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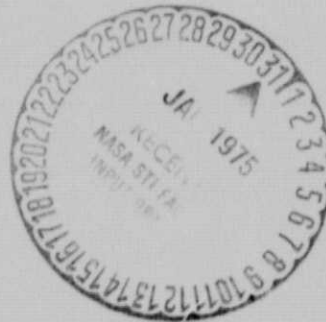
AN EVALUATION: THE POTENTIAL OF DISCARDED
TIRES AS A SOURCE OF FUEL

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TIRES AS A SOURCE OF FUEL

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AN EVALUATION: THE POTENTIAL OF DISCARDED

TIRES AS A SOURCE OF FUEL*

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SUMMARY

The destructive distillation of rubber tire samples was studied by thermogravimetry, differential scanning calorimetry, combustion calorimetry, and mass spectroscopy. The decomposition reaction was found to be exothermic and produced a mass loss of 65 percent. The products from the distillation process were a solid residue with a heating value of approximately -3×10^7 J/kg, a liquid with a heating value of approximately -4×10^7 J/kg, and a combustible gas of undetermined heating value. The gas evolution curves that were obtained indicate that a variety of organic materials are evolved simultaneously during the decomposition of the rubber polymer.

INTRODUCTION

The search for an alternative to petroleum energy has encompassed the investigation of a wide range of materials to determine their suitability as fuel. Materials such as oil shale and coal deposits are obvious energy resources and are being studied and exploited at an accelerated rate; other materials with smaller energy yields are also being considered, although to a lesser degree. One such material is the distillate obtained from the destructive distillation of scrap tires, a process that has been studied by the Firestone Tire and Rubber Company in cooperation with the U.S. Bureau of Mines (ref. 1). The Pittsburgh Energy Research Center of the U.S. Bureau of Mines (ref. 2) has also studied the distillation of tires, and the National Aeronautics and Space Administration is interested in this process.

Substantial quantities of chemical energy remain locked in the rubber structure of discarded automobile tires. This energy can be recovered through distillation in the absence of oxygen. In addition to the ecological advantages inherent in the destruction of discarded tires, the process yields

* Collins, L. W.; Downs, W. R.; Gibson, E. K.; and Moore, G. W.: An Evaluation of Discarded Tires as a Potential Source of Fuel. *Thermochim. Acta*, vol. 10, no. 2, Oct. 1974, pp. 153-159.

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a combustible oil and gas mixture that contains a variety of organic compounds (ref. 1). The composition of the distillate depends on the type of rubber and the compounding procedures used in manufacturing the tires. Four types of rubber (natural, styrene-butadiene rubber (SBR), polyisoprene, and polybutadiene) account for the major portion of rubber used in tire manufacture (ref. 3). These types of rubber are compounded with other materials in varying proportions according to the requirements of the finished product.

The authors thank the National Research Council for extending to L. W. Collins a postdoctoral associateship to work in the laboratories of the Structures and Mechanics Division at the NASA Lyndon B. Johnson Space Center, Houston, Texas.

EXPERIMENT DESCRIPTION

Samples

The tire samples used in this experiment were obtained by cutting 6- by 6-centimeter squares from the tread and sidewall portions (black-wall tires only) of eight passenger tires and two truck tires that were selected in a random manner. These squares were then cut to pass through a 2-millimeter sieve and were thoroughly mixed. Samples were taken from the mixture, and multiple runs were made with each analytical technique to ensure reproducibility. A representative compounding formula for the rubber used in passenger tire treads is given in table I (ref. 3).

Equipment

Thermogravimetric and differential scanning calorimetry (DSC) curves were obtained with a Du Pont model 900 thermal analyzer equipped with the model 950 thermogravimetry accessory. Heating rates (expressed as temperature-rise rates) of 5, 10, 20, and 100 K per minute were used for runs made in nitrogen as well as in vacuo. These rates apply to the specimen heater of the calorimeter.

The computer-controlled thermogravimetry/mass spectroscopy system used in this study is described in reference 4. The combustion calorimeter was manufactured by Parr Instruments and used according to standard procedures (ref. 5).

