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DEGRADATION MECHANISM, HYDROCARBON POLYMERS

Final Technical Report

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Final Technical Report

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# FOREWORD

This document is a final report prepared under Contract NAS7-721,
Degradation Mechanism, Hydrocarbon Polymers.  The research reported
herein was performed at the Santa Susana Field Laboratory of the
Rocketdyne Division of the North American Rockwell Corporation during
the period December 1968 to October 1970.  Dr. E. A. Lawton, Research,
was Program Manager; Dr. F. C. Gunderloy, Jr., the Responsible Engineer,
and Dr. C. L. Hamermesh the Principal Investigator.  Mr. R. Bodemeijer
participated in the laboratory effort.  The technical effort on this
contract was monitored for NASA by Mr. D. D. Lawson and Dr. R. C. Rhein
of the Polymer Branch, Jet Propulsion Laboratory, Pasadena, California.

As a subtask of this program, a comprehensive survey and evaluation of
the literature on saturated hydrocarbon and certain other types of binders
was carried out.  The resultant list of references was considered too
voluminous to include in the present report, and was forwarded to the
Program Monitor as a separate informal document.

# ABSTRACT

A number of functional group terminated hydrocarbon polymers as well as chain extended products thereof were exposed at 275 F for 400 hours both in the presence and absence of ammonium perchlorate. It was observed that for most of the polymers tested, relatively small weight losses occurred. This was also true for the chain extended products.

By contrast, two polyisobutylenes (unextended) with residual functional groups (double bond or hydroxyl) at the chain ends were severely degraded. Chain extension of the hydroxyl polymer with toluene diisocyanate (TDI) or pyromellitic dianhydride (PMDA) reduced the weight loss to the range observed with the other polymers. It was postulated that the sensitive end groups which cause unzipping of the polyisobutylene had been removed by the chain extension reaction. This was confirmed by simple endcapping reactions which do not result in chain extension. The products obtained gave only nominal weight losses.

In all cases, elevated temperature exposure resulted in a substantial fraction of the polymer being rendered insoluble and the presence of AP increased the quantity of insoluble, presumably crosslinked, product. No evidence was obtained to indicate that the presence of tertiary carbon atoms, urethane or ester linkages on the polymer chain made any significant contribution to increased attack by the oxidizer.

All attempts to develop a suitable test device in which the gaseous byproducts from the polymer demonstration could be collected were unsuccessful in that weight losses did not duplicate those obtained in the oven tests. Therefore, no mechanism for polymer degradation or the site of failure could be established conclusively.

# CONTENTS

## TABLES

# INTRODUCTION

In those space programs which involve the landing of a package on other
planets, sterilization is achieved by prolonged heating at elevated
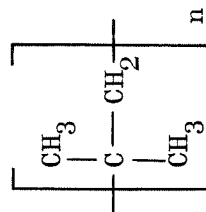temperatures. This has imposed on the materials, propellants, etc.
which are parts of, or are attached to, the package a thermal stability
requirement of 275-300 F for periods up to 400 hours.

Under such conditions, solid propellants containing an unsaturated
binder system based on polybutadiene give unsatisfactory performance due
to a marked deterioration in mechanical properties (Ref. 1). Solid
propellants containing saturated binder systems employing hydrogenated
polybutadienes gave solid propellants which exhibited a high order of
stability. However, to obtain usable flow properties in the uncured
propellant formulations, it is necessary to hydrogenate polybutadienes
having a high (up to 50%) side chain vinyl content (Fig. 1). Every
vinyl group hydrogenated produces a carbon atom containing a tertiary
hydrogen and, for the 50% vinyl polymer, such atoms are present in
every other repeating unit of the polymer chain. It was believed that
these sites may be the points for attack by an oxidizer such as
ammonium perchlorate at elevated temperatures. By contrast, a polymer
based on isobutylene (Fig. 1) has no carbon atoms with tertiary
hydrogens and attack by oxidizer via this route cannot occur. To
date, no demonstration had been made of the relative merits of the two
polymers as binders for thermally stable solid propellants which might
be used in planetary landing applications.

