Products

Further examination of the minor components present in the PEI conversion products shows expected chemical structures, but many also have methyl and ethyl substitutions on phenyl rings. This may indicate that the PEI was also substituted with ethyl groups on the phenyl rings to reduce toxicity. Such ethyl groups would provide a ready source of ethyl and methyl radicals to produce the observed conversion products.

Other Plastic and Organic Materials

A variety of other materials were studied in the Phase I program to determine the versatility and robustness of the catalytic conversion process. These results are representative of potential Air Force waste streams or may be analogous to potential waste streams. Polyurethane (insulation, coatings, construction materials), polycarbonate (transparencies), ABS (engineering thermoplastic), FM-123 epoxy adhesive (structural aircraft bonding), used oil filters (potential hazardous waste stream), and auto fluff (residue from decommissioning projects) are discussed in this section.

The polyurethane studied was a flexible elastomer composition called TU-89. The TU-89 chemistry results in a complex, cross-linked elastomer containing urea, urethane, and allophonate linkages. Upon conversion, the polyurethane film formed an orange tar that coated the surfaces of all the components in the retort, trap, and condenser system. Results from the semivolatile analysis of the polyurethane tar are given in Table XIV.

Despite the complexity of the polyurethane elastomer structure, the results given in Table XIV show that only a few conversion products are extracted in high yield (>85%). These results are very encouraging and may indicate that the low-temperature, catalytic conversion process under investigation may be used to economically form valuable chemical products from most plastics in the waste stream.

The polycarbonate and ABS samples were taken from a used sonobuoy launch tube obtained from the Naval Warfare Supply Center in Crane, IN. Polycarbonate, with some difficulty, converted to a viscous tar. The ABS converted in high yield to liquid product similar to what has been previously observed for polystyrene and the Type V PBM. Analysis of the ABS liquid conversion products is given in Table XV. Conversion products from the ABS and the structure of ABS are shown in Figure 26.

Table XIV

Components of TU-89 Polyurethane Tar

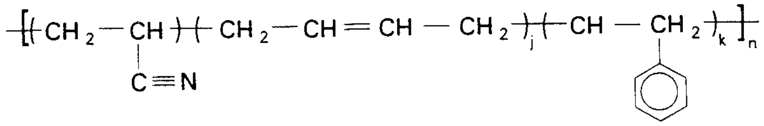
Identified Components	Concentration (percent)	Retention Time (minutes)
Diisopropyl ether	22.2	5.81
1-(1-methylethoxy)-2-propanone	47.9	6.23
Bicyclo[4.2.0]oxta-1,3,5-triene/1,3,5,7-cyclooctatetraene/Ethenyl benzene/ Phenylbutanedioic acid/2-Pyridinecarbonitrile	8.7	8.05
Hexylpentyl ether	6.3*	12.36
2-methyl-1-penten-3-ol	4.2*	25.24
other	10.7	various
*Poor spectral match.		

Table XV

Conversion Products from ABS Sonobouy Launch Tube

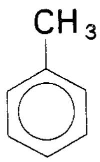
Identified Component	Concentration (percent)	Retention Time (minutes)
methylbenzene	6.0	5.83
ethylbenzene	5.7	8.23
styrene	18.0	9.01
1-methyl styrene	17.1	11.05
1,2-propadienyl-benzene/ 1-propynyl-benzene	4.6	12.34
3-penten-1-yne	5.8*	12.70
benzene butanenitrile	19.6	17.40
other	23.2	various
*Poor spectral match.		

The liquid conversion products from ABS are largely components stabilized by the pendant benzene rings from the styrene in the triblock copolymer. Components not stabilized must form low molecular weight gas species of pentane and below. ABS conversion products are largely unsaturated species useful for plastics production or as chemical intermediates and represent high value compounds.