RESULTS AND DISCUSSION

Thermogravimetry

Thermogravimetric curves for tire samples in a nitrogen atmosphere and in vacuo are shown in figure 1. Decomposition began at approximately 498 K in

nitrogen and appears to have occurred in a single step, whereas decomposition in vacuo appears to be a two-step process beginning at approximately 423 K. The initial mass loss in vacuo appears to be about 10 percent of the original mass and partly overlaps the second step, which begins at approximately 548 K. The decomposition process was complete for both sets of conditions by approximately 723 K after a total mass loss of 65 percent. The residue appeared to be primarily carbon and was stable when the analysis was terminated at 1273 K. The residue also retained the original shape of the sample, which indicates that the sample did not melt during decomposition.

Previous investigators (ref. 1) have reported that the highest yields of liquid products were obtained from tires at a carbonization temperature of 773 K, whereas the highest yields of solid and gaseous products were obtained at 1173 K. This suggests that the heating rate might influence the mass loss observed by thermogravimetry. However, this effect was not observed for heating rates in the range from 5 to 100 K per minute, since all curves showed the same mass loss of 65 percent.

The effluents from the thermobalance were trapped in a preweighed liquid nitrogen cold trap. As each analysis was terminated, the trap was brought to room temperature, dried, and weighed. An average of approximately 85 to 90 percent of the evolved gases remained in the trap at room temperature. The effluent separated into two layers with the bottom layer, constituting approximately 5 to 10 percent by volume, being a colorless liquid that was probably water. The top layer was a dark brownish-yellow liquid that had a pungent odor.

Differential Scanning Calorimetry

The DSC curves for the tire samples in nitrogen and in vacuo are shown in figure 2. These curves show that the decomposition process is exothermic, with the maximum temperature differential (ΔT) for the specimen and its reference (empty pan) occurring at approximately 648 K.

An average decomposition energy of -3×10^5 J/kg was obtained from quantitative measurements made on 20 different curves. (Energy or heat absorbed is positive (+); energy or heat liberated is negative (-).) However, this value can be considered accurate only to within an order of magnitude, because of the difficulty in determining the baseline and the problems associated with reproducibility of sample packing. This first DSC peak coincides with the mass loss region of the thermogravimetric curves.

A second peak was observed in the DSC curve beginning at 713 K with the maximum temperature differential occurring at approximately 748 K. This peak was endothermic and may have partly overlapped the decomposition peak. Since the thermogravimetric curves show that no mass is lost during the temperature interval of this second peak, structural changes are assumed to occur within the carbon residue. This absorption of energy is probably due to the breaking of carbon-carbon bonds in the remaining carbon skeleton. An alternative

explanation is that the peak is due to phase transitions of one or more of the compounding materials. However, the latter explanation seems unlikely because no peak was recorded as the residue was cooled or reheated, which indicates that the original peak resulted from an irreversible process.

The heat of combustion of the tire residue remaining at 1273 K was determined by obtaining the DSC curve of this substance in an oxygen atmosphere. The combustion process was strongly exothermic beginning with ignition (observed visually) at 783 K. Samples larger than 1 milligram produced a temperature jump from 783 K to more than 933 K within an interval of a few seconds, and the aluminum pans were completely melted. Quantitative measurements of the heat of combustion were hampered by the small sample size that had to be used to record a DSC curve, and the measurements included a small contribution from the partial oxidation of the aluminum pans. However, all measurements were of the order of magnitude of the heat of combustion of carbon to carbon dioxide, which is reported as -3.267×10^7 J/kg (ref. 6). The combustion process appeared to be clean with no apparent residue remaining in the pan.

Combustion Calorimetry

Samples of the liquid collected in the nitrogen cold trap from the distillation of the tire samples were ignited in a combustion calorimeter at a pressure of 25×10^5 N/m² of oxygen. The liquid samples were taken from the top layer of the distillates in the cold trap to minimize the water content. The average heat of combustion of the liquid was calculated to be -4×10^7 J/kg, which is slightly less than the heating value of fuel oil. For distillates from different samples, this value varied by approximately 5 percent.

