QUARTERLY PROGRESS REPORT NO. 3
RESEARCH FOR HIGH TEMPERATURE ELASTOMERIC INSULATION MATERIALS

15 November 1962 to 15 February 1962

Contract No. AF 33(657)-8774
Project No. 62-6899-7340
Task No. 734005
15 March 1963

MONSANTO RESEARCH CORPORATION
A SUBSIDIARY OF MONSANTO CHEMICAL COMPANY

Monsanto

BOSTON
LABORATORIES
EVERETT 49, MASSACHUSETTS

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Authors

Lucius Gilman, Project Leader
John E. Wyman
Joseph J. Byrne
Anthony F. Wilde

Contributors

Robert S. Giles
Mildred J. Landon
William R. Smith
William A. Wicks

MONSANTO RESEARCH CORPORATION
BOSTON LABORATORIES
Everett 49, Massachusetts

TABLE OF CONTENTS

I. INTRODUCTION

The objectives of this research are to determine the mechanisms by which an ablating elastomeric insulating material provides thermal protection for a substrate, to determine how much protection each mechanism actually contributes, to determine how much more protection each mechanism could contribute, and finally to show how the various constituents could be selected to maximize the thermal protection.

The study of temperatures and products of thermal decomposition of cured and uncured, saturated and unsaturated rubbers showed that the rubbers decomposed largely to liquid products and a small amount of gaseous hydrocarbons. There was little tendency to form a coherent, carbonaceous char. About 2 phr sulfur cure provided the maximum quantity of carbonaceous residue; increased sulfur had no beneficial effect.

Fillers such as Cabot Sterling R carbon black and Monsanto's Santocel® silica had little effect on the quantity of char produced by thermal decomposition of the rubbers. Additionally, the quantity of carbonaceous char was decreased in nearly all cases when a heating rate for decomposition of 2000°F/minute was employed compared with the results using a heating rate of 30°F/minute.

We have now shown that the quantity of char produced by the rubbers can be significantly increased by using a nickel metal dehydrogenation catalyst as a filler. The increased quantity of char and of hydrogen gas is particularly striking for the saturated butyl and the saturated ethylene-propylene rubbers when they are decomposed using a heating rate of 2000°F/minute.

A considerable portion of the research reported here was conducted using uncured, filled rubbers decomposed at a heating rate of 30°F/minute. These were largely screening tests designed to test rapidly the potential utility of a wide variety of catalytic fillers and other materials. In instances where high temperature vulcanizing agents were employed, comparative information on thermal decompositions could be obtained only with uncured rubber. Screening tests have now been largely completed, and future work will be conducted using cured rubbers decomposed at high heating rates (2000°F/minute).

The precious metals platinum and palladium were tested largely because of their known catalytic activity. Because of their high cost, we do not intend that these catalysts be considered as fillers in actual elastomeric insulation materials. Conveniently, it turned out that the more inexpensive nickel catalysts were, in fact, more active.

II. SUMMARY

The research effort in the first half of the program was concerned largely with a study of the temperatures and products of thermal decomposition of rubbers filled with refractory materials commonly employed in elastomeric insulating materials. These results showed that only small amounts of char and hydrogen gas formed during thermal decomposition. The research of the past quarter has been devoted to a study of methods by which the quantities of char and of hydrogen gas formed by the rubbers can be increased. Calculations have also been completed that show the significant mechanisms by which a rubber absorbs heat during ablation. The subjects to be discussed in this report are listed below:

1. The catalytic activity of both supported metal and metal oxide dehydrogenation catalysts on the formation of char and hydrogen gas by rubbers when they are decomposed at low and high heating rates;
2. The relative charring ability of saturated and unsaturated rubbers filled with dehydrogenation catalysts;
3. The effect of nickel catalyst content on char and hydrogen gas formation by saturated rubbers;
4. The effect of the catalyst support on the catalytic activity of the metal and on the strength of the char;
5. The effect of carbon-to-carbon crosslinkages on the decomposition temperature of the rubber;
6. Calculations that show the significant mechanisms by which a rubber absorbs heat during ablation, the maximum quantity of heat that the rubbers could absorb, the approximate efficiency of rubbers currently used in elastomers insulating materials, and the approximate efficiency of rubbers filled with a supported metal catalyst.

A study of thermal decomposition of a styrene-butadiene and saturated ethylene-propylene rubbers filled with 50 phr catalytic fillers using a heating rate of 30°F/minute showed that the supported metals nickel, platinum, and palladium were most effective in producing increased quantities of carbonaceous residue. Rhodium, vanadium, iron, and cobalt metals were much less effective, and metal oxide dehydrogenation catalysts were practically ineffective. An increase in the quantity of char was always accompanied by an increase in both the molar fraction of hydrogen in the gases not condensible at room temperature and an increase in the total quantity of hydrogen.

In experiments using nickel catalyst as filler and a heating rate of 30°F/minute, unsaturated rubbers (from dienes) generally produced a greater quantity of carbonaceous residue than the saturated rubbers. The cured acrylonitrile-butadiene rubber produced 69 wt-% residue, based on rubber. These compositions produced less carbonaceous residue when they were decomposed using a heating rate of 2000°F/minute.

Contrary to all previous experience, the saturated rubbers filled with nickel catalyst yielded a greatly increased quantity of char at the high heating rate. The saturated butyl rubber produced 45 wt-% char, the ethylene-propylene rubber giving 25 wt-% char. These are the highest yields of residue yet obtained at the high heating rate.

COMPARISON OF CHAR FORMATION BY UNCURED RUBBERS FILLED WITH NICKEL CATALYST*

Rubber	Wt % Char** at Heating Rate 30°F/min.	Wt % Char** at Heating Rate 2000°F/min.
Saturated Butyl	7.0	45.0
Saturated Ethylene-Propylene	4.1	25.1
Acrylonitrile-Butadiene	37	20.5
Styrene-Butadiene	19	7.9

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* 50 phr nickel catalyst (A); see glossary of terms for identification

** Based on weight of polymer.

The amount of nickel catalyst in the saturated butyl and ethylene-propylene rubber can be reduced to about 20 phr and 10 phr, respectively, without significantly decreasing the quantities of char and hydrogen gas produced by thermal decomposition at the high heating rate.

The nature of the catalyst support had a significant effect on the strength of the resulting char as well as on the catalytic activity of the supported metal. A high yield of residue from the rubber did not necessarily give a high strength char. Preliminary experiments showed that the blending of fillers may produce a catalytically active filler that provides a strong char layer. Nickel deposited on silica gel or asbestos was much less active than nickel deposited on kieselguhr or silica-alumina cracking catalyst.

Studies of thermal decomposition of a saturated ethylene-propylene rubber using a heating rate of 30°F/minute have shown that although increased carbon-to-carbon crosslinkages do not increase the yield of carbonaceous residue they do increase the apparent decomposition temperature of the rubber.

Hydrazobenzene and azobenzene decompose at high temperatures to yield free radicals that crosslink an uncured ethylene-propylene rubber as shown by its apparent increased decomposition temperature. On the other hand, compounds that act as free radical traps increase the apparent decomposition temperature of an uncured ethylene-propylene rubber, probably by slowing down the rate of normal thermal decomposition of the polymer. Of course, either one of these different types of additives could be employed in the rubber, but they cannot be used in combination.

Transpirational cooling by hydrogen gas is the most important mechanism of heat absorption by an ablating elastomeric insulation material. Calculations, presented in a subsequent section, of the maximum quantity of heat absorbed by ablation of 100-g quantities of various rubbers show that saturated rubbers can provide more thermal protection than diene rubbers. The heat sink effect of the carbon is significant. The carbon absorbs about 60% as much heat as the hydrogen. The formation of acetylene gas to subsequent reaction of hydrogen with carbon in the char layer absorbs significant quantities of heat only at temperatures above 5000°F. The dissociation of hydrogen absorbs only a small amount of heat. The heat absorbed by thermal decomposition of the rubber is relatively unimportant, and, in fact, the styrene-butadiene and acrylonitrile-butadiene rubbers liberate heat when they are decomposed to the elements.

The efficiency of heat absorption by a butyl rubber is raised from 81% to 92% at an equilibrium temperature of 5000°F when it is filled with a nickel catalyst.

SUMMARY OF EXPERIMENTAL AND COMPUTED RESULTS OF UNCURED RUBBER DECOMPOSITION*

	Butyl	EPR	NBR	SBR
Wt-% Char**	45.0	25.1	20.5	7.9
% of Maximum Value	52.6	29.3	25.4	8.7
Wt-% Hydrogen**	8.3	4.9	2.2	2.3
% of Maximum Value	57.8	34.1	25.7	24.1
Calculated Heat Absorption of 100 g Rubber, to 7000°F, kcal	549	519	367	379
% of Maximum Value	86	77	92	83

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* Filled with 50 phr nickel catalyst (A)

** Weight per cent based on rubber

Butyl = Saturated butyl rubber; EPR = saturated ethylene-propylene rubber;
NBR = high nitrile content acrylonitrile-butadiene rubber;
SBR = styrene-butadiene rubber

III. DISCUSSION

A. THE EFFECT OF CATALYTIC FILLERS ON THE THERMAL DECOMPOSITION OF ELASTOMERS

Prior research on this program has shown that the major products of thermal decomposition of an ethylene-propylene rubber, butyl rubbers, and a styrene-butadiene rubber are hydrocarbons with a wide range of boiling points. The cured elastomers as well as the uncured materials have little tendency to form a carbonaceous residue. The quantity of the residue is substantially increased when the rubbers are filled with dehydrogenation catalysts before they are subjected to thermal decomposition. The best catalytic fillers appear to be nickel, platinum, and palladium metals deposited on the proper support.

1. Thermal Decomposition Using a Heating Rate 30°F/Minute

Preliminary screening tests using uncured styrene-butadiene and ethylene-propylene rubbers have shown that the quantity of carbonaceous residue produced by thermal decomposition is significantly increased when catalytic metals are used as fillers. These metals are usually supported on a ceramic carrier. The data shown in Table 1 were obtained using rubbers with 50 phr of such fillers.

Table 1

THE EFFECT OF SUPPORTED METAL CATALYSTS ON RESIDUE FORMATION FROM UNCURED STYRENE-BUTADIENE AND ETHYLENE-PROPYLENE RUBBERS

Supported Metal	Styrene-Butadiene	Ethylene-Propylene
Platinum	22	9
Palladium	22	4
Nickel (A)	19	4.1
Rhodium	8	1.1
Vanadium	6	-
Iron	5	-
Cobalt	1.5	-
None	0.6	0.4

The catalyst code is shown in the glossary of catalyst nomenclature on the next page.

