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Hydrazine Compatibility with Ethylene-Propylene Elastomers

Prepared by H. H. TAKIMOTO and G. C. DENAULT
Aerodynamics and Propulsion Research Laboratory

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Laboratory Operations
AEROSPACE CORPORATION

Prepared for SPACE AND MISSILE SYSTEMS ORGANIZATION
AIR FORCE SYSTEMS COMMAND
LOS ANGELES AIR FORCE STATION
Los Angeles, California

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FOREWORD

This report is published by The Aerospace Corporation, El Segundo, California, under Air Force Contract No. Fo4701-68-0200.

This report, which documents research carried out from March 1968 to January 1969, was submitted on 22 April to Lieutenant Craig A. Baer, SMTTM, for review and approval.

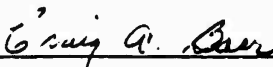
The authors are grateful to Drs. P. C. Marx and P. Breisacher for the analyses of the hydrazine decomposition gases, and to W. R. McDonald for his helpful comments.

Approved



Walter R. Warren, Director
Aerodynamics and Propulsion
Research Laboratory

Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.



Craig A. Baer
2nd Lt., United States Air Force
Project Officer

ABSTRACT

The compatibility of several ethylene-propylene elastomers with hydrazine has been investigated. The gas evolution rate resulting from the catalytic decomposition of hydrazine by elastomers has been determined under ambient conditions. By varying the formulation of one ethylene-propylene rubber (EPR 132), we determined that the carbon black filler material in the elastomer is responsible for promoting the decomposition of the fuel.

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I. INTRODUCTION

Elastomers exhibiting long-term compatibility with hydrazine are required in hydrazine monopropellant systems being developed for many satellite applications. Compatibility of the elastomer with the fuel is particularly important in propellant bladder application in systems where positive expulsion devices are used. This report presents results of an investigation to determine the catalytic decomposition of hydrazine by several ethylene-propylene elastomers at ambient temperatures. The elastomer (EPR 132) composition was modified, and studies were made of ingredients in ethylene-propylene formulations believed responsible for promoting the decomposition.

II. BACKGROUND INFORMATION

Elastomers of ethylene-propylene rubber are used as positive expulsion bladder components in hydrazine monopropellant tanks. Although these elastomers are relatively inert to reaction with the fuel, some decomposition of the hydrazine occurs, with concomitant evolution of gaseous products. The rate of hydrazine decomposition by the elastomers is important, since the presence of gases in the fuel would interfere with the smooth and efficient operation of the monopropellant motor, and result in serious performance problems during flight. Data on gas evolution are essential in determining if the extent of hydrazine decomposition can be tolerated for the duration of the mission.

Ethylene-propylene rubber elastomers are also used as valve seat materials in hydrazine monopropellant systems. Failure of these valves, which have been observed during tests, is attributed in part to swelling of the elastomer valve seat during repeated exposure to the propellant. These elastomers are far superior to other rubbers in their compatibility with hydrazine; however, their properties change considerably under certain conditions. Weight changes of the elastomer specimens after immersion in hydrazine during the gas evolution study were also determined for Stillman Rubbers 721-P80 and 724-90 and for the modified EPR 132; such changes may be related to the degree of swelling.

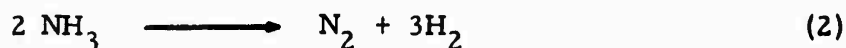
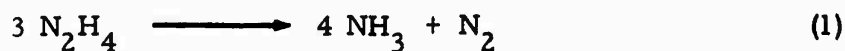
Studies of elastomer compatibility with hydrazine reported by other laboratories (Refs. 1-4) have generally involved the immersion of the specimens in a sealed container and the measurement of pressure increase with time. In the present study the volume of the evolved gases was determined at constant pressure in an essentially all-glass system at ambient temperatures.

III. EXPERIMENTAL PROCEDURE

Specimens approximately 3 in. long by 3/4 in. wide, and 0.05 to 0.09 in. thick were prepared from thin sheets of ethylene-propylene rubber, washed with isopropyl alcohol, and dried before use. These elastomer samples were immersed in 140 ml of 97 percent anhydrous hydrazine (Matheson, Coleman, and Bell), and the evolved gases were collected over the propellant at 1 atm. A drying tube containing "Drierite" and "Ascarite" was used to protect the hydrazine from water and carbon dioxide contained in the atmosphere. An all-glass apparatus was used except for a small Teflon-covered magnetic stirring bar used to remove gas bubbles that formed on the elastomer surface. The effective contact area between the hydrazine and the elastomer sample was decreased if these bubbles were allowed to remain on the surface of the elastomer; however, all bubbles were not removed, even after agitation. The use of glass-covered stirring bars, which tended to break easily, showed a negligible difference in the rate of gas evolution. Volumetric readings were taken immediately after the gas bubbles were manually removed from the elastomer surface and the glass wall.