Gas Evolution/Mass Spectroscopy

The gases that evolved from the thermal decomposition of the tire samples were leaked directly into a mass spectrometer to obtain the gas evolution curves shown in figure 3. These curves represent the intensity of specific mass peaks as a function of sample temperature; therefore, they may represent contributions from molecular fragments and product gases in proportions that cannot be determined. This condition arises because a mixture of gases rather than a pure product is introduced into the mass spectrometer ionization chamber. However, with some knowledge of the possible and probable constituents of the evolved gases, reasonable assignments can be made for some of the peaks to yield conclusions of a general nature.

The gas evolution curves in figure 3 show that the initial mass loss from the tire sample in vacuo is due primarily to water. The gas evolution curve for water, mass/charge (m/e) = 18 as a function of temperature, indicates that the major portion of the water vapor is evolved before the decomposition of the rubber constituents. This initial water loss probably

results from the thermal degassing of adsorbed atmospheric moisture and gases. A typical mass spectrum from this temperature range, such as the spectrum at 423 K shown in figure 4, shows a large water peak with additional peaks that correspond to atmospheric gases such as nitrogen, oxygen, and carbon dioxide. The gas evolution curves in figure 3 show that nitrogen is also evolved before the destruction of the rubber polymer.

The decomposition of the rubber compounds produces a mixture of organic compounds and fragments. However, plots of all significant mass numbers up to $m/e = 100$ as a function of temperature produce a series of gas evolution curves that are identical in shape and will superimpose on each other. These curves are therefore represented by the single gas evolution curve in figure 3. This curve indicates that the rubber decomposes in a manner such that a variety of products are evolved simultaneously rather than different products at different temperatures. The complexity of the distillate mixture is suggested by a typical mass spectrum from this temperature interval, such as the spectrum at 698 K in figure 5. Because of calibration considerations, only that portion of the spectrum from $m/e = 1$ to $m/e = 100$ was recorded in this study. However, previous studies (ref. 1) have shown that well over 100 constituents, some with molecular weights in excess of 300 g/mole, are contained in the effluent from the distillation of tires.

CONCLUSIONS

The calorimetric data obtained in this study indicate that a significant quantity of fuel with a heating value approaching that of fuel oil is recoverable through the destructive distillation of rubber tires. Distillation processes using dynamic heating conditions of 373 K or less per minute yield products in three phases. These phases consist of a solid residue with a heating value of approximately -3×10^7 J/kg, an organic liquid phase with a fuel value of approximately -4×10^7 J/kg, and a gas that was observed to burn but for which no quantitative measurements of heating values were made. Water was also observed as a liquid phase. Decomposition of the tire rubber seems to occur through a mechanism that generates a large variety of organic compounds simultaneously.

A realistic estimate of the quantity of energy recoverable from scrap tires through a large-scale operation would have to include such energy expenditures as transportation, sample grinding and preparation, separation of impurities such as the metal in the tire bead, pollution abatement, and any additional refining required before the fuel is burned. However, since a net energy gain appears feasible and since the process is compatible with existing

technology and is ecologically beneficial, the destructive distillation of discarded tires is probably a logical means of energy conservation.

Lyndon B. Johnson Space Center
National Aeronautics and Space Administration
Houston, Texas, November 15, 1974
982-42-01-00-72

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TABLE I.- TYPICAL COMPOUNDING FORMULAS FOR PASSENGER TIRE TREADS

Component	Natural rubber, percent	SBR cis-polybutadiene, percent
Smoked sheet	57.6	--
SBR 1712	--	46.8
Cis-polybutadiene	--	11.3
Reogen	1.2	--
K-Stay G	--	2.3
Stearic acid	1.4	.9
Zinc oxide	2	1.4
Agerite resin D	.9	.7
Agerite HF	.3	.2
Antozite 67S	2.3	1.8
Microcrystalline wax	.6	.5
Philrich 5	2.9	3.2
HAF	28.8	--
ISAF	--	29.5
Sulfur	1.4	.8
Amox no. 1	.3	--
Amox	--	.7
Redax	.3	--