Another factor which must be considered is that the weakest thermal
link in the binder system may be the structure produced by the reaction
of the polymer and the curative. This site may be considerably more
sensitive than the polymer backbone. Some confirmation of this has been
obtained (Ref. 1) from an evaluation of the behavior on thermal cycling

$$\left[ \begin{array}{c} \overset{*}{\underset{\displaystyle \begin{array}{c} | \\ CH_2 \\ | \\ CH_3 \end{array}}{CH_2-CH-CH_2-CH_2-CH_2-CH_2}} \end{array} \right]_n$$

Saturated Polybutadiene

$$\left[ \begin{array}{c} \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}} - CH_2 \end{array} \right]_n$$
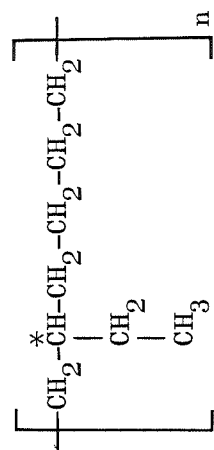
Polyisobutylene

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*Tertiary Carbon Atom

Figure 1. Hydrocarbon Polymer

of hydroxyl-terminated polymers cured with isocyanates versus that of carboxyl-terminated polymer cured with cyclic imines. In both polymers, the backbones were essentially the same. When mixed with oxidizer, the latter binder system was significantly more susceptible to degradation of properties at elevated temperatures.

In this document is described the work performed under Contract NAS7-721. The objective of this effort was the study of the behavior of a number of polymers when exposed to elevated temperatures for prolonged periods of time both in the presence and absence of ammonium perchlorate. From these tests, it was hoped to obtain some insight into the mechanisms of the chemical reactions taking place under these conditions.

# DISCUSSION

Degradation of solid propellant binders at elevated temperatures can occur by (1) chain scission to form low molecular weight fluid products, (2) crosslinking to form hard, brittle products, or (3) a combination of these modes. Since the binder is in intimate contact with an oxidizer, both thermal and oxidative mechanisms may be involved. For a saturated hydrocarbon binder, such as hydroxyl-terminated hydrogenated polybutadiene, attack could possibly occur at several sites along the chain. Besides the tertiary hydrogens in this polymer, the presence of residual unsaturation provides allylic reaction sites. Further, the reaction of the terminal functional groups with crosslinking agent may also give rise to a linkage susceptible to degradation. Finally, residual functional groups, remaining after the curing, may continue to react when the system is exposed to elevated temperatures.

In order to determine which features of the polymer structure are susceptible to degradation and, therefore, should be eliminated in future binder systems, the degradation mechanism must be elucidated. However, determining the structural changes occurring in the polymer in a solid propellant is extremely difficult in that separation of the crosslinked polymer from the other ingredients is not readily achieved. Therefore, in this program, it was decided to use chain extended but uncrosslinked polymers which would have the same structures as those present in the cured solid propellant. This approach has a number of advantages in that (1) separation of the binder from the oxidizer can be achieved readily, (2) crosslinked polymer, if produced under the conditions of exposure, can be detected, and (3) any structural changes occurring as a result of exposure can be examined without interference of oxidizer.

Three functional group terminated hydrocarbon polymers were selected for this study. They were:

(a) Secondary hydroxyl-terminated saturated polybutadiene ($2^0$ OHSPB)

(b) Primary hydroxyl-terminated saturated polybutadiene ($1^0$ OHSPB)

(c) Primary hydroxyl-terminated polyisobutylene ($1^0$ OHPIB)

The properties of these materials are recorded in Table I. It should be noted that with the exception of C, there is residual unsaturation in the polymers.