The data in Table 1 show that platinum, palladium, and nickel are the most active metals. Even greater quantities of carbonaceous residues were formed when these catalysts were used in cured rubber. This is shown in Table 2. The styrene-butadiene rubber was cured as described in the experimental section and it was filled with 50 phr catalyst.

Table 2

THE EFFECT OF SUPPORTED METAL CATALYSTS ON RESIDUE FORMATION FROM A CURED STYRENE-BUTADIENE RUBBER

Supported Metal	Wt-% Residue, Based on Rubber
Nickel (A)	26
Palladium	26
Platinum	25
None	1.6

The results of other screening tests listed in Appendix 2 show that metal oxide dehydrogenation catalysts employing ferric oxide and nickel oxide, respectively, are relatively ineffective.

These data support the postulate that metal oxide dehydrogenation catalysts are active only after they have been reduced to the metal by hydrogen produced by the cracking reaction. Surprisingly, freshly prepared silica-alumina and silica-alumina-magnesia cracking catalysts produced very little char in spite of their known high coking activity (ref. 1).

Heated at 30°F/minute, the acrylonitrile-butadiene rubbers produced the greatest quantity of char of any of the rubbers studied to date when they were filled with 50 phr of nickel catalyst (A). As will be seen later, this was not true at greater heating rate. In general, diene rubbers such as acrylonitrile-butadiene and styrene-butadiene produced a significantly greater quantity of char than the saturated rubbers such as ethylene-propylene and butyl rubbers. The data shown in Table 3 were obtained using a heating rate of 30°F/minute. The rubber was filled with 50 phr catalyst and it was cured as described in the experimental section.

GLOSSARY OF CATALYST NOMENCLATURE

Designation	Composition
[1]Nickel (A)	67 wt-% metal on kieselguhr (Girdler G-49A)
Nickel (B)	5 wt-% metal on asbestos
Nickel (C)	10 wt-% metal on silica-alumina cracking catalyst
Nickel (D)	10 wt-% metal on alumina
Nickel (E)	5 wt-% metal on silica
Nickel (F)	10 wt-% metal on silica
Nickel (G)	5 wt-% metal on silica-alumina cracking catalyst
Nickel (H)	15 wt-% metal on asbestos
[1]Platinum	5 wt-% metal on charcoal
[1]Palladium	5 wt-% metal on charcoal
[1]Rhodium	5 wt-% metal on alumina
Vanadium	10 wt-% metal on silica-alumina cracking catalyst
Iron	20 wt-% metal on kieselguhr
[1]Cobalt	Girdler T-323
[1]Nickel Oxide	Girdler T-316
[1]Iron Oxide	Girdler G-48A
[1]Silica-Alumina	American Cyanamid Co. Aerocat 75/85
[1]Silica-Alumina-Magnesia	American Cyanamid Co. Aerocat 3C-12-75/85

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[1] These catalysts were obtained from commercial sources. The others listed above were prepared as described in the experimental section.

Table 3

THE EFFECT OF NICKEL CATALYST (A) ON CHAR FORMATION OF A HIGH NITRILE CONTENT ACRYLONITRILE-BUTADIENE RUBBER

Material	Wt-% Residue, Based on Rubber
Cured Rubber	
Filled*	69
Unfilled	24.4
Uncured Rubber	
Filled*	37
Unfilled	15.2

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*50 phr Nickel Catalyst A

The carbonaceous residue resulting from thermal decomposition of saturated and unsaturated butyl, ethylene-propylene, and natural rubbers filled with other catalysts is shown in Appendix 3.

The increase in carbonaceous residue formed by uncured rubbers with 50 phr catalytic fillers was accompanied by an increase in the molar fraction of hydrogen in the gases not condensable at room temperature as shown in Table 4.

Table 4

THE EFFECT OF CATALYTIC FILLERS ON HYDROGEN FORMATION

Rubber	Mole-% Hydrogen in Non-Condensable Gases: Unfilled	Silica Filled	Nickel (A) Catalyst Filled
Styrene-Butadiene	27	45	76
Acrylonitrile-Butadiene	9	40	90

2. Thermal Decomposition Using a Heating Rate 2000°F/Minute

Previous research during this program has shown that in general the cured and uncured rubbers studied to date, either unfilled or filled with inert fillers, produced less char when they were decomposed using a heating rate of 2000°F/minute than at a heating rate of 30°F/minute. This has been attributed to more vigorous chain scission occurring at these high heating rates and high ultimate temperatures necessary to achieve these high rates. Presumably, the initial decomposition products travel out of the hot zone before they can decompose to a carbonaceous residue.

However, contrary to all previous experience, saturated rubbers such as the ethylene-propylene and butyl rubbers filled with 50 phr catalytic fillers produced more carbonaceous residue when they were decomposed using a heating rate of 2000°F/minute than at a heating rate of 30°F/minute. The quantities of char and hydrogen gas formed by a representative saturated and unsaturated rubber at a heating rate of 2000°F/minute are shown in Table 5.

Table 5

QUANTITY OF CHAR AND HYDROGEN GAS PRODUCED AT A HEATING RATE OF 2000°F/MINUTE

Filler or Catalyst*	Saturated Ethylene-Propylene Rubber		Styrene-Butadiene Rubber	
	Wt-% Char**	Wt-% Hydrogen**	Wt-% Char**	Wt-% Hydrogen**
Nickel (A)	25.1	4.9	7.9	2.3
Platinum	7.2	2.2	13.4	2.3
Palladium	5.5	1.6	13.1	1.8
Rhodium	5.1	1.8	3.4	1.1
Silica	0.8	1.4	< 1	0.7
Carbon	<1	1.0	< 1	0.8
None	0.3	0.4	0.3	0.3

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* 50 phr

**Based on weight of polymer

The silica was Monsanto Chemical Company Santocel^{R} and the carbon was Cabot Sterling R.

The data in Table 5 show that the best catalysts produced the most hydrogen as well as the most char.

The effect of heating rate on the quantity of char produced by the catalyst-filled rubbers is shown in Table 6, which combines data from Tables 1 and 5.

Table 6

QUANTITY OF CHAR FORMED AT DIFFERENT HEATING RATES

	Weight % Char at Heating Rate Shown			
	Saturated Ethylene/ Propylene Rubber		Styrene-Butadiene Rubber	
Supported Metal	30°F/min.	2000°F/min.	30°F/min.	2000°F/min.
Nickel (A)	4.1	25.1	19	7.9
Platinum	9	7.2	22	13.4
Palladium	4	5.5	22	13.1
Rhodium	1.1	5.1	8	3.4

As would be expected, the proportions of hydrocarbon gases such as ethylene, propane, and propylene contained in the gases not condensable at room temperature are much lower for the elastomers filled with catalytic fillers than with the uncatalyzed materials. Analyses of products are included in Appendix 2.

Highly saturated rubbers filled with 50 phr of nickel catalyst (A) produced more carbonaceous residue than the rubbers with a greater degree of unsaturation. The data shown in Table 7 compare the quantity of char produced by uncured rubbers filled with 50 phr of nickel catalyst (A at heating rates of 30°F/minute and 2000°F/minute, respectively.

Table 7

COMPARISON OF CHAR FORMATION BY UNCURED RUBBERS FILLED WITH NICKEL CATALYST A

Rubber	Heating Rate of 2000°F/minute Wt-% Char*	Heating Rate of 30°F/minute Wt-% Char*
Saturated Butyl	45.0	7.0
Unsaturated Butyl	39.8	<1
Saturated Ethylene-Propylene	25.1	4.1
Acrylonitrile-Butadiene	20.5	37
Unsaturated Ethylene-Propylene	16.0	6.3
Styrene-Butadiene	7.9	19

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*Based on weight of polymer

The data in Table 7 show that the butyl rubbers produce the greatest quantity of char of any rubber studied to date when they are decomposed at the high heating rate. This is contrary to refinery experience where unsaturated materials are more susceptible to coking than are saturated paraffins.

The content of nickel catalyst (A) can be lowered to about 20 phr in the uncured saturated butyl rubber and to about 10 phr in the uncured saturated ethylene-propylene rubber without significantly decreasing the quantities of char and hydrogen gas produced at the higher heating rate.

The quantities of hydrogen gas and carbonaceous residue are shown in Tables 8 and 9 and they are graphed in Figures 1 and 2. Complete analyses are shown in the appendix.

Table 8

THE EFFECT OF CONTENT OF NICKEL CATALYST ON THERMAL DECOMPOSITION OF A SATURATED BUTYL RUBBER

Composition in Parts by Weight			% Products, Based on Rubber	
Rubber	Catalyst	Silica	Carbonaceous Residue	Hydrogen Gas
100	50	0	45.0	8.3
100	25	25	45.0	8.2
100	15	35	37.0	6.6
100	8	42	13.8	3.1
100	0	50	<1	0.9
100	0	0	0.5	0.6

Table 9

THE EFFECT OF CONTENT OF NICKEL CATALYST ON THERMAL DECOMPOSITION OF A SATURATED ETHYLENE-PROPYLENE RUBBER

Composition in Parts by Weight			% Products, Based on Rubber	
Rubber	Catalyst	Silica	Carbonaceous Residue	Hydrogen Gas
100	50	0	25.1	4.9
100	25	25	24.0	4.2
100	8	42	20.4	3.9
100	4	46	8.2	2.4
100	0	50	0.8	1.5
100	0	0	0.3	0.4

With both polymers, the production of hydrocarbon gases increased as content of catalyst and production of hydrogen decreased. Analyses appear in Appendix 2.