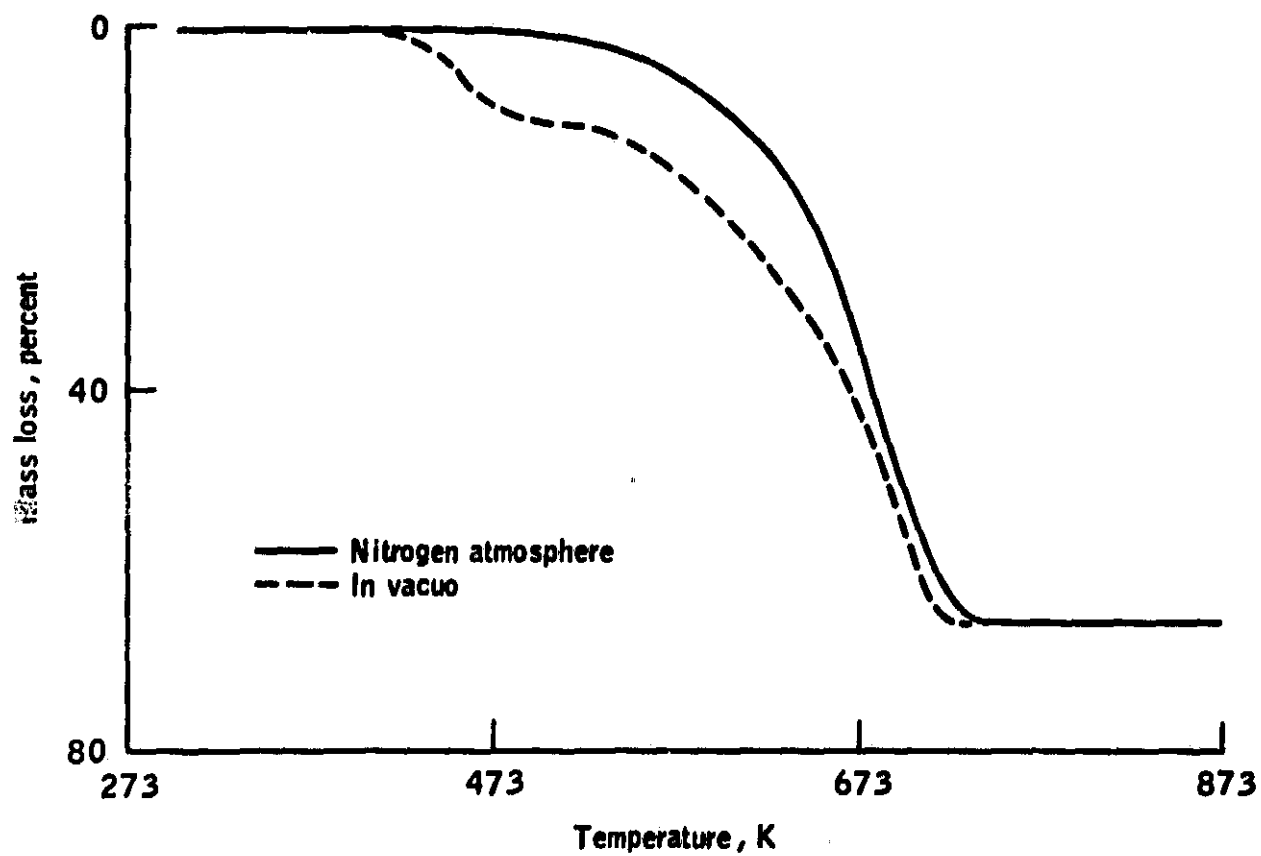


Figure 1.- Thermogravimetric curves for tire samples at a temperature-rise rate of 10 K/min.