### TABLE I

### PROPERTIES OF INITIAL POLYMER

| Polymer | Functionality[a] | Unsaturation[b] | Molecular Weight[c] |
|---------|------------------|-----------------|---------------------|
| $2^0$ OHSPB | 1.62 | 0.25 | 2022 |
| $1^0$ OHSPB | 1.43 | 0.63 | 2400 |
| $1^0$ OHPIB | 2.02 | 0 | 1721 |

a. Hydroxyl groups per polymer molecular weight
b. Milliequivalents of I per gram
c. Determined via Mechrolab Vapor Phase Osmometer

### PREPARATION OF CHAIN EXTENDED POLYMERS

Two chain extending agents, toluene diisocyanate (TDI) and pyromellitic dianhydride (PMDA) were employed. Reaction of an hydroxyl-terminated polymer with the former yields urethane linkages and, with proper stoichiometry, no residual functional groups should be present in the

product. The stoichiometry of the reaction with PMDA was such as to merely open the anhydride rings and produce one ester linkage per anhydride ring. Therefore, the products therefrom would have carboxyl groups present along the polymer chain.

Chain extension of the saturated butadiene polymers with TDI was attempted under a variety of conditions including the use of different solvents (benzene, toluene), different stoichiometric levels (excess polymer to excess TDI), and at various concentrations of reactants (10 to 85% total active ingredients in solution). In all cases, methanol was added at the end of the reaction to destroy any isocyanate end groups as well as to precipitate the polymer. After precipitation and trituration with methanol, the polymer was redissolved in toluene, precipitated with methanol, and vacuum dried overnight at 50 C.

Regardless of the conditions employed, no chain extended products with molecular weights in excess of 15,000 were obtained. In light of the functionality and molecular weight of the starting polymers, this was not surprising in that, at the 1:1 ratio, products with a molecular weight no higher than 15,000 would be anticipated. The low functionality of the polymers indicates the presence of monofunctional material which acts as a chain stopping agent. By contrast, the hydroxyl-terminated polyisobutylene which had a functionality of 2.02 gave a TDI extended product (from reaction in refluxing toluene) with a molecular weight of 31,500, more than twice the value obtained for the other two polymers (Table II).

Chain extension with PMDA of polymers similar to those employed in this program had been attempted previously (Ref. 2) and only very modest increases in molecular weights were obtained. Since the anhydride is insoluble in aromatic solvents, these reactions were run in tetra-hydrofuran (THF) which gave a homogeneous system. Despite this and

## TABLE II

### CHAIN EXTENSION OF POLYMERS

| Polymer | Functionality[a] | Molecular Weight[b] | Molecular Weight | | |
|---------|------------------|---------------------|------------------|---|---|
| | | | After TDI Reaction | After PMDA Reaction | |
| | | | | In Solution | In Bulk |
| $2^o$ OHSPB | 1.62 | 2022 | 11–12,000[c] | 2,200[d] | 10,000[c] |
| $1^o$ OHSPB | 1.43 | 2400 | 13–14,000[c] | 3,000[d] | 10,000[c] |
| $1^o$ OHPIB | 2.02 | 1721 | 31,500[c] | 4,000[d] | 13,000[c] |

a. Hydroxyl groups per molecule
b. Before chain extension, determined using Mechrolab Vapor Phase Osmometer
c. Determined using Mechrolab membrane osmometer
d. Determined using Mechrolab Vapor Phase Osmometer

all attempts at varying reaction conditions, the molecular weights of the products were quite low (Table II). Again, the isobutylene material gave the higher value. Subsequently, it was observed that more viscous, higher molecular weight products could be obtained if the polymers were reacted in bulk with the PMDA.

## EXPOSURE TESTS

### Differential Thermal Analysis

Several of the chain extended polymers were dissolved in toluene (or THF for the PMDA products), mixed with an equal weight of ammonium perchlorate (Lot 310 provided by JPL), and vacuum dried. Differential thermal analysis (DTA) of these mixtures exhibited the same two peaks as is observed with AP alone. The curves can best be described as those for an "impure" AP.

## Thermal Gravimetric Analysis

An equal weight mixture of a TDI-extended secondary hydroxyl-terminated saturated polybutadiene and AP was exposed for 400 hours at 275 F in a helium environment in a thermal gravimetric apparatus (TGA). After 400 hours, the mixture had lost less than 1% of its initial weight. It would therefore appear that the TGA technique is of little value in detecting polymer-AP interactions under the conditions employed.