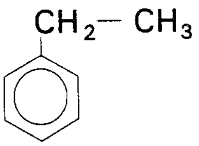


$\left[(CH_2-\underset{C\equiv N}{CH})(CH_2-CH=CH-CH_2)_j(CH-CH_2)_k\right]_n$

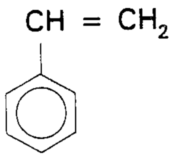
acrylonitrile butadiene styrene (ABS)



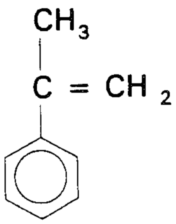
methylbenzene



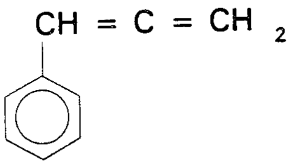
ethylbenzene



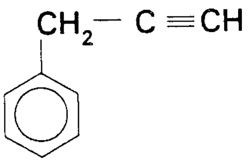
styrene



1-methylstyrene



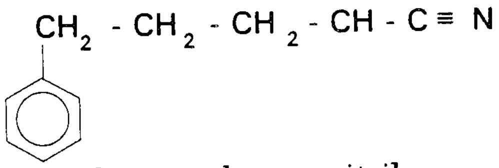
1,2-propadienylbenzene



1-propynylbenzene

$HC\equiv C-HC=CH-CH_3$

3-penten-1-yne



benzene butanenitrile

Figure 26. Chemical Structure and Conversion Products of ABS

FM-123 adhesive is a 350°F curing epoxy structural adhesive commonly used in the aerospace industry. The FM-123 system may be toughened with a second phase of nylon thermoplastic. Conversion products for the FM-123 adhesive are given in Table XVI.

Table XVI

Conversion Products of FM-123 Adhesive

Identified Component	Concentration (percent)	Retention Time (minutes)
cyclopentanone/2-hexene	6.9*	6.75
2,3,3-trimethyl-1-butene	5.6*	7.12
N,N-dimethyl-1,2-ethanediamine	27.5*	9.14, 12.69
phenol	18.1	10.40-11.25
1-(hydroxymethyl)-5,5-dimethyl-2,4-imidazolidinedione	20.2	17.42
5-methyl-2,4-imidazolidinedione	20.2	18.34
other	1.5	various
*Poor spectral match.		

The conversion products from the FM-123 adhesive (Table XVI) show a surprising difference compared to the epoxy matrix composites (Tables VIII and X). The FM-123 shows a number of aliphatic compounds and some complex heterocyclics. These results indicate that the adhesive has an aliphatic amine curing agent and that the nylon toughener is rearranging into the heterocyclic structures, perhaps combining with the scissioned groups from the epoxy curing agent.

The processing of used oil filters provides an interesting variation of the low-temperature catalytic conversion technology. Legislation has passed in some states and is pending in many others, including New Mexico, to classify used oil filters as hazardous waste, preventing their introduction into landfills. The conversion process produced a clear yellow oil that looked like new motor oil. The residue from the filter paper was a carbon powder that could be used as plastic filler or reprocessed into toner- or ink-grade carbon black.

Samples of auto shredder residue (auto "fluff") were also successfully converted. That material is a complex mixture that comprises what is left from shredding whole cars after the metal is removed. Auto fluff is thus an oily mixture of many plastic types (polyurethane foam seats, polyolefin insulation on wires, polyvinyl chloride upholstery, high-temperature packaging materials for engineered components, light lenses, *etc.*) with bits of wire and plenty of dirt.

Conversion of the auto fluff resulted in a dark viscous tar and a substantial carbon residue. These results show that the low-temperature catalytic conversion process under investigation can be successfully applied to complex mixtures that could be encountered by the Air Force such as in decommissioning projects.

BENCH-SCALE REACTOR DEVELOPMENT

Feasibility studies using our small laboratory glassware reactor have proved that chemical recycling of waste plastics is a viable and productive technology. In order to take this technology into the marketplace, large volumes of plastic waste will have to be broken down at one time. To achieve this goal Adherent Technologies has built two bench-scale reactors capable of breaking larger amounts of plastic waste. Two different approaches were tried, one machine used a batch process in which large amounts of plastic waste are dumped into the reactor and recycled at one time. This machine closely mimics the laboratory glassware setup. The second machine is a continuous-feed design that allows plastic waste to be continually fed into the machine analogous to the tire recycling system (Appendix A). Several benefits associated with the continuous-feed design are evident. There is no need to cool the reactor while new waste material is added; in addition, waste products (carbon black, dirt and ash) are removed from the system while the system is in operation, and the agitation of the plastic waste during transport through the reactor improves the efficiency of this conversion reaction.