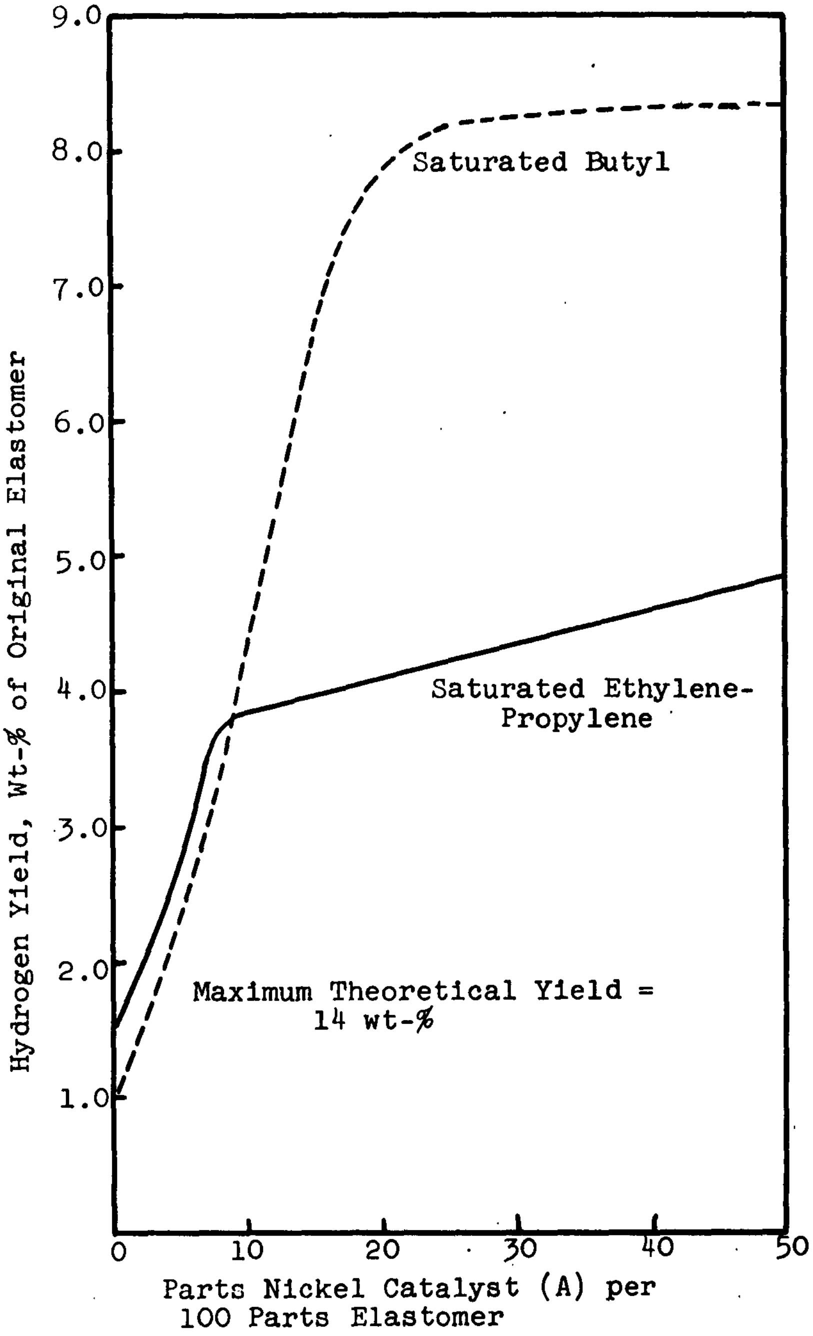

Figure 1. Hydrogen Yield as a Function of Nickel Catalyst Content.

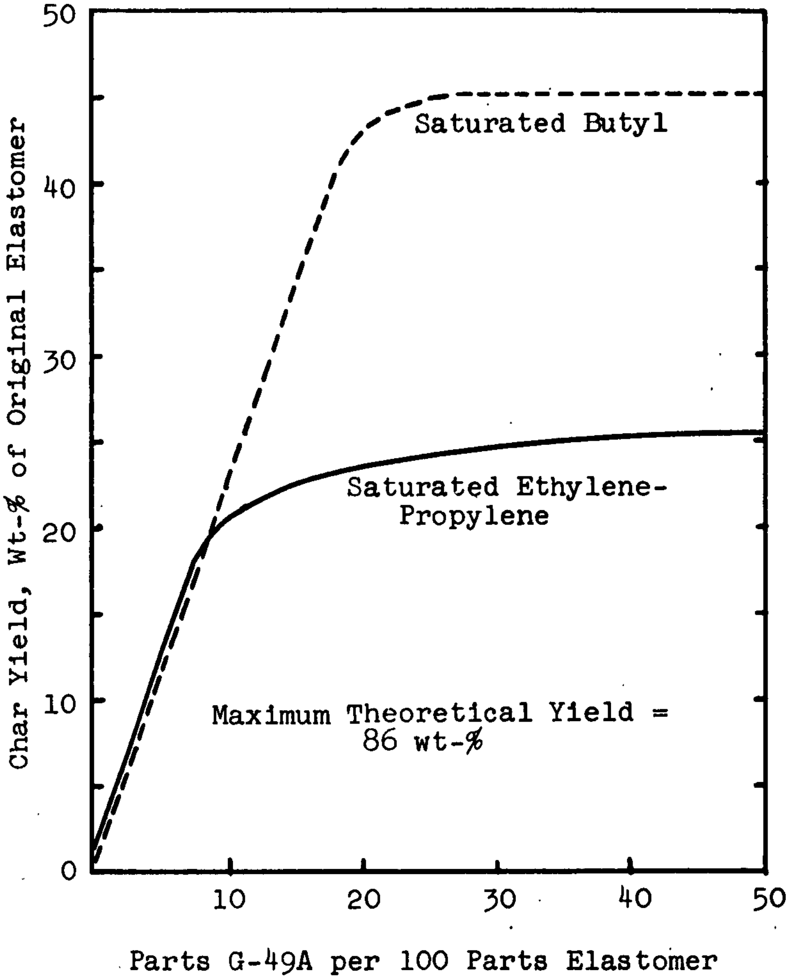

Figure 2. Char Yield as a Function of Nickel Catalyst Content

The effect of catalyst content on the decomposition products of an unsaturated butyl rubber showed that the yield of carbonaceous residue and hydrogen gas was not markedly decreased until the catalyst content was reduced to less than 15 phr. The carbonaceous residue and hydrogen gas yield are shown in Table 10. Complete decomposition product analyses are shown in the appendix.

Table 10

THE EFFECT OF NICKEL CATALYST CONTENT ON THERMAL DECOMPOSITION OF AN UNSATURATED BUTYL RUBBER

Composition, Parts by Weight			Wt % Products, Based on Rubber	
Rubber	Catalyst	Silica	Carbonaceous Residue	Hydrogen Gas
100	50	0	39.8	8.1
100	25	25	33.1	6.7
100	15	35	32.5	5.8
100	0	0	0.2	0.5

Above 15 phr of catalyst, the gases consisted almost exclusively of hydrogen and methane. Thus, results are similar to those for the saturated butyl rubber.

B. THE EFFECT OF CATALYST SUPPORT ON CATALYTIC ACTIVITY AND CHAR STRENGTH

Fortunately, the effectiveness of various nickel catalysts does not depend entirely on the per cent of nickel present. In fact, the most effective catalyst tested contained only 5% nickel compared with as much as 57% nickel in other, less effective catalysts. A comparison is shown in Table 11. The cause of the differences has not been established but may be due, for example, to either the differences in identity of supporting material or differences in area of exposed nickel.

Table 11

EFFECTIVENESS OF NICKEL CATALYSTS WITH UNCURED STYRENE-BUTADIENE POLYMER

Heating Rate = 30°F/min.

Catalyst[a]		
Support	Wt-% Ni[b]	% Carbonaceous Char[c]
SiO_2-Al_2O_3 cracking catalyst	5	22
Kieselguhr	67	19
Silica	10	14
Asbestos	15	3

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[a] 50 parts catalyst per 100 parts (by wt) polymer

[b] % Ni of combined Ni and support

[c] Based on wt of original polymer

The bulk density of the silica decreases during catalyst impregnation and calcining. This could be due to a collapse of structure, which could bury the active nickel. In fact, catalytic activity of nickel deposited on the silica is improved when the silica is wetted and calcined before the nickel is deposited. The catalytic activity of various nickel-on-silica catalysts in promoting formation of a carbonaceous residue from a styrene-butadiene rubber decomposed using a heating rate of 30°F/minute is shown in Table 12. Details of the catalyst preparation are described in the experimental section.

Table 12

THE EFFECT OF CATALYST PREPARATION ON CATALYTIC ACTIVITY

Catalyst	Wt % Residue, Based on Rubber
5 Wt-% nickel on silica	
No pretreatment	5
Prewetting and calcining at 1000°F	9
10 Wt-% nickel on silica	
No pretreatment	9
Prewetting and calcining at 1000°F	14

The silica-alumina cracking catalysts are more compact than the silica and they have less tendency to collapse when they are calcined at 1000°F. In addition, they are synthesized with a high degree of pore openings accessible by large organic molecules. In effect, the cracking catalyst has more usable surface area than the low bulk density silica gel.

Qualitative observation show that rubbers filled with silica or with nickel deposited on kieselguhr produce stronger chars than rubbers containing other fillers. The chars produced by rubbers filled with silica or with nickel deposited on kieselguhr retain their shape during thermal decomposition, and they have the best crushing strength of the chars examined to date. Charcoal and asbestos-containing chars retain their shapes but they are more easily crushed. Chars containing alumina and silica-alumina cracking catalyst both with and without deposited metal have very poor crushing strength and they seldom retain their original shape.

Initial experiments show that good char strength and a high yield of carbonaceous residue can be achieved simultaneously by blending fillers. The data in Table 13 were obtained by decomposing an uncured styrene-butadiene rubber containing 50 phr filler using a heating rate of 30°F/minute. The char strength listed in the table is a qualitative observation of the relative ease with which the chars were crushed using a spatula.

Table 13

THE EFFECT OF VARIOUS CATALYSTS ON RELATIVE CHAR STRENGTHS

Filler	Wt-% Residue, Based on Rubber	Char Strength
50 phr 5 wt % nickel on silica	9	Superior
50 phr 5 wt % nickel on silica-alumina cracking catalyst	22	Poor
25 phr silica + 25 phr 10 wt % nickel on silica-alumina cracking catalyst	21	Good

The competing requirements of a refractory filler used in an insulating material are (1) to produce a char layer with good strength and abrasion resistance and (2) to cause maximum formation of carbonaceous residue and hydrogen gas from the rubber during ablation. It has not been shown that any one filler will result in maximum performance in both ways. Different fillers will probably have to be combined during subsequent formulation and testing of rocket liner formulations to trade off one requirement to satisfactorily fulfill the other.

C. THE EFFECT OF CARBON TO CARBON CROSSLINKAGES ON THERMAL DECOMPOSITION OF AN ETHYLENE-PROPYLENE RUBBER

Increased carbon-to-carbon crosslinkages do not significantly increase the quantity of carbonaceous residue formed by thermal decomposition of an ethylene-propylene rubber using a heating rate of 30°F/minute. However, they do raise the temperature of volatilization of the hydrocarbon decomposition products. The temperatures at which 50% and 100% weight loss occurs with a saturated ethylene-propylene rubber cured with divinyl benzene, or when it is treated with high temperature radical forming materials is shown in Table 14. The data are also illustrated in Figure 3.