IV. RESULTS AND DISCUSSION

The decomposition of hydrazine generally occurs with the formation of ammonia and nitrogen. Ammonia further decomposes to produce hydrogen and more nitrogen; thus, the following equations can be written for the hydrazine decomposition reaction:



The gaseous products from one elastomer run (EPR 132) were investigated using a mass spectrometer. At least 99 percent of the evolved gases collected over hydrazine was found to be nitrogen; no hydrogen was detected. The catalytic decomposition of the propellant by the elastomer appeared to proceed via Eq. (1). Apparently the further decomposition of ammonia (Eq. 2) does not occur at room temperature under the conditions of our study. Equation (1) shows that 4 moles of ammonia were formed for every 1 mole of nitrogen, and thus the evolved gases totaled five times the observed values. The solubility of ammonia in hydrazine at room temperature and 1 atm pressure is approximately 0.05 mole fraction,¹ as compared with 10^{-5} mole fraction for nitrogen (Ref. 5); therefore, although ammonia was the major product formed, its high solubility in hydrazine precluded its presence in large amounts in the gases trapped over the liquid.

Results (average of two specimens) of the gas evolution study are shown in Table 1 and Fig. 1. For long-term storage, Uniroyal 3015 exhibited the best compatibility behavior with hydrazine, despite its rapid rate of gas evolution that persisted for several days. In fact, during the first day, the

¹ E. T. Chang, N. A. Gokcen, and T. M. Poston, unpublished work.

evolved gases amounted to more than ten times the volume of the stabilized rate; stabilization occurred after about five days. It may be possible that a pretreatment with the fuel would eliminate some of the initial rapid surge of gas evolution, since a temporary increase in gas evolution was noted when fresh hydrazine was added. Of the elastomers tested, only the solutions in which the Uniroyal elastomer was immersed turned yellow in color, indicating the extraction of some material from the rubber into the solution.

Both SR 721-P80 and SR 724-90 (Table 1) are elastomers that are generally used as valve seat materials. In such applications only a very small portion of the elastomer surface is exposed to fuel, and gas evolution characteristics of the elastomers are not as critical as other properties; e. g., hardness and swelling. After 15 days of immersion in hydrazine at 73°F, SR 721-P80 and SR 724-90 increased in weight by 1.89 and 2.14 percent, respectively.

Two samples of EPR 132 (from Martin Marietta Corp., Denver, Colo.) were coated with Kraton 101,² a styrene-butadiene block copolymer, and tested with dissimilar results. The specimen coated with a thin layer of Kraton 101 (0.358 g coating on 2.262 g elastomer) had a considerably faster rate of gas evolution than the specimen coated with a heavier layer (0.427 g coating on 2.223 g elastomer). Although the coating on both specimens appeared clear and transparent before initiation of tests, only the latter became whitish-opaque in color during the tests. The coating on this specimen (the better sample in terms of compatibility) became detached from the elastomer when the specimen was washed with water after conclusion of the test.

A considerable discrepancy in gas evolution rates was obtained for the two samples of EPR 132 from different sources. The first sample was cut from an actual propellant bladder obtained from Martin Marietta Corp. This bladder had been exposed to hydrazine during two five-day slosh tests, in addition to a 48-hr soak prior to its receipt in our laboratory. The rate of gas evolution at 70±2°F during four days was 0.0096 in.³/in.²/day; at the end of the fourth day agitation of the immersed specimen was stopped and the

²Elastomer specimens were coated by W. R. McDonald, Materials Sciences Laboratory, The Aerospace Corporation.

Table 1. Elastomer-Hydrazine Gas Evolution at 70°F

| Elastomer | Gas Evolved, ^a in. ³ / in. ² / day |
|---------------------------------|--|
| Parker E515-8 | 0.0101 |
| Uniroyal 3051 | 0.0044 ^b |
| EPR 132 coated with Kraton 101 | 0.0099 and 0.0040 ^c |
| EPR 132 ^d (sample 1) | 0.0096 ^e |
| EPR 132 ^f (sample 2) | 0.0236 ^g |
| SR-721-P80 | 0.0127 ^g |
| SR-724-90 | 0.0372 ^g |

^a Volume of gas evolved per area of elastomer exposed in one day.

^b Rate of gas evolution stabilized after about five days. Rate of gas evolution on first day: 0.0512 in.³/in.²/day.

^c Coating delaminated after elastomer was removed from propellant.

^d Obtained from Martin Marietta Corp. Previously exposed to hydrazine.

^e Rate of gas evolution at 90°F: 0.0270 in.³/in.²/day.

^f Prepared by AFML.