Batch Reactor

The batch reactor shown in Figure 27 is constructed of 316 stainless steel and has a maximum volume of eight cubic feet for waste plastic. The reactor is fired using natural gas. All gases produced during the process are fed through a chilled water cooled condensing column and allowed to condense.

Gases that do not condense are compressed and stored in a pressurized collection tank. This compressed gas can serve as a combustion source to run the burners of the reactor replacing the natural gas fuel as is done with the tire recycling system. Liquid conversion products are collected in containment vessels located in various parts of the system. Temperature is monitored with thermocouples located above the burners in the waste plastic conversion retort.

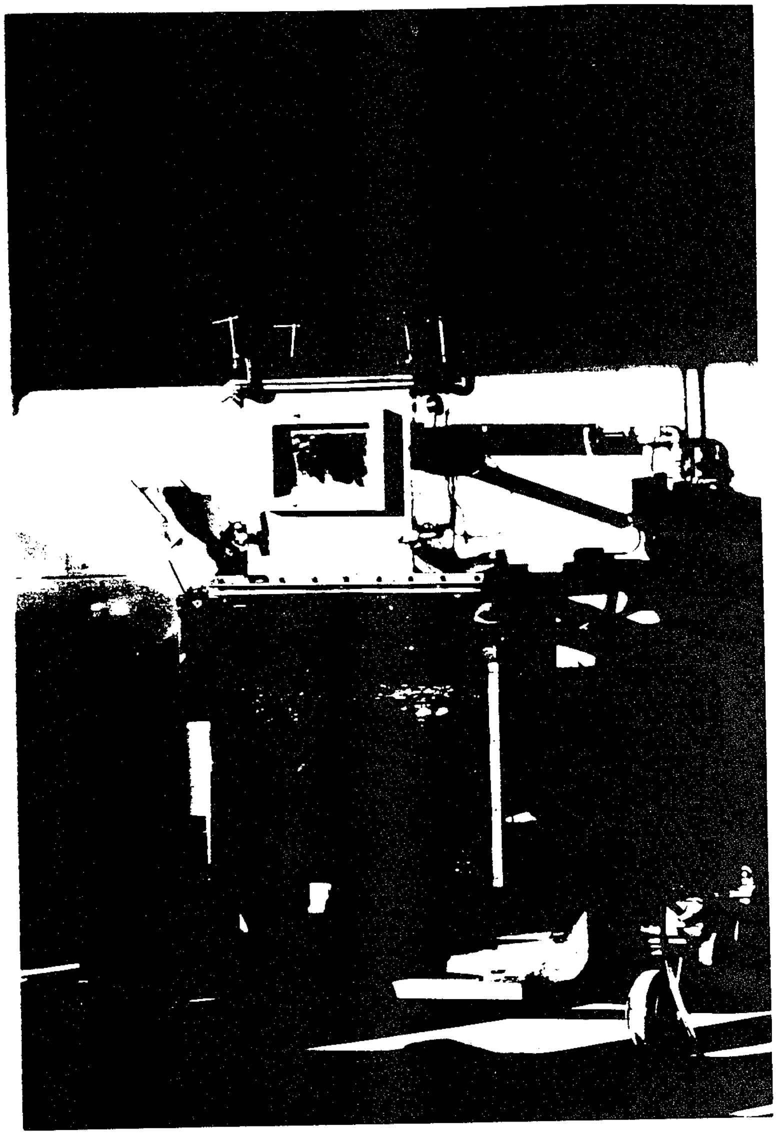


Figure 27. Batch Process Reactor

Several runs were made with the batch reactor. Initial runs made with rubber and rubber/polypropylene mixtures produced excellent results. Although gas and liquid products were produced from plastics, the reaction did not proceed with the speed or efficiency observed in the laboratory and often conversion was incomplete. Plastic conversion was hampered by the buildup of plastic waste in various states of decomposition and melting that appeared to reduce access of the bulk plastic to the catalyst and activated gas species. Small volumes of plastic waste materials and composites were successfully broken down, producing gas and liquid by-products similar to that observed in the laboratory glassware apparatus. It was concluded that agitation of the material while the process is running is necessary to the speed and efficiency of the reaction.

Continuous-Feed Reactor

The batch reactor proved to be time consuming and inefficient in breaking down large amounts of plastic waste. Before a continuous-feed reactor could be built, several problems had to be addressed. These included maintaining a vacuum in the system, controlling the rate at which waste plastic enters the machine, agitating the waste plastic to help increase the rate of reaction, and removing solid by-products while the reaction was running.