Table 14

THE EFFECT OF CARBON-TO-CARBON CROSSLINKAGES ON A SATURATED ETHYLENE-PROPYLENE RUBBER

Material, Additive	Temperature, °F, for 50% Weight Loss	Temperature, °F, for 100% Weight Loss	Wt-% Residue, Based on Rubber
Uncured, unfilled	827	870	< 1
Uncured, 5 phr hydrazobenzene	862	935	< 1
Uncured, 5 phr azobenzene	865	955	< 1
Cured with 2.6 phr Dicumylperoxide + 2.5 phr divinylbenzene	835	925	< 1
Cured with 5.0 phr Dicumylperoxide + 5.0 phr divinylbenzene	845	930	< 1
Cured with 8.0 phr Dicumylperoxide + 8.0 phr divinylbenzene	858	930	2.4
Cured with 8.0 phr Dicumylperoxide, 8.0 phr divinylbenzene, 50 phr nickel catalyst A	-	-	7.0
Uncured, 4 phr 2,6-ditertiary-butylbenzoquinone	865	930	< 1
Uncured, 4 phr 4,4'-thiobis-(6-tert-butyl-m-cresol)	875	940	< 1
Uncured, 4 phr 4,4'-butylidene-bis(6-tert-butyl-m-cresol)	870	945	< 1

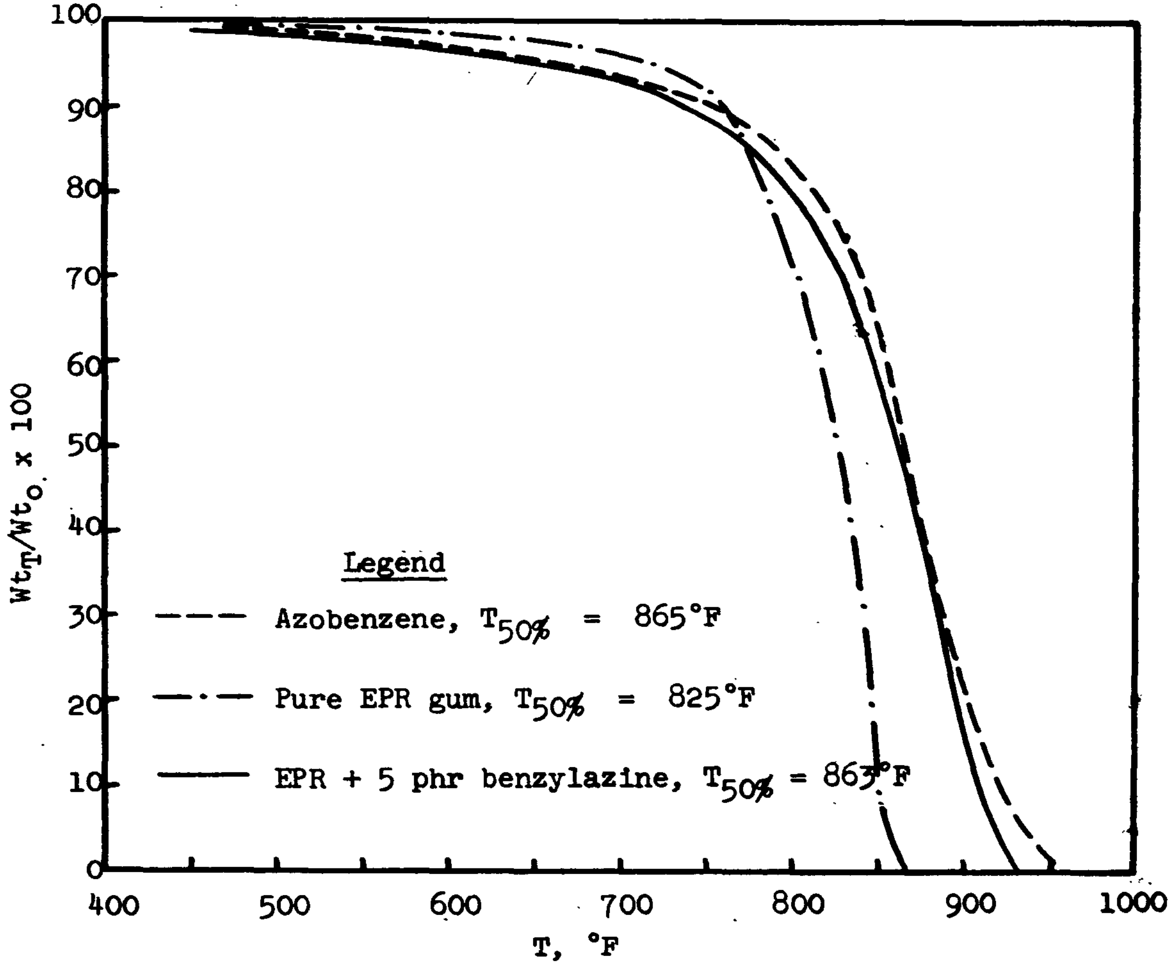

Figure 3. Thermal Gravimetric Analysis of Cured and Uncured EPR

The rubbers were cured using a 30-minute press cure at 320°F followed by a 2-hour postcure at 320°F and atmospheric pressure.

The data in Table 14 show that increased carbon-to-carbon crosslinkages raise the apparent decomposition temperature of the rubber as determined by thermogravimetric analysis. Hydrazobenzene and azobenzene are known to decompose to form free radicals at high temperatures, and apparently these radicals cause the rubber to form carbon-to-carbon crosslinkages below the normal decomposition temperature of the rubber. On the other hand, the 4,4'-thiobis(6-_tert_-butyl-_m_-cresol) and 4,4'-butylidenebis-(6-_tert_-butyl-_m_-cresol) are free radical traps, and they too appear to raise the apparent decomposition temperature. This seeming anomaly may be caused by the compounds' acting as free radical traps and decreasing the rate of chain scission of the polymer induced by radicals formed during normal thermal decomposition of the rubber. Either one of these two types of additives may be useful in final compositions but undoubtedly they cannot be employed simultaneously.

The data in Table 15 show that the saturated ethylene-propylene rubber filled with 50 phr nickel catalyst (A) and cured with 8.0 phr of divinylbenzene and dicumylperoxide yields a greater quantity of carbonaceous residue than a similar sample of filled but uncured rubber. The data were obtained using a heating rate of 30°F/minute.

Table 15

THE EFFECT OF CURING ON THE QUANTITY OF CHAR

Ethylene-Propylene Rubber*	Wt-% Residue, Based on Rubber
Cured	7.0
Uncured	4.1

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*Filled with 50 phr nickel catalyst A

These results show that the catalytic fillers are more effective in producing carbonaceous residue at higher temperatures than at lower temperatures since the data in Table 14 show that introducing carbon-to-carbon crosslinkages into the polymer raises the apparent decomposition temperature. This effect might be more pronounced when the rubber is decomposed using a heating rate of 2000°F/minute.

D. THERMAL DECOMPOSITION OF COMMERCIAL ELASTOMERIC INSULATION MATERIALS

Thermal decomposition of two uncured commercial elastomeric insulating materials (Stoner Rubber Company SMR 6-10 and SMR 7-12) using a heating rate of 2000°F/minute showed that the rubber in these compositions formed a relatively small amount of carbonaceous residue under these conditions. Since the formulations were not known, the quantity of carbon in the char was estimated by the weight loss that occurred when the residues were fired in air. It is known that SMR 6-10 contained a phenolic resin, so the data shown in Table 16 include that for pyrolysis of a highly cured phenolic resin. Complete analysis of the gases are shown in Appendix 2.

Table 16

THERMAL DECOMPOSITION OF COMMERCIAL ELASTOMERIC INSULATION MATERIALS

		Wt-% Products, Based on Volatile Material		
Material	Wt % Non-Volatile Filler	Gas	Liquid	Carbonaceous Residue
SMR 6-10	8.5	14.3	65.9	19.8
SMR 7-12	53.1	20.9	75.1	4.0
Phenolic Resin	-	7.2	40.6	>52.2

The phenolic resin was Plaskon V-204, cured at 400°F for 24 hours. The char yield of the phenolic resin shown in Table 16 is a minimum value since a small amount of char was lost by mechanical erosion of the powdery residue by the gases produced at the high heating rate.

E. CALCULATED HEAT ABSORPTION BY ABLATING ELASTOMERIC INSULATING MATERIALS

The purpose of these calculations is (1) to show the significant mechanisms by which the rubber in an ablating elastomeric insulating material absorbs heat, (2) to show the maximum quantity of heat the rubbers might absorb, (3) to show the approximate efficiency of each rubber at present, and (4) to show the approximate efficiency when the rubbers are used with catalytic fillers. To be meaningful, these calculations must consider all the possible mechanisms of heat absorption by the rubber and its decomposition products. In addition, the same mechanisms must be considered for each rubber in order to achieve self-consistent values. However, we have neglected in all cases the heat absorbed by possible endothermic reactions of the carbon in the char layer with a refractory such as silica and the heat absorbed by vaporization of carbon. These mechanisms may absorb a significant amount of heat but they are affected more by the nature of the refractory filler and the conditions in the combustion chamber than by the nature of the rubber employed in the rocket liner. The calculations presented here are sufficiently complete and accurate to show the significant mechanisms of heat absorption and to compare the prospective utility of various rubbers that could be used subsequently to formulate improved insulating materials. Complete calculations and the assumptions and estimations used are contained in Appendix 1.

Maximum combustion chamber temperatures of 5000, 6000, and 7000°F were chosen even though most current solid propellants have combustion temperatures around 5000°F. Projected propellant compositions may have combustion temperatures as high as 7000°F.

The maximum quantity of heat that could be absorbed by complete thermal decomposition of 100 grams of each of four representative rubbers is shown in Table 17. The values are those if the rubbers decompose completely to carbon and hydrogen, the products achieve thermal equilibrium at the relevant temperatures, and equilibrium concentrations of acetylene and atomic hydrogen are formed by subsequent reaction of hydrogen with the carbon in the char layer and dissociation of the gaseous hydrogen.

Table 17

MAXIMUM HEAT ABSORBED BY DECOMPOSITION OF 100 GRAMS OF UNCURED RUBBERS

Rubber	Heat Absorbed, kcal		
	5000°F	6000°F	7000°F
Saturated Ethylene-Propylene	367	508	677
Saturated Butyl	331	473	641
Styrene-Butadiene	229	334	459
Acrylonitrile-Butadiene (high nitrile content)	196	291	401

These values show clearly the potential superiority of saturated rubber The temperature of 932°F for composition of the rubber was chosen since nearly all the rubbers examined to date are decomposed at this temperature.

The calculated quantity of heat absorbed by heating the rubbers to 932°F with subsequent decomposition at this temperature is shown in Table 18. A plus sign (+) indicates that heat is absorbed and a minus sign (-) indicates that heat is liberated.

Table 18

MAXIMUM HEAT ABSORBED BY 100 GRAMS OF RUBBERS UP TO 932°F

	Heat Absorbed, kcal			
Process	Ethylene-Propylene	Butyl	Styrene-Butadiene	Acrylonitrile-Butadiene
Heating Rubber at 77-932°F	+26	+19	+16	+16
Rubber Decomposition at 932°F	+70	+41	- 5	-20
Total	+96	+60	+11	- 4

The styrene-butadiene and acrylonitrile-butadiene rubbers have positive heats of formation and liberate heat when they are decomposed to carbon, hydrogen, and nitrogen.