## Oven Tests

Experimental Procedure. All polymers, either alone or in equal weight mixtures with ammonium perchlorate, were exposed in a 275 F oven for 400 hours in a helium environment. The AP mixtures were prepared by deposition of the polymer on the AP from solutions of toluene (or THF for PMDA extended materials), followed by vacuum drying to remove the solvent prior to testing. Weight loss of the samples were, in some cases, checked during the period of exposure and for all samples after 400 hours[*].

After exposure, the polymers were separated from the AP mixture. Two methods were used. In one, the mixtures were stirred in a Waring blendor with a mixture of equal amounts of water and toluene. With an ethylene-propylene binary copolymer (EPR) mixture, three phases were obtained: (1) water containing AP, (2) toluene containing low molecular weight polymer (presumably) and (3) insoluble polymer. The high molecular weight polyisobutylene-AP combination gave only water and toluene soluble phases. No insoluble products were isolated.

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[*]Prior to the start of the tests, temperatures at various locations in the oven were measured and it was found that a variation of no more than 5 degrees occurred between these positions.

When this method was applied to the TDI-extended polymers, very stable emulsions were produced. To overcome this, the procedure was altered so that the mixture was first stirred with water to remove AP and then with toluene. Although the emulsion problem was overcome, not all the polymer isolated was soluble.

The entire mass of polymer (soluble and insoluble) was isolated, extracted with refluxing toluene in a Soxhlet apparatus, and the quantity of insoluble material (presumably crosslinked) and the molecular weight of the soluble fractions determined. In addition, the molecular weight distributions for the chain extended polymers both before exposure and after exposure alone and with AP were measured.

RESULTS

Starting Polymers

In addition to the three saturated polymers listed above, samples of a number of other polymers were exposed in oven tests. As can be seen from Table III, these included two high molecular weight commercial polymers, an ethylene-propylene binary copolymer and a polyisobutylene. Both polymers are presumed to be non-functional (however, see below) and would represent the main chain of the hydrocarbon polymer at a molecular weight roughly comparable with that of the chain extended materials. In addition, two hydroxyl-containing ethylene-propylene terpolymers provided by Dr. H. E. Marsh, Jet Propulsion Laboratory, were evaluated.

It can be seen from Table III that with the exception of the isobutylene polymers, all the starting materials including the unsaturated polymers showed very little weight loss regardless of the condition of exposure (with or without AP). For the Butarez polymers (FGT

TABLE III

EFFECT OF EXPOSURE[a] ON POLYMER WEIGHT LOSS

| Polymer | Molecular Weight | Weight Loss, % | |
| --- | --- | --- | --- |
| | | Exposed Alone | Exposed with AP[b] |
| HTPB II | 5,000 (ca) | 2 | 5 |
| CTPB II | 5,000 (ca) | 4 | 5 |
| $2^o$ OHSPB | 2,022 | 13 | 15 |
| $1^o$ OHSPB | 2,400 | 10 | 3 |
| $1^o$ OHPIB | 1,721 | 94 | 48 |
| EPR | 50,000 | 20 | 18 |
| PIB | 50,000 | 43 | 57 |
| 28FMS-106[c] | 1,479 | 25 | 20 |
| 9170-73-3B[d] | 1,647 | 18 | 18 |

a.  400 hrs., 275 F oven, helium environment
b.  AP weight loss – 3%
c.  Ethylene-propylene-2 methyl butenol terpolymer
d.  Ethylene-propylene-vinyl alcohol terpolymer

polybutadiene, Philips) regardless of the type of functional group present or condition of exposure, considerable hardening had occurred and shrinkage cracks were evident.  It is apparent that considerable crosslinking had occurred in both cases and that exposure with AP resulted qualitatively in a greater hardening of the polymer.  The antioxidant which is normally present in the Butarez polymers did not appear to inhibit this behavior to any great extent.  This discrepancy

between weight loss and change in mechanical properties of the exposed samples is indicative of the difficulties inherent in studying polymer degradation. Both parameters are significant and not wholly inter-dependent. The importance of one over the other is a function of the application in which the polymer (and propellant) is being employed. Mechanical properties may be influenced by physical interaction of perchlorate and binder to a considerable extent. In this instance, examination of the isolated polymer or weight loss measurements will give no valid information. Weight loss may also give erroneous infor-mation in that it may pertain to the removal of nonfunctional low molecular weight impurity rather than to a degradation of the main bulk of the polymer.