The design of the continuous-feed reactor contained the following features:

- All areas of the reactor that contact gas or liquid by-products are made of 316 stainless steel.
- Temperature is monitored with thermocouples in the reaction chamber.
- The reactor chamber for testing purposes is constructed of high-temperature glass. (A glass reaction chamber makes it possible to watch the reaction as it progresses and to define any mechanical problems.)
- The glass reactor is 3 ft long with a 1.53-in. diameter.
- Plastic waste material is moved through the glass reactor with a stainless steel auger 4 ft long and 1.5 in. in diameter.
- The auger is belt driven with very little tension on the belt to avoid any stress that could occur if plastic waste becomes trapped between the auger and the glass. (With an auger system, the amount of plastic waste entering the machine can be controlled and the depth of the plastic waste can be controlled by varying the depth of the auger flights.)
- Solid reaction by-products are pushed through the reaction chamber by the auger into a collection chamber.
- Reaction gases are run through two condenser columns to remove condensable products.
- Gases that do not condense will be compressed and stored or injected back into the reaction chamber to help assist in the breakdown of new material.

A photograph of the continuous-feed reactor is shown in Figure 28.

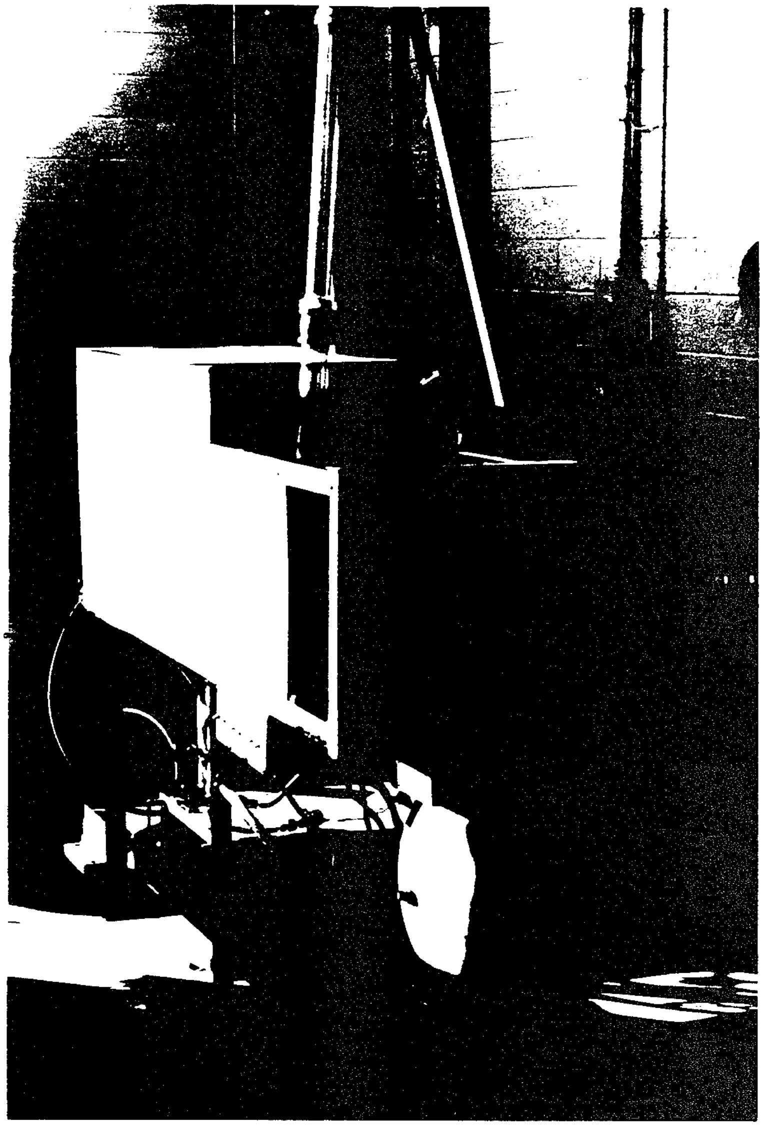


Figure 28. Bench-Scale Continuous-Feed Tertiary Recycling Reactor

Results from the continuous-feed system show that the agitation of waste plastics is critical to the rapid breakdown of the material. Reinjection of gas conversion products back into the reaction chamber also increases the speed of reaction. All plastic wastes run in the continuous reactor showed evidence of chemical breakdown, although several higher molecular weight plastics had to be run at a very slow speed to increase transit time in the reaction chamber. Carbon/epoxy composite samples were also run through the reactor with similar results as the waste plastics.