The difference in heat absorption between the butyl and ethylene-propylene rubbers at all temperatures listed in Table 17 is due solely to the difference in specific heat and heat of decomposition of the rubber. Both materials have the same empirical formula, $(CH_2)_n$, and the products absorb identical quantities of heat between 932°F and 7000°F.

Gaseous hydrogen can absorb the greatest quantity of heat when the decomposition products are heated from 932°F to 5000°F. The carbon absorbs a lesser amount. Formation of acetylene and dissociation of hydrogen absorb only relatively minor quantities of heat.

When the products are heated to 6000 and 7000°F, the fraction of the total quantity of heat absorbed by the hydrogen is lowered and the fraction of the total quantity of heat which is absorbed by the formation of acetylene and dissociation of hydrogen increases, particularly at the higher temperature. In all cases, however, hydrogen absorbs the greatest quantity of heat. The results of the calculations for ethylene-propylene and butyl rubbers are shown in Table 19.

Table 19

HEAT ABSORPTION BY VARIOUS MECHANISMS FROM 932°F TO MAXIMUM TEMPERATURES

	Heat Absorbed, kcal(% of Total Heat Absorbed		
Process	932-5000°F	932-6000°F	932-7000°F
Heating Hydrogen	+130 (48)	+166 (40)	+203 (35)
Heating Carbon	+ 92 (34)	+117 (28)	+141 (24)
Acetylene Formation	+ 29 (11)	+ 89 (22)	+168 (29)
Hydrogen Dissociation	+ 20 (7)	+ 40 (10)	+ 69 (12)
Total	271 (100)	412 (100)	581 (100)

These results show clearly the advantage of using a binder with a high hydrogen content and cracking the polymer completely to carbon and hydrogen. Although the greatest quantity of heat is absorbed by the gaseous hydrogen, the formation of acetylene becomes increasingly important at the higher temperatures. In this mechanism also, the greater the quantity of hydrogen produced by thermal decomposition of the binder, the greater will be the quantity of acetylene produced at equilibrium.

The styrene-butadiene rubber has a lower carbon-hydrogen ratio than either the ethylene-propylene or butyl rubbers. Consequently, the products of decomposition of 100 g of the rubber absorb a lesser quantity of heat when they are heated to 5000, 6000 and 7000°F than the decomposition products from 100 g of the saturated rubbers. The major portion of the heat absorbed is due to the heating of carbon, but the formation of acetylene becomes increasingly important at the higher temperatures. The calculations are listed in Table 20.

Table 20

HEAT ABSORPTION BY VARIOUS MECHANISMS FROM 932°F TO MAXIMUM TEMPERATURES (STYRENE-BUTADIENE RUBBER)

	Heat Absorbed, kcal (% of Total Heat Absorption)		
Process	932-5000°F	932-6000°F	932-7000°F
Heating Carbon	+ 97 (44.5)	+ 123 (38)	+149 (33)
Heating Hydrogen	+ 88 (40.5)	+ 113 (35)	+138 (31)
Hydrogen Dissociation	+ 13 (6)	+ 27 (8)	+ 47 (10.5)
Acetylene Formation	+ 20 (9)	+ 60 (19)	+114 (25.5)
Total	218 (100)	323 (100)	+448 (100)

The lesser quantity of hydrogen accounts for the fact that the styrene-butadiene rubber has a maximum calculated potential heat absorption of only 67% as high as the ethylene-propylene rubber and about 72% as high as the butyl rubber when they are heated to 7000°F.

The acrylonitrile-butadiene rubber had the lowest calculated potential heat absorption of the rubbers considered in these calculations, largely because of its low hydrogen content. Similar to the styrene-butadiene rubber, the greatest quantity of heat was absorbed by the carbon, and at all temperatures it was greater than the heat absorbed by the hydrogen gas. The formation of acetylene accounted for nearly 25% of the total heat absorbed at 7000°F. The calculations are listed in Table 21.

Table 21

HEAT ABSORPTION BY VARIOUS MECHANISMS FROM 932°F TO MAXIMUM TEMPERATURE (ACRYLONITRILE-BUTADIENE RUBBER)

Process	Heat Absorbed, kcal (% of Total)		
	932-5000°F	932-6000°F	932-7000°F
Heating Carbon	+85 (425)	+108 (37)	+130 (32)
Heating Hydrogen	+77 (38.5)	+ 99 (33)	+121 (30)
Acetylene Formation	+17 (8.5)	+ 53 (18)	+100 (25)
Hydrogen Dissociation	+12 (6)	+ 24 (8)	+ 41 (10)
Heating Nitrogen	+ 9 (4.5)	+ 11 (4)	+ 13 (3)
	200 (100)	295 (100)	405 (100)

The calculated quantity of heat absorbed by actual thermal decomposition of 100 g of the cured but unfilled rubbers again shows that the saturated rubbers have a higher potential heat absorption than either the styrene-butadiene or acrylonitrile-butadiene rubbers. The results of the calculations are shown in Table 22. The number in parentheses beside each calculated value represents the percentage of the possible theoretical maximum value of heat absorption for each rubber shown in Table 17. The number in parentheses, then, represents the approximate efficiency of each rubber. The quantities of gas, liquid, and carbonaceous residue obtained by thermal decomposition of the rubbers using a heating rate of 2000°F/minute were employed in the calculation. It was assumed that the liquid products did not undergo further cracking in the char layer. The assumptions are completely discussed in Appendix 1.

Table 22

HEAT ABSORBED BY DECOMPOSITION OF 100 GRAMS OF CURED RUBBER

Rubber	5000°F (% Efficiency)	6000°F (% Efficiency)	7000°F (% Efficiency)
Saturated Ethylene-Propylene	307 (83)	376 (74)	446 (66)
Saturated Butyl	268 (81)	338 (72)	411 (64)
Acrylonitrile-Butadiene	242 (123)	300 (103)	358 (89)
Styrene-Butadiene	237 (103)	295 (88)	355 (88)

The high efficiencies shown by the acrylonitrile-butadiene and styrene-butadiene rubber are due to the fact that the polymers decompose largely into liquids with high positive heats of formation. The heat liberated when the polymers decompose to carbon, hydrogen, and nitrogen lowers the total maximum heat which can be absorbed, particularly at low temperature. These data show that the saturated rubbers can absorb the greatest quantity of heat even though their efficiencies are lower than the diene rubbers. Although the calculations were made using cured but unfilled rubbers, the heat absorbed by rubbers filled with inert fillers are expected to be very similar since the products of thermal decomposition of cured, unfilled and cured, inert filled rubbers are quite similar.

The calculated heat absorption by thermal decomposition of rubbers filled with 50 phr, 67 wt-% nickel-on-kieselguhr catalyst shows that increased quantities of carbonaceous residue and hydrogen gas improves the potential thermal protection. The data in Table 23 were calculated using the results of thermal decomposition at a heating rate of 2000°F of uncured rubbers filled with 50 phr nickel catalyst. The number in parentheses beside each calculated value represents the percentage of the possible theoretical maximum value of heat absorption for each rubber shown in Table 17.

Table 23

HEAT ABSORBED BY DECOMPOSITION OF 100 GRAMS OF RUBBER FILLED WITH 50 phr CATALYST

Rubber	5000°F (% Efficiency)	6000°F (% Efficiency)	7000°F (% Efficiency)
Saturated Ethylene-Propylene	326 (89)	418 (82)	519 (77)
Saturated Butyl	303 (92)	418 (88)	549 (86)
Acrylonitrile-Butadiene	229 (117)	297 (102)	367 (92)
Styrene-Butadiene	246 (107)	315 (94)	379 (83)

The ethylene-propylene, saturated butyl, and styrene-butadiene rubbers filled with nickel catalyst can absorb a greater quantity of heat at all three temperatures than the unfilled sample. The filled butadiene-acrylonitrile rubber can absorb more heat at 7000°F than the unfilled material. This is due to the greater quantity of hydrogen gas produced by the samples filled with nickel catalyst. The butyl rubber filled with nickel catalyst produces a much greater quantity of hydrogen than the filled ethylene-propylene rubber, and it can absorb a greater quantity of heat at 7000°F. The potential efficiency of the butyl rubber has been significantly improved.

In summary, these calculations show that transpirational heating of hydrogen gas is the most significant mechanism by which an ablating elastomeric insulating material can absorb heat. Additionally, the formation of acetylene by the reaction of the hydrogen with carbon in the char layer can absorb a considerable quantity of heat, particularly at 6000°F and higher. The heat absorbed by heating the carbon in the char layer is also significant, particularly for styrene-butadiene and acrylonitrile-butadiene rubbers, which have a lower hydrogen content than the butyl and ethylene-propylene rubbers. The possible heat absorption by thermal decomposition of the rubbers is relatively insignificant, and for the acrylonitrile-butadiene and styrene-butadiene rubbers, heat is liberated by complete thermal decomposition to carbon, hydrogen, and nitrogen. Dissociation of hydrogen gas absorbs a relatively small fraction of the total quantity of heat, even at 7000°F.

The calculations show clearly that ethylene-propylene and butyl rubbers can provide more thermal protection than diene rubbers and that their efficiency can be improved by the use of catalytically active fillers.

IV. EXPERIMENTAL DETAILS

The apparatus and procedure described in the first quarterly progress report were used in analyzing products of decomposition of the rubbers and for thermogravimetric analysis. The procedure and apparatus used for controlled pyrolyses at a heating rate of 2000°F/minute (radiofrequency induction heating of a graphite rod) were described in the second quarterly report.

The styrene-butadiene and acrylonitrile-butadiene rubbers were cured using the procedure described in the first quarterly report. The ethylene-propylene rubbers and butyl rubbers were cured using the following recipe:

100	parts rubber
50	parts filler
1	part calcium stearate
2.75	parts dicumyl peroxide
0.33	parts sulfur
1.0	part divinylbenzene

The materials were added to the gumstock on a cold, tight mill, and the mixture was press-cured for 30 minutes at 300°F and postcured 4 hours at 150°F.

The supported metal catalysts were all prepared by the same general procedure. The preparation of nickel metal deposited on silica-alumina cracking catalyst is illustrative.

A slurry of silica-alumina cracking catalyst in a water solution of nickel nitrate was evaporated to dryness on a hot plate with stirring. The quantity of nickel nitrate employed was sufficient to provide the desired weight per cent reduced metal on the support. The resulting green powder was dried for two hours in a circulating air oven controlled at 250°F. The material was then poured into a Pyrex tube held horizontally in a tube furnace and it was fired at 750°F in a current of air for 30 minutes. The tube was purged with dry nitrogen and the material was reduced by hydrogen at 750-840°F until no more water vapor condensed in the cool end of the tube. The catalyst was then allowed to cool to room temperature under a nitrogen atmosphere and was stored in a sealed bottle protected from air.