The two ethylene-propylene terpolymers experienced the bulk of their weight loss during the first 168 hours of exposure. Therefore, it would appear that these polymers consist of a low molecular weight fraction which is readily removed during the exposure test and a higher molecular weight polymer which is of good thermal stability. In light of the oven tests, improvement in these products can probably be achieved by removal of the lighter ends prior to use.

The very high weight loss of the isobutylene polymers is not unanticipated. The commercial polymer is nonfunctional in the sense that it has neither hydroxyl nor carboxyl end groups. However, it does have a double bond at one chain end and this is the site for thermal degradation and polymer unzipping. It appears that hydroxyl end groups function in a manner similar to double bonds in polyisobutylene.

Since the hydroxyl groups at the end of the polyisobutylene appeared to be the site of instability, a series of experiments were run in which these groups were reacted with either TDI or phenyl isocyanate in a 1:2 molar ratio. This resulted in an end capped but unextended polymer. When these products were exposed in oven tests, weight losses of 8.5

and 5.8%, respectively, were obtained. This would appear to confirm
the hydroxyl group as the unstable moiety in the polymer. Work on
the chain extended polymers described below offers additional confir-
mation of this point.


## TDI Chain Extended Polymers

The polymers which were chain extended with TDI gave in all cases
products of high thermal stability (Table IV). Reaction of the poly-
isobutylene with the diisocyanate obviously stabilizes the polymer.
This effect is consistent with the elimination of sensitive groups
from the polymer chain ends.

TABLE IV

WEIGHT LOSS OF CHAIN EXTENDED POLYMERS

| Polymer | % Weight Loss | |
| --- | --- | --- |
| | Exposed Alone | Exposed with AP |
| TDI – $2^o$ OHSPB | 2 | 14 |
| TDI – $1^o$ OHSPB | 0 | 14 |
| TDI – $1^o$ OHPIB | 0 | 14 |

Regardless of the condition of exposure, all the polymers, after
exposure, were only partially soluble in toluene as opposed to total
solubility prior to testing. Samples of these materials were extracted
with refluxing toluene for 3 days in a Soxhlet apparatus and the quantity
of insoluble products determined (Table V). In all instances, polymers
exposed in the presence of AP yielded larger quantities of insolubles
than did the polymer samples exposed alone. The insoluble and presumably
crosslinked polymers observed in the latter case may be due to the
residual unsaturation in these polymers.

TABLE V

EFFECT OF EXPOSURE ON POLYMER SOLUBILITY

| | % Insoluble Product | |
| Polymer | Exposed Alone | Exposed with AP |
|---|---|---|
| TDI $- 2^o$ OHSPB | 15 | 42 |
| TDI $- 1^o$ OHSPB | 22 | 33 |
| TDI $- 1^o$ OHPIB | 25 | 50 |

The average molecular weights of the soluble fractions from the extraction procedure described above were measured using a membrane osmometer (Table VI). However, since major portions of the samples were insoluble, it is difficult to attach any significance to the observed difference in molecular weight. Similarly, the molecular weight distribution for two polymers before and after exposure was determined via gel permeation chromatography (Table VII). Here too, the high percentage of insolubles makes this data difficult to interpret. However, it is probable that no drastic change in molecular weight distribution has occurred.

Infrared spectra of the TDI-extended polymers before exposure, after exposure alone, or after separation from the AP mixture which had been exposed showed no significant changes in structural detail.