ECONOMIC ANALYSIS

The economics of low-temperature, catalytic conversion of aircraft plastics and composites is difficult to assess accurately at this early stage of development. There are numerous unknowns such as gathering and transportation costs for the waste, volumes of waste available, and markets for the conversion products. Nevertheless, it is beneficial to ignore these unknowns and perform an elementary economics analysis. Two analyses have been conducted. One for a 100-ton per day polystyrene recycling plant, and one for a 10-ton per day carbon/epoxy composite recycling plant.

Polystyrene is similar to the Type V acrylic PBM and ABS in product yields and value. For every pound of polystyrene processed, 0.9 lb of fluid hydrocarbons can be recovered with the remainder of the materials transformed into proportions of 0.07 lb of hydrocarbon gas and 0.03 lb of residue. Styrene comprises 0.8 lb of the fluid hydrocarbons.

Styrene can be marketed at about $0.25 per pound and hydrocarbons at $0.06-0.10 per pound. A unit dedicated to polystyrene recycling with a 100-ton capacity operated 330 days per year should yield yearly revenues in the following amounts:

Styrene (52.8 x 10^6 lb @ $0.25)	$13,200,000.00
Hydrocarbons (11.2 x 10^6 lb @ $0.08)	$897,600.00
Total	$14,097,600.00

Even with operating expenses of $1,500,000 (three times the tire recycling operating expenses), this yields a total of $12,597,600 in pre-tax income. Assuming a total initial capital outlay for construction of the facilities of $10,000,000 (three times the cost of a tire recycling plant), the revenues generated would result in a return of the total investment in a polystyrene plastics recycling plant in a year or less.

Currently, the plastics industry has formed a joint task force to deal with polystyrene alone, the National Polystyrene Recycling Consortium, on which it has spent over $45 million without yet coming up with a viable solution to this exponentially increasing problem. Since most polystyrene is used in packaging and disposable goods, a significant amount of polystyrene being produced is landfilled. One hundred 100-ton per day units would be required to recycle current levels of polystyrene being produced.

A minimum economic analysis for the hydrocarbons from other plastics yields one-quarter the revenues from the sale of the by-products compared to the polystyrene recycling process. The estimated gross yearly income from a similarly scaled unit dedicated to their recycling would be approximately \$3.2 million. A facility dedicated to recycling composite materials could be even more lucrative. Carbon fibers originally cost \$20-\$1,000 per pound depending upon the type and resultant mechanical properties. The lower cost carbon fibers are generally used in aircraft structures. Boron fibers sell for about \$50 per pound. Reclaiming these valuable products for reuse will ensure that the conversion process is economical. Chemical products from the epoxy resins will also add to the process economics.

For each pound of carbon composite material processed, 0.6 lb of fibers and 0.4 lb of polymer hydrocarbons (which can be sold for about \$0.08 per pound) will be recovered. Because of the lower volume of waste composite materials available compared to commodity plastics, the analysis is based on a 10-ton per day recycling plant. A 10-ton unit operated 330 days per year can recycle 6.6 million pounds of composite or 16.5% of DoD production. Such a plant could be expected to yield the following annual revenues if the carbon fibers were sold for use in molding compounds at \$2.00 per pound, which is equivalent to the cost of buying virgin glass with the superior properties of carbon fibers:

Fibers (3.96 x 10^6 lb @ \$2.00)	\$7,920,000.00
Hydrocarbons (2.64 x 10^6 lb @ \$0.08)	\$211,200.00
Total	\$8,131,200.00

As the technology would entail no additional costs for adaptation to composites recycling or operation, there is a very realistic potential for \$6,631,200 of gross income after estimated operating expenses of \$1,500,000 from a single year's operation.