The precalcined and presintered metal deposited on silica catalysts were prepared by a similar procedure. The silica was wetted, dried, and fired in air before it was slurried with the nickel nitrate solution.

Metal nitrates were generally used for the preparation of the catalyst with the exception that ammonium metavanadate was used to prepare the supported vanadium catalyst.

V. CONCLUSIONS

The results of the research to date show that the quantity of carbonaceous residue formed by thermal decomposition of the rubber can be increased by using a supported nickel catalyst for at least part of the refractory normally used in an elastomeric insulating material. Nickel metal catalysts are more effective in saturated rubbers than in diene rubbers. The initial decomposition products from a butyl rubber appear to be more susceptible to catalytic cracking than those from an ethylene-propylene rubber since a saturated butyl rubber gave nearly twice as much char as the former material when they were decomposed using a heating rate of 2000°F/minute. Introducing saturation into the saturated rubber appears to decrease the quantity of char produced by the rubber.

In all cases, the increased yields of carbonaceous residue were accompanied by an increase in the total quantity of hydrogen gas.

Qualitative observations show that the refractory support used for the nickel metal catalyst greatly influences the activity of the catalyst and appears to affect the strength of the resulting char layer. A high yield of carbonaceous residue does not guarantee high char strength. Initial experiments indicate, however, that blending refractory fillers will result in an insulating material which will have a high strength char as well as a high yield of char.

Increasing the amount of carbon-to-carbon crosslinkages in an ethylene-propylene rubber does not increase the quantity of char but it does raise the apparent decomposition temperature. Materials that decompose to form free radicals at high temperatures apparently increase the amount of carbon-to-carbon crosslinkages and raise the apparent decomposition temperature also. Compounds that act as free radical traps apparently decrease the amount of chain scission and raise the observed decomposition temperature. This effect may prove to be significant in increasing the quantity of char in rubbers using catalytically active fillers.

Thermal decomposition of two uncured commercial elastomeric insulating materials has shown that the rubbers employed yield only a small amount of char. The insulating material that yields the greatest quantity of char was filled with an unknown amount of phenolic resin. Thermal decomposition of a cured phenolic resin using a heating rate of 2000°F/minute yielded about 53% carbonaceous residue. By comparison, the saturated butyl rubber filled with nickel catalyst yielded 45% carbonaceous residue, based on rubber.

Calculations have shown that transpirational heating of hydrogen gas is the most important mechanism by which a thermally decomposing rubber can absorb heat in an ablating elastomeric insulating material. The heat sink effect of the carbon is the next most important mechanism at relatively low (5000°F) temperatures. The formation of equilibrium amounts of acetylene is an increasingly significant mechanism of heat absorption at 6000 and 7000°F. The dissociation of hydrogen gas is a relatively unimportant mechanism at high temperatures.

The calculations show that saturated rubbers can absorb considerably more heat than diene rubbers. Additionally, the efficiency of a saturated butyl rubber, for example, can be raised from 81% to 92% at an equilibrium temperature of 5000°F by using a nickel catalyst filler.

VI. FUTURE WORK

The screening tests employing uncured rubbers decomposed using a heating rate of 30°F/minute have been largely completed. Thermal decomposition of prospective materials in the future will be studied using cured rubbers and a heating rate of 2000°F/minute.

During the coming quarter we will prepare, characterize, and test a very limited number of improved elastomeric insulating materials to confirm the results of our laboratory tests. We will concentrate largely on materials using ethylene-propylene and butyl rubbers since the calculations have shown them to be more advantageous than diene rubbers.

Specifically, we will examine qualitatively the strength of chars resulting from thermal decomposition of butyl rubbers filled with a minimum of 20 phr Girdler G-49A 67 wt-% nickel-on-kieselguhr catalyst and increasing amounts of silica or asbestos fiber to find the filler content providing optimum char strength consistent with acceptable mechanical properties and maximum thermal protection from the rubber. We will use an ethylene-propylene rubber in a similar manner. We will then examine the effect of a dicumyl peroxide/divinyl benzene cure on the mechanical properties and on the quantity of char produced by thermal decomposition. We will measure the tensile strength and tensile elongation at low temperature as well as at room temperature and the highest anticipated service temperature for the most promising compositions. We will also determine the specific heat, thermal conductivity, and specific gravity of these compositions.

We will compare the performance of our materials with currently used commercial elastomeric insulation in an electric arc plasma torch.

APPENDIX 1

CALCULATED HEAT ABSORPTION BY RUBBER DECOMPOSITION

The assumptions and estimations used in calculating the heat absorbed during ablation of 100-gram quantities of various rubbers are described below.

1. The rubbers were assumed not to decompose at all during heating from 77°F to 930°F. At 930°F the rubbers were assumed to decompose sharply.
2. The heat capacity of the rubbers was assumed to remain constant over the temperature range of 77°F to 930°F.
3. All carbon formed by the rubbers was assumed to be graphite.
4. Hydrocarbon fragments formed by the rubber decomposition were assumed not to crack further in the hot char layer.
5. Molecular hydrogen was assumed to dissociate to atomic hydrogen in equilibrium quantities at the temperatures considered in the calculations and at a pressure of 68 atmospheres. This pressure was assumed to be due solely to atomic and molecular hydrogen. The hydrogen species was assumed to behave ideally so that the heat of dissociation was independent of pressure.
6. Molecular hydrogen was assumed to react with solid carbon to form equilibrium quantities of acetylene, which behaved ideally so that the heat of formation of acetylene was independent of pressure.
7. The liquid products of decomposition of the rubbers were assumed to consist of a simple constituent whose composition corresponded to the average composition of the liquid.
8. The heat capacity of hydrocarbons above 2200°F, if not listed in the literature, was estimated by the following technique. The ratio of the heat capacity of ethane at a specific temperature up to 7000°F to the heat capacity at 1340°F was computed and the heat capacity of the hydrocarbon at 1340°F was multiplied by this ratio to give the heat capacity at this given temperature. The validity of this method was tested by calculating the heat capacities of methane and ethylene, and the values were found to agree with the published values within about ± 5%.

9. The heat capacity of the hypothetical compound comprising the liquid product from styrene-butadiene rubber, which corresponded to n-dodecylbenzene with four double bonds, was estimated by analogy to the heat capacity differences between n-pentane, 1-pentene, and 1,4-pentadiene. The heat capacity for the hypothetical compound from the nitrile rubber decomposition was assumed to be the same as that of the hypothetical styrene-butadiene liquid compound.

10. The heats of formation of any organic molecules that were not listed in the published tables were estimated by the bond energy method.

SATURATED ETHYLENE-PROPYLENE RUBBER
HEAT ABSORBED BY COMPLETE DECOMPOSITION OF 100 GRAMS OF RUBBER

Empirical Formula = (CH_2)

No. of Moles of Elements/100 g

C	H_2
7.15	7.15

Temp., °F	Process	ΔH, Kcal	Cumulative ΔH, Kcal			
			930°F	5000°F	6000°F	7000°F
77 - 930	Heating Rubber	+ 26				
930	Rubber Decomposition	+ 70	+ 96			
930-5000	Heating Carbon	+ 92				
	Heating Hydrogen	+130				
	Hydrogen Dissociation	+ 20				
	Acetylene Formation	+ 29				
		271		+367		
930-6000	Heating Carbon	+117				
	Heating Hydrogen	+166				
	Hydrogen Dissociation	+ 40				
	Acetylene Formation	+ 89				
		412			+508	
930-7000	Heating Carbon	+141				
	Heating Hydrogen	+203				
	Hydrogen Dissociation	+ 69				
	Acetylene Formation	+168				
		581				+677

SATURATED ETHYLENE-PROPYLENE RUBBER
HEAT ABSORBED BY DECOMPOSITION OF 100 g OF CURED, UNFILLED RUBBER

Product Species	No. of Moles/ 100 g	ΔHf kcal/mole	ΔHf kcal	Heat Absorbed (kcal) Heating from 77°F to		
				5000°F	6000°F	7000°F
Liquid	0.385	-64.2	-24.7	177	226	276
H_2	0.360	0	0	6.6	8.4	10.2
CH_4	0.541	-20.7	-11.2	26.1	33.6	41.1
C_2H_6	0.070	-24.4	- 1.7	5.6	7.2	8.8
C_2H_4	0.388	+ 9.9	+ 3.8	23.8	30.4	37.0
C_3H_8	0.020	-30.0	- 0.6	2.3	2.9	3.4
C_3H_6	0.028	+ 0.9	0	2.7	3.4	4.1
				244.1	311.9	380.6

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal 930°F	5000°F	6000°F	7000°F
77-930	Heating Rubber	+ 26				
930	Decomposition	+ 36	+62			
930-5000	Heating Products	+244				
	Hydrogen Dissociation	+ 1				
		245		+307		
930-6000	Heating Products	+312				
	Hydrogen Dissociation	+ 2				
		314			+376	
930-7000	Heating Products	+381				
	Hydrogen Dissociation	+ 3				
		384				+446

SATURATED ETHYLENE-PROPYLENE RUBBER
HEAT ABSORBED BY DECOMPOSITION OF 100 g OF RUBBER WITH NICKEL CATALYST

Product Species	No. of moles/100 g	ΔHf, kcal/mole	ΔHf, kcal	Heat Absorbed, kcal, Heating from 77°F to		
				5000°F	6000°F	7000°F
Char (assumed all carbon)	2.09	0	0	27	34	41
Liquid	0.246	-64.2	-15.8	113	145	177
H_2	2.48	0	0	45	58	70
CH_4	0.565	-20.7	-11.7	27	35	43
C_2H_6	0.101	-24.4	- 2.5	8	10	13
C_2H_4	0.345	+ 9.8	+ 3.4	21	27	33
			-26.6	241	309	377

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal			
			930°F	5000°F	6000°F	7000°F
77-930	Heating Rubber	+ 26				
930	Rubber Decomposition	+ 43	69			
930-5000	Heating Products	+241				
	Hydrogen Dissociation	+ 7				
	Acetylene Formation	+ 9				
		257		+326		
930-6000	Heating Products	+309				
	Hydrogen Dissociation	+ 14				
	Acetylene Formation	+ 26				
		349			+418	
930-7000	Heating Products	+377				
	Hydrogen Dissociation	+ 24				
	Acetylene Formation	+ 49				
		450				+519

SATURATED BUTYL RUBBER
HEAT ABSORBED BY COMPLETE DECOMPOSITION OF 100 GRAMS OF RUBBER

Empirical Formula = (CH_2)