PMDA Extended Polymers

As indicated previously, the PMDA extended materials prepared in solution were of lower molecular weight than those produced in bulk reactions. This difference is reflected in that weight loss behavior

TABLE VI

MOLECULAR WEIGHT OF SOLUBLE FRACTION

AS A FUNCTION OF EXPOSURE

| Polymer | Condition | Molecular Weight, Soluble Fraction |
|---|---|---|
| TDI - 2° OHSPB | Before Exposure<br>Exposed Alone<br>Exposed with AP | 11-12,000<br>12,500<br>12,200 |
| TDI - 1° OHSPB | Before Exposure<br>Exposed Alone<br>Exposed with AP | 13-14,000<br>10,200<br>10,500 |
| TDI - 1° OHPIB | Before Exposure<br>Exposed Alone<br>Exposed with AP | 31,500<br>14,500<br>15,500 |

TABLE VII

GPC EVALUATION OF POLYMERS

(Elution Solvent - THF)

| Polymer | Solubility in THF, % | Retention (Counts) | Peak ($A^o$) | Molecular Wt.[a] at Peak |
|---|---|---|---|---|
| TDI-extended secondary hydroxyl-terminated saturated polybutadiene (A) | 75 | 23.5 | 890 | 36,800 |
| TDI-extended primary hydroxyl-terminated polyisobutylene (B) | 50 | 23.4 | 950 | 39,200 |
| (A) After 400 hr. exposure | 50 | 23.7 | 800 | 32,700 |
| (B) After 400 hr. exposure | 10 | 23.9 | 710 | 29,500 |
| (A) After 400 hr. exposure with AP | 75 | 23.7 | 800 | 32,700 |

[a]Based on the molecular weight of polystyrene sample absorbed at this peak.

(Table VIII) in that the former gave inconsistent results while the latter gave losses comparable to those obtained with the TDI extended polymers. However, regardless of the polymer molecular weight, the products isolated after exposure were wholly insoluble in tetrahydrofuran. It is probable that this is the result of ester interchange with the residual carboxyl groups and that extensive crosslinking has occurred.

TABLE VIII

EFFECT OF PMDA EXTENSION ON WEIGHT LOSS

| Polymer | Molecular Weight | Weight Loss, % | |
|---------|------------------|----------------|---|
| | | Exposed Alone | Exposed with AP |
| PMDA $-$ $2^o$ OHSPB | Low | 58 | 30 |
| | High | 8.7 | 8.5 |
| PMDA $-$ $1^o$ OHSPB | Low | 2 | 17 |
| | High | 4.4 | 9.7 |
| PMDA $-$ $1^o$ OHPIB | Low | 11 | 35 |
| | High | 7.4 | 15.0 |

In the work described above, no attempt had been made to isolate and collect the products generated in the decomposition of the polymer. Without this information, neither the site of initiation of the degradation nor the mechanism thereof can be arrived at conclusively. Therefore, several gas collection devices were constructed and tested. The first employed a pear-shaped vessel containing the polymer sample. The bottom of this vessel was immersed in an oil bath at 135 C. Attached to the vessel was glass tubing leading to an $LN_2$ trap. Prior to the start of the test, the system was flushed with helium and then closed. In this test, as in the subsequent experiments, only the hydroxyl terminated polyisobutylene was used since it had exhibited the highest weight loss of any material exposed in the oven.

After 400 hours, the polymer sample had lost less than 3 percent by weight and no condensable material was found in the trap. It was concluded that these results may have been due to the relatively small surface area of polymer exposed and to the failure to continually sweep the system with helium. However, a second test apparatus in which an Erlenmeyer flask replaced the pear-shaped vessel and where a continual helium purge was maintained gave equally unsatisfactory results (10 percent weight loss in 300 hours). No condensables were found in the $LN_2$ trap but a trace of wax-like substance was observed in the tube leading to the $LN_2$ trap.

The setups described above were so designed that only part of the equipment containing the polymer sample was heated. In a subsequent design, it was decided that the entire apparatus up to the exit tube from the vessel containing the polymer sample should be heated. To accomplish this, a Hickman still was used. It was placed in two halves of a heating mantle which was packed with glass insulation so that heating would be uniform throughout the still. To the exit tube of the still was attached an uncooled trap which in turn was connected by tubing to the $LN_2$ trap. As in the previous experiment, a continual helium purge was employed. Despite these changes, no better correlation with the oven tests was obtained then in prior tests (5 percent weight loss, no wax-like material isolated). A drop of water had condensed in the $LN_2$ trap but it may have been in the system initially rather than being produced during the polymer degradation.