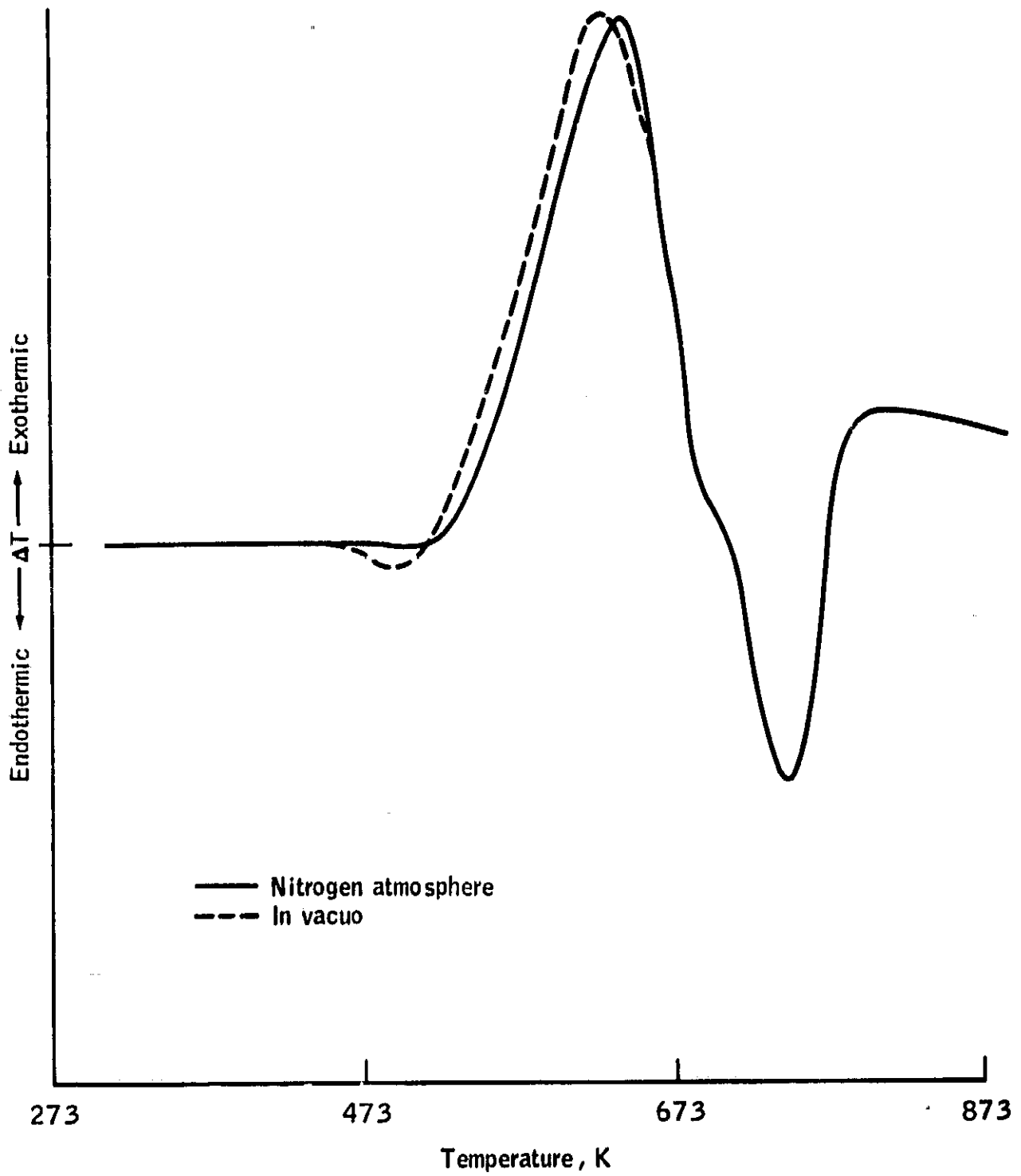


Figure 2.- Differential scanning calorimetry curves for tire samples at a temperature-rise rate of 10 K/min.