^g Sample at 73°F.

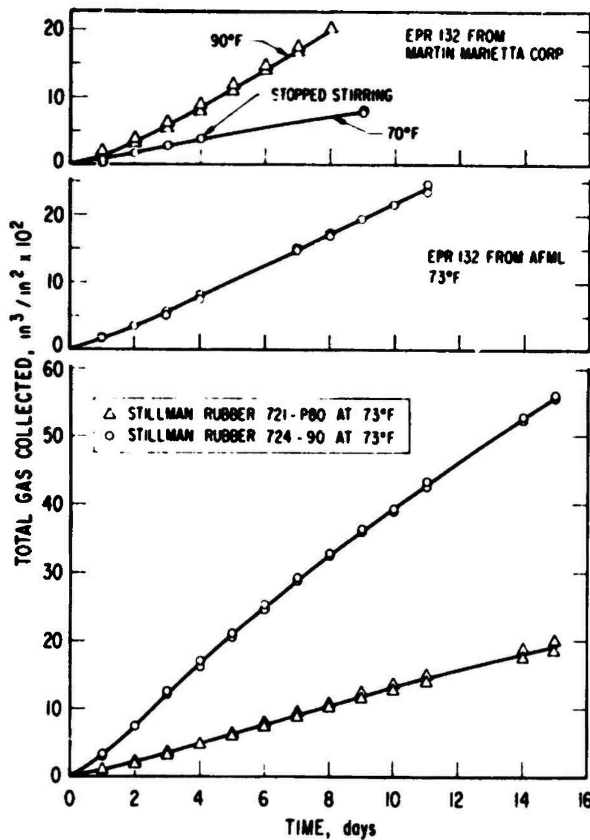
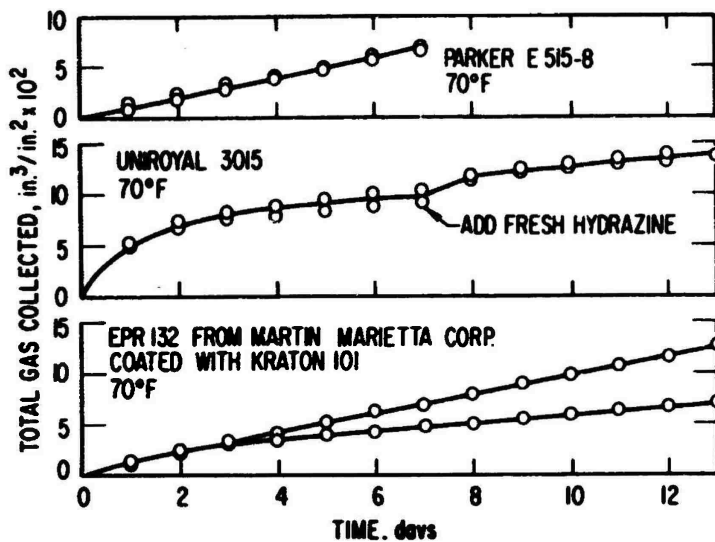


Fig. 1. Elastomer-Hydrazine Gas Evolution at 70°F

rate of gas evolution decreased to 0.0084 in.³/in.²/day. The same EPR 132 formulation fabricated at AFML had a considerably higher rate of gas evolution of 0.0236 in.³/in.²/day at 73°F. This difference in behavior can be attributed to the batch-to-batch variations in properties so common in elastomer fabrication, and/or to the prior exposure of the rubber to the propellant in the case of the elastomer fabricated at Martin Marietta.

In order to determine the ingredient in elastomer formulations responsible for the catalytic decomposition of hydrazine, different compositions of EPR 132 were prepared by AFML.³ The standard EPR 132 (Ref. 4) is fabricated of 100 parts ethylene-propylene rubber (Enjay 404), 50 parts carbon black (Statex R, HAF), and 10 parts Di-cup 40C (Hercules Powder Company). Di-cup 40C is 40 percent dicumyl peroxide and 60 percent calcium carbonate. The following modifications were made to the standard EPR 132:

| <u>Designations</u> | <u>Formulations</u> |
|---------------------|--------------------------------------|
| EPR 132A | Cured with Di-cup 40-HAF |
| EPR 132B | Cured with Di-cup R-HAF |
| EPR 132C | Cured with Di-cup R; no carbon black |

Di-cup R is recrystallized dicumyl peroxide. Two sets of the above formulations were obtained for testing, one with the standard press-cure of 40 min at 300°F and the second with an additional postcure of 16 hr at 200°F. The additional postcure eliminated the peroxide decomposition products from the elastomer but did not appreciably change its physical properties.

³ Prepared by J. K. Sieron, Elastomers and Coatings Branch, Non-Metallic Materials Div., Air Force Materials Laboratory.