CONCLUSIONS

The low-temperature catalytic conversion process under development has been shown to be extremely versatile for breaking down all types of organic materials into low molecular weight hydrocarbons for reuse. Earlier results obtained on waste commodity plastics were complimented by a wide variety of polymer chemistries investigated during the Phase I program. Even high thermal stability thermosetting polymers were converted to valuable low molecular weight organic compounds. One thermoset system, Type II urea-formaldehyde PBM, was removed from a mixture of stripped paint classified as hazardous waste. By removing the plastic from the mixture, the volume of hazardous waste is drastically reduced and means for reprocessing it into its elements become available. A prototype continuous-feed reactor was designed, built, and demonstrated in the Phase I program. Results show that plastics and composites may be processed on a continuous basis similar to what is now being done with tires. This versatile process may be used to solve many current and future solid and hazardous waste problems within the Air Force and the country. In addition, economic analyses show that recovery of valuable hydrocarbons and fillers from these wastes can be highly profitable.

RECOMMENDATIONS

Results from the Phase I program show that the chemical recycling process under development is effective with a wide variety of plastics and composite materials. Future work should focus on a particular waste stream such as the PBM and demonstrating a large-scale recycling system for that waste stream. Design issues that must be addressed in the demonstration unit include transport of material through the reactor, liquid and gas conversion product containment, handling of solid residues, catalyst placement and lifetime, and incorporation of safety features. Additional work also needs to be expended on identifying means of handling toxic conversion products and residues and in identifying uses and markets for the conversion products. Means to tailor product composition through the use of mixtures of wastes should also be addressed.

ACKNOWLEDGMENTS

Many people contributed to the success of this program demonstrating the feasibility of recycling Air Force waste plastic materials. We would especially like to thank Lt. Phillip Brown, our technical monitor, for his substantial efforts in identifying plastics waste streams, obtaining representative substrate materials, and for valuable technical discussions. Mr. Jim Seely at Assaigai Analytical Laboratories provided a significant amount of help in interpreting the chemical analysis data as did Dr. Joseph Wander at Tyndall AFB. Mr. Jeff Wilder and Mr. Dana Finley of TRTC contributed their mechanical and electrical skills and experience with the large-scale tire recycling machine toward the successful construction of both bench-scale reactors. Mr. J.D. Christensen at Hill AFB helpfully provided the PBM substrates. Mr. Brian Gilmore at Hexcel Corp. and Ms. Nancy Hall at Fiberite Corp. generously provided the aerospace composite samples. Finally, Ms. Susan Switzer-Allred contributed her technical writing skills and energy in preparing this document.

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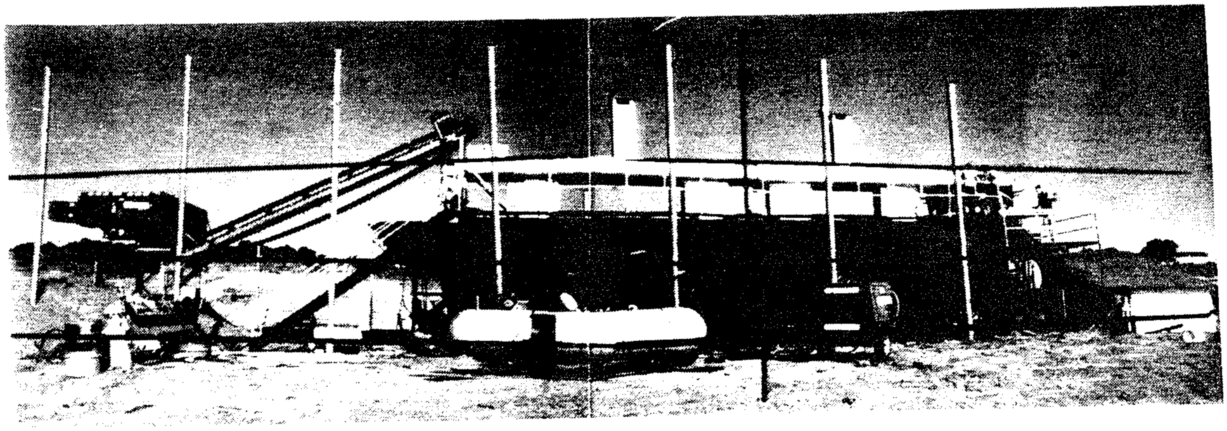
APPENDIX A

TIRE RECYCLING



Tire Recycling Prototype Plant

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Disposal of used tires is an enormous problem. One used tire is generated per person per year in the United States. That number is higher for Europe and Japan. Used tires cannot be placed in conventional landfills, and they take nearly 500 years to biodegrade. For this reason, used tires are accumulating in large volumes along the nation's highways and in used tire dumps. The EPA estimates that as many as 3 billion used tires are stockpiled in the United States. Extensive searches for uses for used tires in paving and roofing materials have not significantly diminished the annual accumulation of used tires.