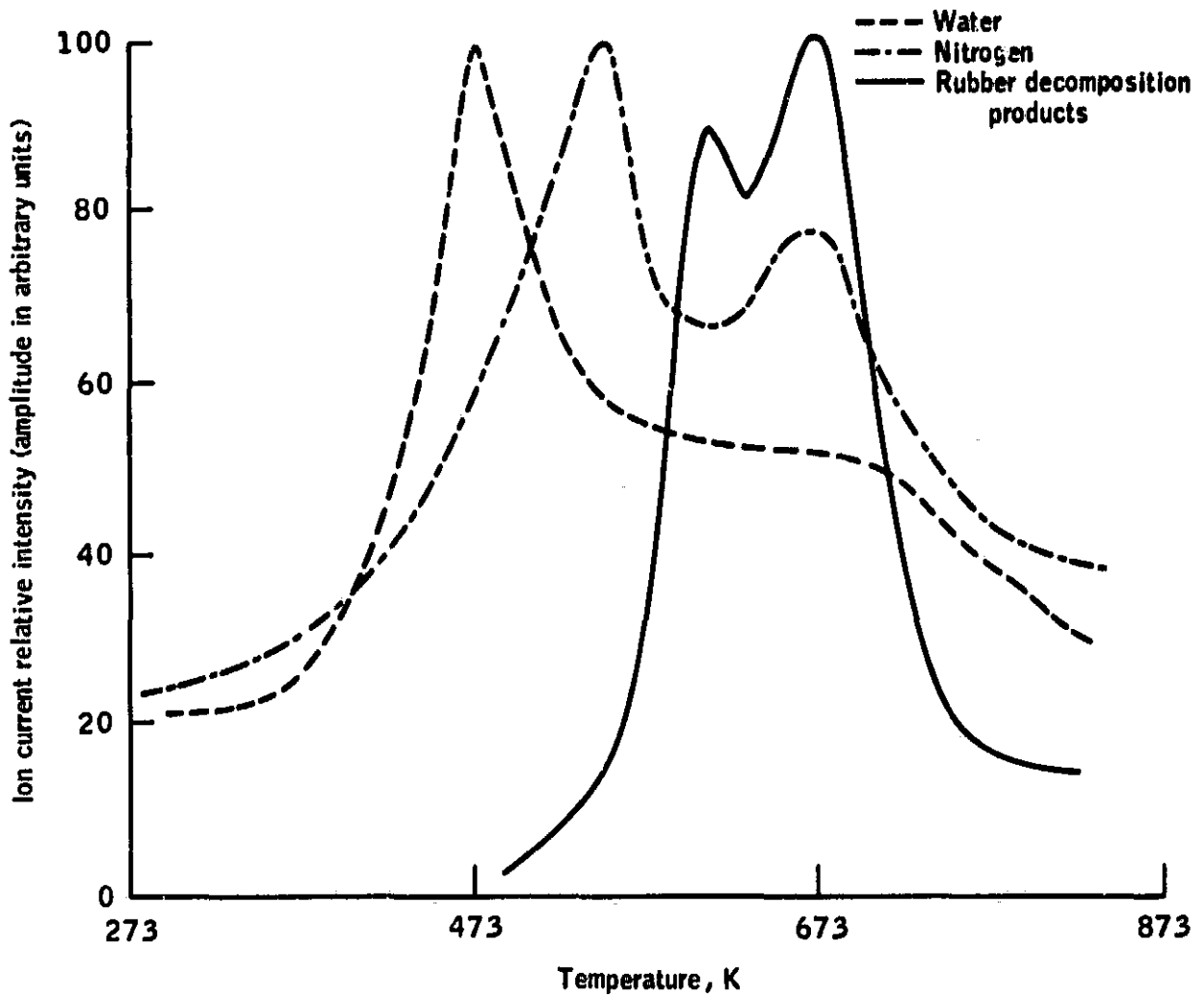


Figure 3.- Mass spectrometric measurement of gas evolution curves for water, nitrogen, and rubber decomposition products resulting from the thermal decomposition of tire samples at a temperature-rise rate of 6 K/min in vacuo. Data reduction was performed according to the procedure described by Gibson (ref. 4).