The results of the compatibility studies of modified EPR 132 are shown in Table 2 and Fig. 2. Comparison of the gas evolution rates indicates that the carbon black used as filler material is primarily responsible for the catalytic decomposition of hydrazine. The additional postcure appears to cause a slight increase in the rate of decomposition. Calcium carbonate used as a peroxide dispersing agent in Di-cup 40C has little effect, if any, on the rate of decomposition.

The edge effect of the specimens on the catalytic decomposition of hydrazine was not investigated. However by keeping the specimen dimensions relatively constant, it was possible to compare the gas evolution rates with more significant results.

Table 2. Compatibility of Modified EPR 132 in Hydrazine at 73°F

| Designation | Immersion Time, days | Weight Increase, Percent | Gas Evolved, ^a in. ³ /in. ² /day |
|-------------------------|-------------------------|-----------------------------|--|
| EPR 132 | 11 | 3.75 | 0.0218 |
| EPR 132 ^b | 16 | 4.19 | 0.0236 |
| EPR 132A | 16 | 3.85 | 0.0259 |
| EPR 132A ^b | 11 | 3.97 | 0.0265 |
| EPR 132B | 18 | 3.66 | 0.0275 |
| EPR 132B ^b | 15 | 3.24 | 0.0289 |
| EPR 132C ^c | 18 | 0.76 | 0.0005 |
| EPR 132C ^{b,c} | 16 | 1.84 | 0.0009 |

^a Volume of gas evolved per area of elastomer exposed in one day.

^b Postcured 16 hr at 200°F after standard 40-min press-cure at 300°F.

^c No carbon black.

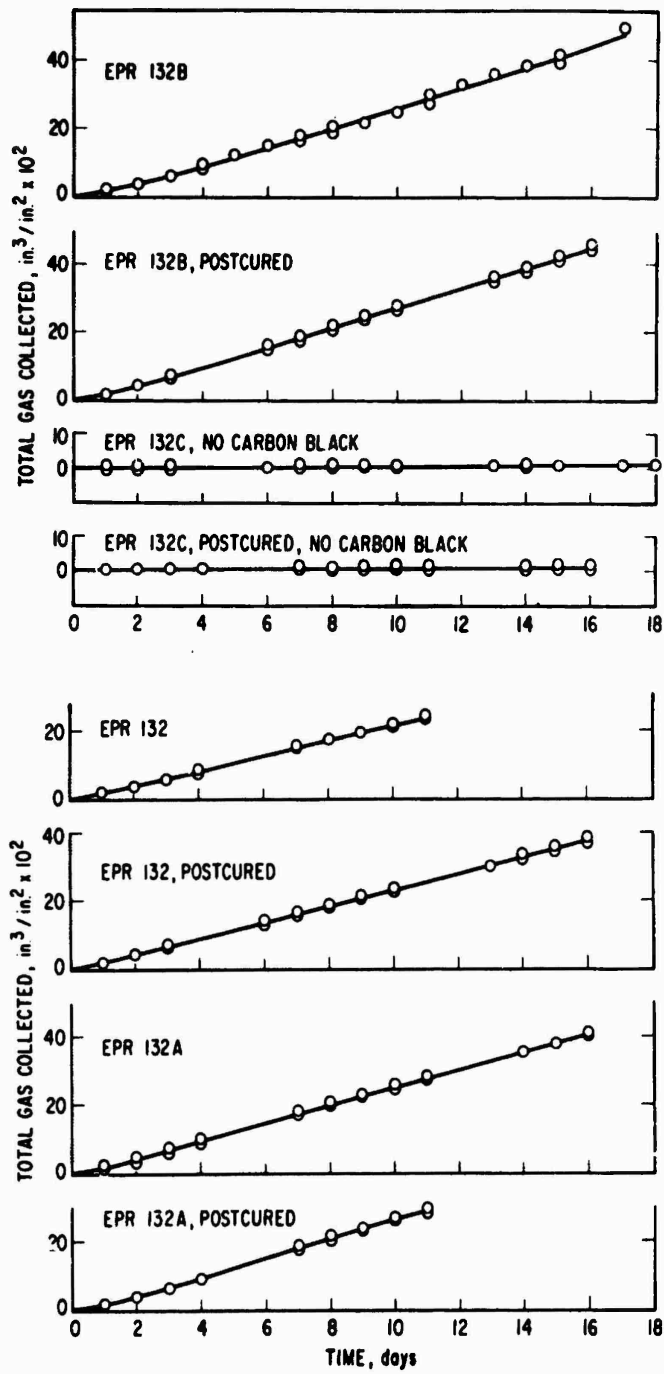


Fig. 2. Compatibility of Modified EPR in Hydrazine at 73°F

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Abstract (Continued)

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