A solution to the used tire disposal problem has been found by inventor Floyd Wallace. The Wallace Process is a unique low-temperature, catalytic conversion technology; is nonpolluting; and returns the tires to their primary ingredients: oil, gas, carbon black, and steel (Figure A-1). Each of these products is resold and processed for new uses. This is a pure form of recycling or reclamation.

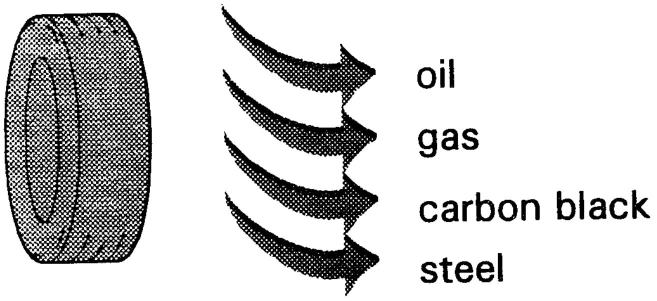

Figure A-1. Results of the Catalytic Conversion Process for Tires

The Wallace Process has been implemented on a large scale by TRTC. A photograph of the TRTC prototype tire recycling facility located in Bradley, OK, is shown on the cover page of this Appendix. This facility has a demonstrated capability of processing 60-100 tons of used tires per day. A schematic of the process is given in Figure A-2.

In the plant shown on the cover and in Figure A-2, tire chips are fed into the conversion retort with the conveyer on the left side. The chips then pass through the drying tube traversing the top of the retort. The drying tube is heated with what would be waste heat from the retort burner flue gases. Next, the dried chips enter the retort and are heated to 400°F in the presence of the catalyst. Under the influence of low heat and the catalyst, the rubber is broken down into a complex mixture of low molecular weight hydrocarbon (HC) gas and oil in the retort (HC gas stream, Figure A-2). Results of a standard distillation test on the oil (liquid HC, Figure A-2) obtained are given in Table A-I.

Analysis of the gas fraction produced from reverse polymerization of tires is given in Table A-II. The majority of the gas is stored onsite and used to fire the retort burners.