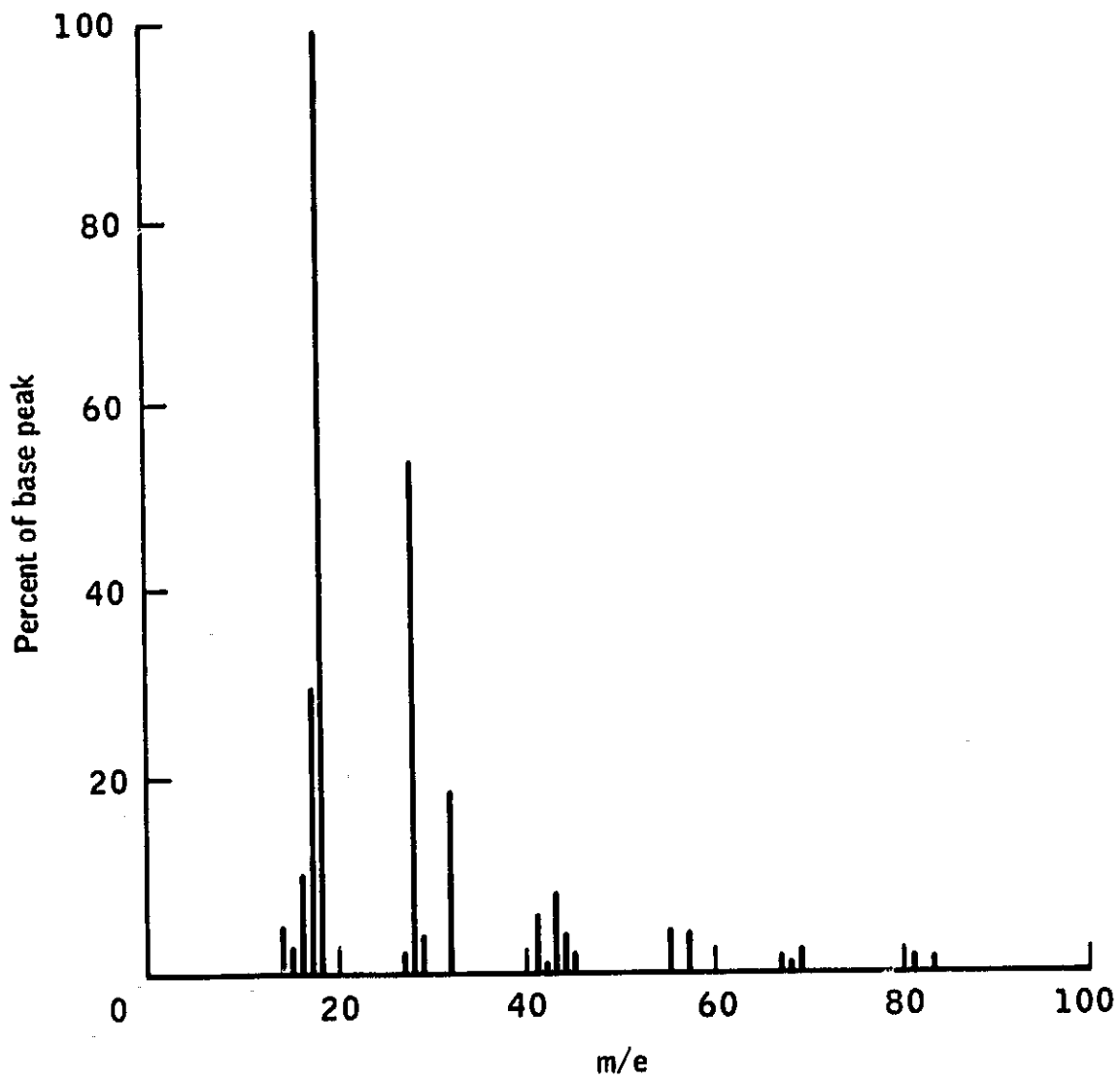


Figure 4.- Mass spectrum of gases evolved from the thermal decomposition of rubber tires at 423 K.