The failure to duplicate the weight loss behavior observed in oven tests in the several attempts at collecting the gaseous products made it impossible to employ this approach as a means for determining the mechanism of polymer degradation. However, while no mechanism for degradation of the polymers in the presence of AP can be offered, it is evident that both the urethane and ester linkages are not primary sites of attack. Nor does it appear that the presence of tertiary

carbon atoms on the polymer chain (as is the case with the saturated polybutadienes) has any significant effect on polymer-AP interactions. Thus, the crosslinking of the polyisobutylene polymer was at least as great or larger than was observed for the saturated polybutadienes. In the latter polymers, the presence of some residual unsaturation has increased the quantity of insoluble fraction over that which would have been observed for an entirely hydrogenated product.

These results which rule out any significant contribution to crosslinking of the tertiary carbon atoms on the polymer appear to be consistent with data reported by Grassie (Ref. 3). In examining the rate of oxidation of a series of isomeric hexanes (Fig. 2), it was observed that the rate of oxidation decreases with the increase in the number of methyl groups in the compound. This is contrary to the anticipated effect which predicts that the molecule with the greatest number of tertiary carbon atoms should be most readily oxidized. Grassie suggests that the rate controlling reaction is not the formation of a hydroperoxide but rather its decomposition. Therefore, in the latter case, the presence of the methyl groups will tend to stabilize the hydroperoxide and result in the molecule being more oxidation resistant that the straight chain material or those of lesser methyl (or tertiary carbon atom) content.

It is recognized that the Grassie data involves rates of reaction rather than the equilibrium conditions observed in this program. In addition, evidence for the formation of hydroperoxides by reaction of polymer with AP is not wholly conclusive. It is felt, however, that these data do complement each other and in any event do rule out the influence of the tertiary carbon atom.

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_3$$

1

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - CH_2 - CH_3$$

12

$$CH_3 - CH_2 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_3$$

60

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{CH} - CH_2 - CH_2 - CH_3$$

560

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$

1580

Figure 2.  Rate of Oxidation of Paraffins
as a Function of Branching

# CONCLUSIONS

1. Except for the polyisobutylenes, all of the initial polymers (hydroxyl containing or straight hydrocarbon) tested lose relatively little weight on exposure to heat under the conditions employed. In some cases where such weight losses occur during the first 200 hours, this is the result of the removal of a low molecular weight fraction rather than of a product of the thermal decomposition of the polymer.

2. Except for the polyisobutylenes, chain extension of the polymer by either toluene diisocyanate or pyromellitic dianhydride has little effect on weight loss behavior.

3. The polyisobutylenes show high weight losses indicating degradation by unzipping. Endcapping of the hydroxyl groups or chain extension reduces the weight loss to the range observed with the other polymer. This occurs due to the removal of the thermally unstable hydroxyl groups on the polymer.

4. In all cases, exposure at elevated temperature results in chain extension and/or crosslinking of the polymers.

5. The presence of ammonium perchlorate has relatively little effect on the weight loss suffered by the polymer but results in a higher quantity of insoluble product than when the polymer is exposed alone.

6. The relatively small weight losses observed for the polymers may be misleading in evaluating their utility in specific applications in that mechanical properties as evidenced by increased hardness, shrinkage, and cracks have been significantly altered by exposure.

7.  While no mechanism based on unequivocal data can be offered, it would appear from the oven tests that:

    a.  Neither the urethane nor ester linkage is the site of degradation.

    b.  The presence of tertiary carbon atoms do not represent a weak point in the polymer.

# FUTURE WORK

It is recommended that future programs examine the change in mechanical properties of chain extended uncrosslinked systems such as those studied as a function of exposure and the presence or absence of AP. Correlation of such results to the chemical changes such as increased crosslinking (as measured by reduced solubility) would be extremely valuable.

# REFERENCES

1.  C. Robillard, AIAA Meeting on Solid Propellants, Sacramento, California, March 1967.

2.  Jet Propulsion Laboratory Space Program Summary, 37-52, Vol. 3, p. 97, 31 August 1968.

3.  Grassie, N., "Chemistry of High Polymer Degradation Processes," p. 231, Butterworths Scientific Publications, 1956.