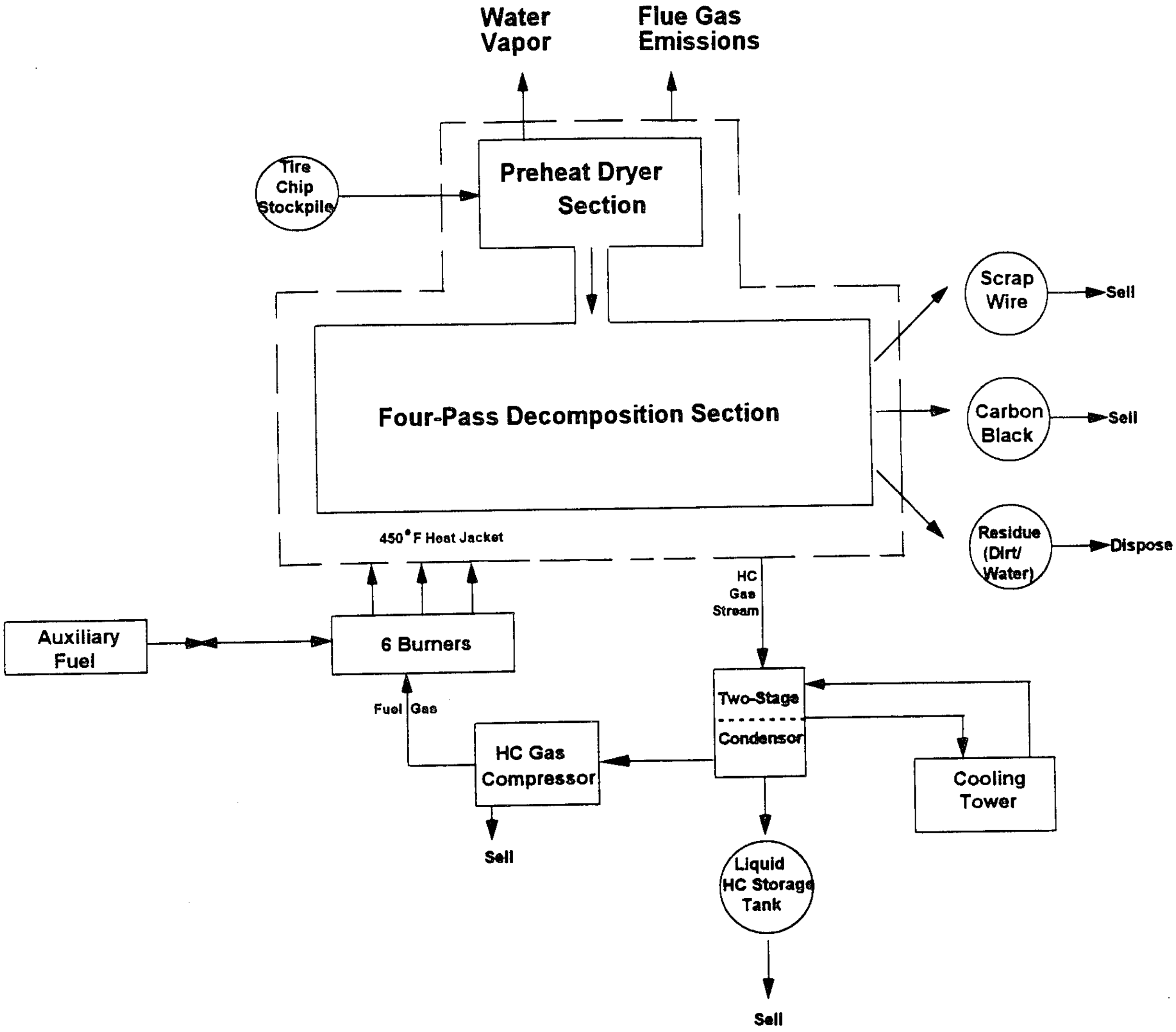

Figure A-2. Tire Recycling Process Schematic

As seen in Tables A-I and A-II, the catalytic conversion process provides valuable fuel and chemical resources from what was unsightly and unusable waste. The low-temperature catalytic process is the key to making valuable hydrocarbons rather than burning to form atmospheric pollutants. The recovered carbon black is of a high enough quality that it is readily usable for inks, toners, and plastic fillers. Other, higher temperature, processes convert the carbon black to a char that cannot be used in many of these applications. Finally, the steel tire reinforcements are recovered and sold to steel mills for reprocessing.

Table A-I

Recycled Tire Oil Distillation Results

Component	Percent
Gasoline; EP @ 375°F	23
Naptha; EP @ 425°F	8
Kerosene; EP @ 550°F	21
Fuel Oil; bottoms	48

Table A-II

Gas Analysis From Recycled Tires

Component	Mole Percent
Oxygen	not detected
Nitrogen	60.13
Carbon Dioxide	13.38
Methane	13.54
Ethane	3.44
Propane	4.62
i-Butane	0.94
n-Butane	not detected
i-Pentane	0.06
n-Pentane	2.38
Hexanes plus	1.51
Total	100.00

The entire tire recycling process is a closed system. The only emissions are the exhaust gases from firing the retort burners. Because methane and the other components of the gas fraction are clean burning, release of pollutants to the atmosphere is minimal. The only nonresaleable materials from the process are the small quantities of ash and dirt produced that are landfilled.

The economics of the tire recycling process may be evaluated based on 100 tons of used tire chips per day operating 330 days per year. A single plant generates $3-7 million in revenues per year at current prices for oil ($20 per barrel), carbon black $0.05-0.30), steel ($30-60 per ton) and an acceptance charge for processing at $0.10 per tire. In one year, 3 million tires are removed from the nation's landfills, highways, and tire dumps. There are no additional raw material or fuel costs required, and only four people per shift are needed to operate the plant shown in Figure A-1.

Advantages similar to those of the tire process may be obtained by applying this technology to the recovery of raw materials from plastics packaging and consumer and industrial products.