No. of Moles of Elements/100 g

C	H_2
7.15	7.15

Temp. °F	Process	ΔH, kcal	930°F	5000°F	6000°F	70C
77-930	Heating Rubber	+ 19				
930	Rubber Decomposition	+ 41	+ 60			
930-5000	Heating Carbon	+ 92				
	Heating Hydrogen	+130				
	Hydrogen Dissociation	+ 20				
	Acetylene Formation	+ 29				
		271		+331		
930-6000	Heating Carbon	+117				
	Heating Hydrogen	+166				
	Hydrogen Dissociation	+ 40				
	Acetylene Formation	+ 89				
		412			+472	
930-7000	Heating Carbon	+141				
	Heating Hydrogen	+203				
	Hydrogen Dissociation	+ 69				
	Acetylene Formation	+168				
		581				+641

SATURATED BUTYL RUBBER
HEAT ABSORBED BY DECOMPOSITION OF 100 g OF CURED, UNFILLED RUBBER

Product Species	No. of moles/100 g	ΔHf kcal/mole	ΔHf, kcal	Heat Absorbed, kcal, heating from 77°F to 5000°F	6000°F	7000°F
Liquid	0.334	-64.2	-24.4	153	197	240
H_2	0.373	0	0	7	9	11
CH_4	0.700	-20.7	-14.5	34	43	53
C_2H_6	0.031	-24.4	- 0.8	2	3	4
C_2H_4	0.094	+ 9.9	+ 0.9	6	7	9
C_3H_8	0.017	-30.0	- 0.5	2	2	3
C_3H_6	0.110	+ 0.9	+ 0.1	10	13	16
1-C_4H_8	0.243	- 8.8	- 2.1	31	40	49
			-38.3	245	314	385

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal 930°F	5000°F	6000°F	7000°F
77-930	Heating Rubber	+ 19				
930	Rubber Decomposition	+ 3	+ 22			
930-5000	Heating Products	+245				
	Hydrogen Dissociation	+ 1				
		246		+268		
930-6000	Heating Products	+314				
	Hydrogen Dissociation	+ 2				
		316			+338	
930-7000	Heating Products	+385				
	Hydrogen Dissociation	+ 4				
		389				+411

SATURATED BUTYL RUBBER
HEAT ABSORBED BY DECOMPOSITION OF 100 g RUBBER WITH NICKEL CATALYST

Product Species	No. of Moles/100 g	ΔHf, kcal/mole	ΔHf, kcal	Heat Absorbed, kcal, Heating from 77°F to 5000°F	6000°F	7000°F
Char (assumed carbon)	3.75	0	0	48	61	74
Liquid	0.192	-64.2	-12.3	88	113	138
H_2	4.18	0	0	76	97	119
CH_4	0.560	-20.7	-11.6	27	35	43
			-23.9	239	306	374

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal 930°F	5000°F	6000°F	7000°F
77-930	Heating Rubber	+ 19				
930	Rubber Decomposition	+ 17	+ 36			
930-5000	Heating Products	+239				
	Hydrogen Dissociation	+ 11				
	Acetylene Formation	+ 17				
		267		+303		
930-6000	Heating Products	+306				
	Hydrogen Dissociation	+ 24				
	Acetylene Formation	+ 52				
		382			+418	
930-7000	Heating Products	+374				
	Hydrogen Dissociation	+ 40				
	Acetylene Formation	+ 99				
		513				+549

STYRENE BUTADIENE RUBBER
HEAT ABSORBED BY COMPLETE DECOMPOSITION OF 100 GRAMS OF RUBBER

Empirical Formula (approx.) = (C_4H_5)

No. of Moles of Elements/100 g

C	H_2
7.53	4.84

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal 930°F	5000°F	6000°F	7
77-930	Heating Rubber	+ 16				
930	Rubber Decomposition	- 5	+11			
930-5000	Heating Carbon	+ 97				
	Heating Hydrogen	+ 88				
	Hydrogen Dissociation	+ 13				
	Acetylene Formation	+ 20				
		+218		+229		
930-6000	Heating Carbon	+123				
	Heating Hydrogen	+113				
	Hydrogen Dissociation	+ 27				
	Acetylene Formation	+ 60				
		+323			+334	
930-7000	Heating Carbon	+149				
	Heating Hydrogen	+138				
	Hydrogen Dissociation	+ 47				
	Acetylene Formation	+114				
		448				

STYRENE-BUTADIENE RUBBER
HEAT ABSORBED BY DECOMPOSITION OF 100 GRAMS OF CURED, UNFILLED RUBBER

Product Species	No. of Moles/100 g	ΔHf, kcal/mole	ΔHf, kcal	Heat Absorbed, kcal, Heating from 77°F to		
				5000°F	6000°F	7000°F
Liquid	0.528	+44	+23.3	176	224	273
H_2	0.503	0	0	9	12	14
CH_4	0.277	-20.7	- 5.7	13	17	21
C_2H_6	0.033	-24.4	- 0.8	3	3	4
C_2H_4	0.092	+ 9.9	+ 0.9	6	7	9
				207	263	321

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal			
			930°F	5000°F	6000°F	7000°F
77-930	Heating Rubber	+ 16				
930	Rubber Decomposition	+ 13	+29			
930-5000	Heating Products	+207				
	Hydrogen Dissociation	+ 1				
		208		+237		
930-6000	Heating Products	+263				
	Hydrogen Dissociation	+ 3				
		266			+295	
930-7000	Heating Products	+321				
	Hydrogen Dissociation	+ 5				
		326				+355

STYRENE-BUTADIENE RUBBER
HEAT ABSORBED BY DECOMPOSITION OF 100 GRAMS OF RUBBER WITH NICKEL CATALY

Product Species	No. of Moles/100 g	ΔHf, kcal/mole	ΔHf, kcal	Heat Absorbed, kcal, Heating from 77°F to 5000°F	6000°F	7000°F
Char (assumed carbon)	0.658	0	0	9	11	13
Liquid	0.482	+44	+21.2	160	204	249
H_2	1.16	0	0	21	27	33
CH_4	0.177	-20.7	- 3.7	9	11	13
C_2H_6	0.033	-24.4	- 0.8	3	3	4
C_2H_4	0.119	+ 9.9	+ 1.2	7	9	11

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal 930°F	5000°F	6000°F	7000°
77-930	Heating Rubber	+ 16				
930	Rubber Decomposition	+ 13	+29			
930-5000	Heating Products	+209				
	Hydrogen Dissociation	+ 3				
	Acetylene Formation	+ 5				
		+217		+246		
930-6000	Heating Products	+265				
	Hydrogen Dissociation	+ 7				
	Acetylene Formation	+ 14				
		+286			+315	
930-7000	Heating Products	+323				
	Hydrogen Dissociation	+ 11				
	Acetylene Formation	+ 16				
		+350				+379

ACRYLONITRILE-BUTADIENE RUBBER, HIGH NITRILE CONTENT
HEAT ABSORBED BY COMPLETE DECOMPOSITION OF 100 GRAMS OF RUBBER

Empirical Formula (approx.) = $C_{58}H_{75}N_8$

No. of Moles of Elements/100 g

C	H_2	N_2
6.57	4.25	4.53

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal			
			930°F	5000°F	6000°F	7000°
77-930	Heating Rubber	+ 16				
930	Rubber Decomposition	- 20	-4			
930-5000	Heating Carbon	+ 85				
	Heating Hydrogen	+ 77				
	Heating Nitrogen	+ 9				
	Hydrogen Dissociation	+ 12				
	Acetylene Formation	+ 17				
		200		+196		
930-6000	Heating Carbon	+108				
	Heating Hydrogen	+ 99				
	Heating Nitrogen	+ 11				
	Hydrogen Dissociation	+ 24				
	Acetylene Formation	+ 53				
		295			+291	
930-7000	Heating Carbon	+130				
	Heating Hydrogen	+121				
	Heating Nitrogen	+ 13				
	Hydrogen Dissociation	+ 41				
	Acetylene Formation	+100				
		405				+401

ACRYLONITRILE-BUTADIENE RUBBER, HIGH NITRILE CONTENT
HEAT ABSORBED BY DECOMPOSITION OF 100 g OF CURED, UNFILLED RUBBER

Product Species	No. of Moles/100 g	ΔHf, kcal/mole	ΔHf, kcal	Heat Absorbed, kcal, Heating from 77°F to 5000°F	6000°F	7000°F
Liquid	0.561	+ 80	+ 45	171	218	266
H_2	0.283	0	0	5	7	8
CH_4	0.239	- 20.7	- 4.9	12	15	18
C_2H_6	0.036	- 24.4	- 0.9	3	4	5
C_2H_4	0.166	+ 9.9	+ 1.6	10	13	16
C_3H_6	0.034	+ 0.9	0	3	4	5
			+ 40.8	204	261	318

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal 930°F	5000°F	6000°F	700
77-930	Heating Rubber	+ 16				
930	Rubber Decomposition	+ 21	+37			
930-5000	Heating Products	+204				
	Hydrogen Dissociation	+ 1				
		205		+242		
930-6000	Heating Products	+261				
	Hydrogen Dissociation	+ 2				
		+263			+300	
930-7000	Heating Products	+318				
	Hydrogen Dissociation	+ 3				
		321				+35

ACRYLONITRILE-BUTADIENE RUBBER, HIGH NITRILE CONTENT
HEAT ABSORBED BY DECOMPOSITION OF 100 GRAMS OF RUBBER WITH NICKEL CATALYST

Product Species	No. of Moles/100 g	ΔHf, kcal/mole	ΔHf, kcal	Heat Absorbed, kcal, Heating from 77°F to 5000°F	6000°F	7000°F
Char (assumed carbon)	1.71	0	0	22	28	34
Liquid	0.448	+ 80	+ 35.8	137	175	213
H_2	1.07	0	0	19	25	30
CH_4	0.175	- 20.7	- 3.6	8	11	13
C_2H_6	0.030	- 24.4	- 0.7	2	3	4
C_2H_4	0.105	+ 9.9	+ 1.0	6	8	10
			+ 32.5	194	250	304

Temp. °F	Process	ΔH, kcal	Cumulative ΔH, kcal 930°F	5000°F	6000°F	7000°F
77-930	Heating Rubber	+ 16				
930	Rubber Decomposition	+ 12	+28			
930-5000	Heating Products	+194				
	Hydrogen Dissociation	+ 3				
	Acetylene Formation	+ 4				
		+201		+229		
930-6000	Heating Products	+250				
	Hydrogen Dissociation	+ 6				
	Acetylene Formation	+ 13				
		+269			+297	
930-7000	Heating Products	+304				
	Hydrogen Dissociation	+ 10				
	Acetylene Formation	+ 25				
		+339				+367