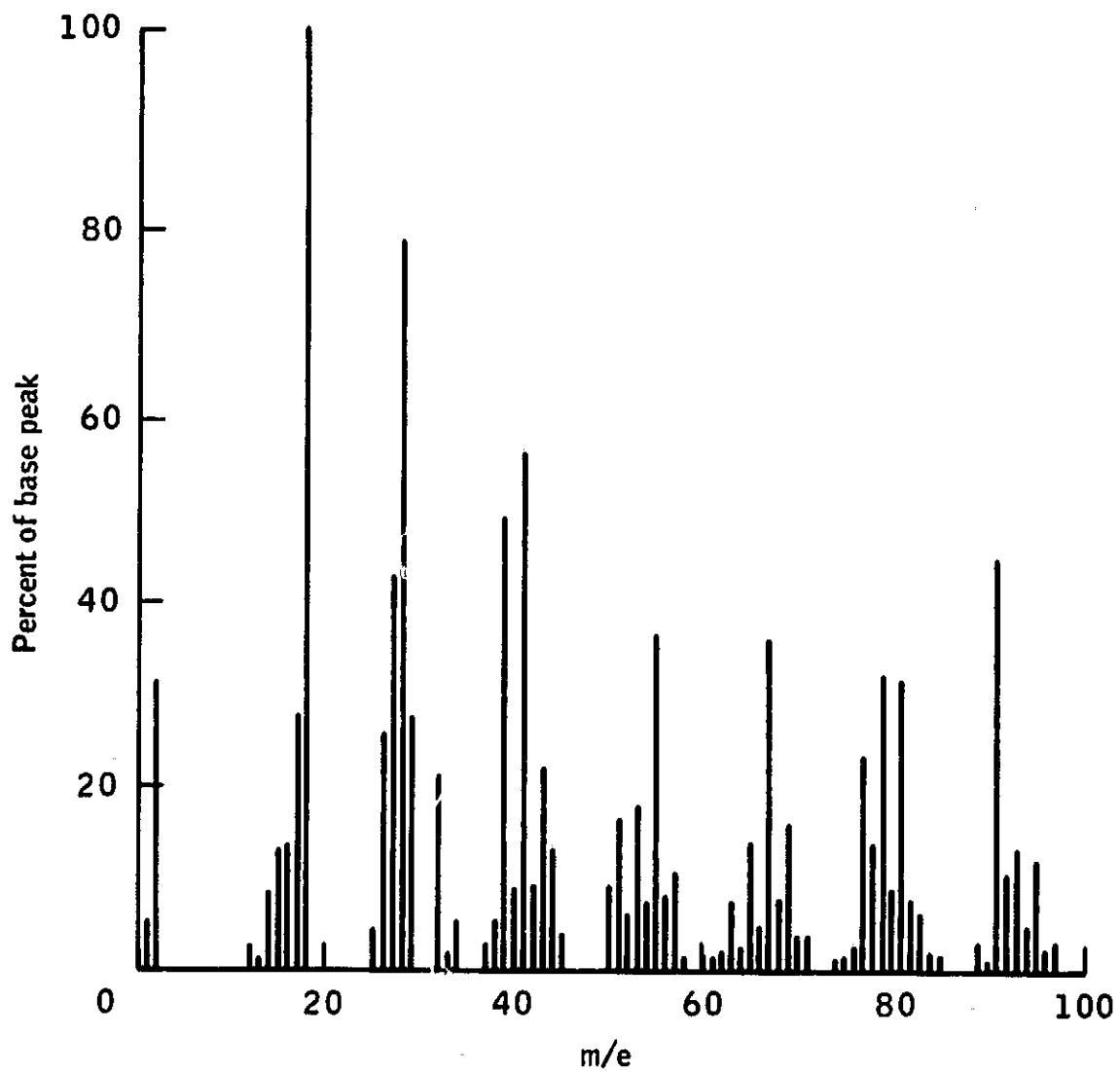


Figure 5.- Mass spectrum of gases evolved from the thermal decomposition of rubber tires at 698 K.