APPENDIX 2

THERMAL DECOMPOSITION DATA FOR FILLED RUBBERS USING 2000°F/MINUTE HEATING RATE

THERMAL DECOMPOSITION DATA FOR VARIOUS FILLED RUBBERS

Formulation	Parts by Weight	Avg. Mol. Wt. Gas	Wt-% Products Based on Rubber Gas	Wt-% Products Based on Rubber Liquid	Wt-% Products Based on Rubber Char	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	iso C_4H_8
Styrene-butadiene Silica-alumina-magnesia catalyst	100 50	15.5	11.6	86.3	2.1	36.9	30.7	5.5	21.9	trace	5.0	trace	
Styrene-butadiene Silica-alumina catalyst	100 50	16.2	9.7	87.9	2.4	36.9	30.3	4.7	18.5	trace	9.6	trace	
Styrene-butadiene Nickel (G) catalyst	100 50	8.1	6.9	much residue lost by erosion		68.3	18.4	2.9	10.4	trace	trace	0	
Ethylene-propylene, saturated Nickel (G) catalyst	100 50	20.0	31.1	much residue lost by erosion		26.6	30.0	4.5	21.9	1.1	15.9	0	
Styrene-butadiene Nickel (E) catalyst	100 50	13.7	15.8	81.2	3.0	41.1	30.9	3.6	24.3	trace	trace	0	
Unsaturated butyl Nickel (E) catalyst	100 50	18.2	46.6	46.0	7.4	35.7	36.6	1.8	9.4	trace	5.3	0	11.1
Styrene-butadiene Asbestos	100 50	16.7	13.5	86.5	0	35.1	27.5	4.8	25.8	0.4	6.5	trace	
Ethylene-propylene, saturated Nickel (E) catalyst	100 50	16.8	45.9	47.3	6.8	32.9	32.1	2.9	24.1	0.7	7.4	0	
Saturated butyl Nickel (B) catalyst	100 50	23.2	54.6	40.7	4.7	24.3	36.2	1.8	9.5	trace	7.9	0	20.3
Acrylonitrile-butadiene (40% nitrile content) Nickel (A) catalyst	100 50	6.4	8.8	70.7	20.5	77.5	12.7	2.2	7.6	trace	0	0	
Unsaturated ethylene-propylene Nickel (A) catalyst	100 50	8.8	24.1	59.9	16.0	66.9	15.6	4.5	13.0	trace	trace	0	

EFFECT OF NICKEL CATALYST CONTENT UPON THERMAL DECOMPOSITION OF UNCURED SATURATED ETHYLENE-PROPYLENE RUBBER (EPR 404)

Composition, Parts by Weight			Products, Wt-% Based on Rubber			Avg. Mol. Wt.	Gaseous Products in Wt-% Based on Rubber							
EPR 404	Nickel (A)	SiO$_2$	Char	Liquid	Gas	Gas	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	iso-C_4H_8
100	50	0	25.1	48.2	26.7	7.7	4.9	9.1	3.0	9.7	trace	0	trace	0
100	25	25	24.0	36.0	40.0	10.7	4.2	13.8	3.4	18.6	trace	trace	trace	0
100	8	42	20.4	29.6	50.0	12.0	3.9	20.7	2.8	22.6	trace	trace	trace	0
100	4	46	8.2	39.5	52.3	15.7	2.4	16.8	2.3	21.5	trace	9.3	0	0
100	0	50	0.8	49.0	50.2	18.4	1.5	15.0	3.1	20.4	1.0	9.2	0	0
100	0	0	0.3	80.6	19.1	21.3	0.4	4.1	1.5	6.8	0.9	5.1	0.3	0

EFFECT OF NICKEL CATALYST CONTENT UPON THERMAL DECOMPOSITION OF UNCURED SATURATED BUTYL RUBBER (BUTYL 268)

Composition, Parts by Weight			Products, Wt-% Based on Rubber			Avg. Mol. Wt.	Gaseous Products in Wt % Based on Rubber							
Butyl 268	Nickel (A)	SiO_2	Char	Liquid	Gas	Gas	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	iso C_4H_8
100	50	0	45.0	37.7	17.3	3.6	8.3	9.0	0	0	0	0	0	0
100	25	25	45.0	38.3	16.7	3.6	8.2	8.5	trace	trace	0	trace	0	trace
100	15	35	37.0	39.7	23.3	5.4	6.6	16.7	trace	trace	trace	trace	0	trace
100	8	42	13.8	40.2	46.0	13.4	3.1	20.2	1.1	8.4	trace	5.9	0	7.3
100	0	50	<1.0	≈50.0	48.9	22.0	0.9	15.8	1.6	7.4	trace	6.5	0	16.7
100	0	0	0.5	45.5	54.0	28.9	0.6	10.5	1.2	4.8	trace	6.7	0	30.2

EFFECT OF NICKEL CATALYST CONTENT UPON THERMAL DECOMPOSITION OF UNCURED, UNSATURATED BUTYL RUBBER

Composition, Parts by Weight			Products, Wt-% Based on Rubber			Avg. Mol. Wt	Gaseous Products in Wt-% Based on Rubber							
Butyl MD-502	Nickel (A)	SiO_2	Char	Liquid	Gas	Gas	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}	iso-C_4H_8
100	50	0	39.8	44.1	16.1	3.5	8.1	8.0	trace	0	0	0	0	0
100	25	25	33.1	52.6	14.3	3.8	6.7	7.6	trace	trace	trace	trace	0	trace
100	15	35	32.5	42.9	24.6	6.0	5.8	18.8	trace	trace	trace	trace	0	trace
100	0	0	0.2	58.7	41.1	28.6	0.5	7.6	1.0	3.3	1.0	7.2	0	20.5

THERMAL DECOMPOSITION DATA FOR COMMERCIAL UNCURED INSULATING MATERIALS

Material	Wt-% Non-Volatile Filler (estimated)	Avg. Mol. Wt Gas	Wt-% Products Based on Volatile Material			Gas Composition, Mole-%						
			Gas	Liquid	Char	H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}
Stoner Rubber Co., SMR 6-10	8.5	10.9	14.3	65.9	19.8	54.9	24.3	3.8	16.9	trace	trace	0
Stoner Rubber Co., SMR 7-12	53.1	14.2	20.9	75.1	4.0	36.1	37.3	3.6	22.9	trace	trace	0
Phenolic Resin	-	5.6	7.2	$<$40.6	$>$52.2	74.2	25.8	trace	0	0	0	0

THERMAL DECOMPOSITION DATA FOR UNCURED STYRENE-BUTADIENE RUBBER

50 phr Catalyst or Filler

Catalyst or Filler*	Avg. Mol. Wt. Gas	Wt-% Gas	Wt-% Liquid	Wt-% Char	Gas Composition, Mole-% H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}
None	17.4	8.1	91.6	0.3	35.8	29.4	3.8	21.5	trace	4.1	0
Carbon	14.5	16.0	≈83.0	<1.0	36.9	33.4	4.0	25.7	trace	trace	0
Silica	14.5	13.6	≈86.0	<1.0	37.0	33.1	4.5	25.3	trace	trace	0
Platinum	6.9	10.7	75.9	13.4	74.8	13.7	2.5	8.9	trace	trace	0
Palladium	8.6	11.6	75.3	13.1	65.6	19.7	3.1	11.6	trace	trace	0
Rhodium	9.3	8.2	88.4	3.4	63.3	19.5	3.7	13.5	trace	trace	0
Nickel (A)	6.4	9.5	82.6	7.9	78.0	11.9	2.2	8.0	0	trace	0

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*See glossary of terms for catalyst identification

THERMAL DECOMPOSITION DATA FOR UNCURED SATURATED ETHYLENE-PROPYLENE
50 PHR CATALYST OR FILLER

Catalyst or Filler*	Avg. Mol. Wt Gas	Wt-% Gas	Wt-% Liquid	Wt-% Char	Gas Composition, Mole-%						
					H_2	CH_4	C_2H_6	C_2H_4	C_3H_8	C_3H_6	C_4H_{10}
None	21.3	19.1	80.6	0.3	22.3	29.0	5.4	26.9	2.2	13.7	0.6
Carbon	19.8	41.8	≈58.0	<1.0	23.9	31.5	4.8	27.6	1.1	11.0	trace
Silica	18.4	50.2	49.0	0.8	26.4	34.3	3.8	26.8	0.8	8.0	0
Platinum	14.8	37.3	55.5	7.2	43.6	26.6	3.8	17.1	1.1	7.8	trace
Palladium	17.0	36.8	57.7	5.5	36.5	27.6	6.2	18.0	1.8	9.9	trace
Rhodium	16.4	39.5	55.4	5.1	37.7	27.5	3.7	21.3	0.9	8.9	trace
Nickel (A)	7.7	26.7	48.2	25.1	71.0	16.2	2.9	9.9	trace	0	trace

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*See glossary of terms in text for catalyst identification

APPENDIX 3

SCREENING TESTS OF THE CHARRING ABILITY OF CATALYTIC FILLERS IN VARIOUS RUBBERS: HEATING RATE 30°F/MINUTE

Catalytic Filler[a]	Wt-% Residue, Based on Rubber
STYRENE-BUTADIENE RUBBER, UNCURED	
Platinum	22
Palladium	22
Rhodium	8
Nickel (A)	19
Nickel (B)	3
Nickel (C)	26
Nickel (E)	9
Nickel (F)	14
Nickel (G)	21
Nickel (H)	3
Cobalt	1.5
Vanadium	6
Iron	5
Nickel Oxide	1.5
Iron Oxide	6.3
Silica-Alumina	5.0
Silica-Alumina-Magnesia	4.0
None	0.6
STYRENE-BUTADIENE RUBBER, CURED	
Platinum	25
Palladium	26
Nickel (A)	26
Silica[b]	1.9
Carbon[c]	1.3
Asbestos[d]	1.5
Glass	1.0
Alumina	1.5
None	1.6
SATURATED ETHYLENE-PROPYLENE RUBBER, UNCURED	
Platinum	9
Palladium	4
Rhodium	1.1
Nickel (A)	4.1
Nickel (G)	2.4
Nickel (E)	0.5
Nickel Oxide	2.0
Iron Oxide	1.8
Silica-Alumina	2.0
None	0.4

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[a] 50 phr

[b] Monsanto Chemical Co. Santocel®

[c] Cabots Sterling®

[d] Johns-Manville JM-301

Catalytic Filler[a]	Wt-% Residue, Based on Rubber
ACRYLONITRILE-BUTADIENE UNCURED (HIGH NITRILE CONTENT)	
Nickel (A)	37
None	15.2
ACRYLONITRILE-BUTADIENE, CURED (HIGH NITRILE CONTENT)	
Nickel (A)	69
None	24.4
SATURATED BUTYL, UNCURED	
Nickel (A)	7
Nickel (B)	<1
Nickel (C)	1.5
Nickel (D)	<1
Vanadium	1.5
None	<1