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LOX/GOX SENSITIVITY OF FLUOROELASTOMERS

By: NORMAN KIRSHEN and THEODORE MILL

Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA 34812

Attention: S&E-ASTN-MNR
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ABSTRACT

The effect of formulation components and the addition of fire retardants on the impact sensitivity of Viton B fluoroelastomer in liquid oxygen was studied with the objective of developing a procedure for reliably reducing this sensitivity.

Component evaluation, carried out on more than 40 combinations of components and cure cycles, showed that almost all the standard formulation agents, including carbon, MgO, Diak-3, and PbO_2, will sensitize the Viton stock either singly or in combinations, some combinations being much more sensitive than others. Cure and postcure treatments usually reduced the sensitivity of a given formulation, often dramatically, but no formulated Viton was as insensitive as the pure Viton B stock. Coating formulated Viton with a thin layer of pure Viton gave some indication of reduced sensitivity, but additional tests are needed. From these results we conclude that sensitivity in formulated Viton arises from a variety of sources, some physical and some chemical in origin.

Our studies of the effect of polymer fire retardants on the sensitivity of fully formulated and cured Viton B indicate that among the six retardants or combinations tried, only SbOCl was effective in significantly reducing the sensitivity at loadings of 17 and possibly 4.3 pph. These results with SbOCl give us some confidence that a satisfactory procedure can be found for desensitizing formulated Viton and other fluoroelastomers without significantly sacrificing their physical properties.

Elemental analyses for all the formulated Vitons are reported as are the results of a literature search on the subject of LOX impact sensitivity.

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INTRODUCTION

This is the final report prepared for this program under Contract No. NAS8-28898. The objective of this work was to study the chemical and physical factors that influence the liquid oxygen (LOX) impact sensitivity of Viton B fluoroelastomer so as to reduce this sensitivity without sacrificing the useful properties of this material.

Viton and related fluoroelastomers are used extensively in spacecraft construction because of their superior properties under extreme environments. Extensive LOX impact testing of Viton over many years has shown that batches of formulated and cured elastomer can pass the strict test requirements,[1] but that among many batches of Viton products otherwise identical some will pass and some will fail. During the last few years NASA/Marshall has found that Viton products are increasingly variable in their LOX impact sensitivity.

The SRI investigation of LOX impact sensitivity of Viton B was based on the assumption that either the source of variability of sensitivity could be uncovered by a systematic examination of formulation components and procedures or that whatever the source or sources of variability, certain additives or treatments might desensitize all Viton samples. If successful, either approach would provide a reliable source of LOX-insensitive Viton-B materials for NASA and eliminate or markedly reduce the need for time-consuming and expensive batch testing.

Accordingly, this program was divided into two phases. Phase I was an evaluation of the separate and combined effects of standard special formulation components on a particular Viton B elastomer composition in conjunction with a study of the effects of press cure and postcure on impact sensitivity. Phase II was an examination of the effects of selected fire retardants and treatments on the LOX/GOX impact sensitivity of a particular Viton fluoroelastomer.

BACKGROUND

Viton B, a Du Pont terpolymer of vinylidene fluoride, hexafluoropropylene, and a small amount of tetrafluoroethylene,[2] is only one of several fluoroelastomers used by NASA. However, since Viton-B is one of the more extensively used and impact-tested, it was chosen for investigation in this initial study with the reasonable assumption that any effective desensitizing agents or techniques developed for Viton-B could be applied usefully to other elastomers.

A useful working elastomer is prepared from raw stock by milling together elastomer and several formulation components and then heating the mixture for prescribed periods at several temperatures. The usual Viton elastomeric formulation used in LOX environments contains a crosslinking diamine such as Diak-3, MgO acid acceptor, carbon black filler, and PbO_2, which provides a "tighter" cure but has no clearly established function. These components are milled together and then cured and postcured to produce a vulcanized elastomer that possesses the desired physical properties. The chemistry of the curing process is complex, requiring removal of HF, addition of amine groups, and possibly cycloaddition between polymer chains.[3]

It is currently assumed that the increased sensitivity of the cured elastomer is a result of the separate or additive effects of the formulation components in conjunction with the press cure and postcure cycles or is a result of physical and chemical changes associated with vulcanization. These effects were studied in Phase I of this program.

The success of fire retardant agents in plastics used in ambient atmospheres suggest that the same materials may be effective in reducing the impact sensitivity of Viton elastomers in LOX. The compounds that find the greatest use as conventional fire retardants are bromine compounds, phosphate esters such as tri-o-cresyl phosphate, bromoalkyl and chloroalkyl phosphate esters, mixtures of highly chlorinated organic compounds with antimony oxide, and certain borates such as zinc borate.

What little information that is available on the response of phosphate esters and halogen compounds to LOX impact does not allow a prediction of their efficacy as fire retardants for elastomers for LOX service. Previous work done at SRI[4] for NASA showed that certain organobromine compounds markedly reduced the impact sensitivity of simple organic compounds such as benzene. No other LOX sensitivity data on bromine compounds or their effect as desensitizers are available. The report of Hauser et al[5] gives impact sensitivities determined for tri-o-cresyl phosphate, triphenyl phosphate, and a number of chlorinated organic liquids. The phosphate esters have an intermediate sensitivity to LOX impact. The sensitivity threshold of the chlorine compounds increases as hydrogen atoms are replaced by chlorine atoms. The highly chlorinated compounds for which data are available have low impact sensitivities. Test data for polyvinyl chloride, polyvinylidene chloride, and a chlorinated polyether show a low order of sensitivity for all three polymers. Phase II of this program sought to establish the possible value of several fire retardants in reducing the LOX sensitivity of fully formulated and cured Viton B.

COMPONENT EVALUATION

Procedure

Most Viton formulations described in this section were based on the following NASA-Marshall specified recipe:

Component	Parts Per Hundred	Source
Viton B	100	Du Pont
Maglite Y	7	C. P. Hall Co.
NS carbon black	20	Cabot Corporation
Lead dioxide	7	Fisher Scientific
Diak 3	4	Du Pont

A standard procedure for preparing Viton elastomer formulations was devised with two objectives: (1) to keep any unspecified variables in the preparation procedure constant and (2) to prepare homogeneous samples with clean, dust-free surfaces. In this procedure, Viton formulation components are weighed, then milled together on a 6-in., 2-roll rubber mill (Reliable No. 1982) for exactly 30 minutes using batch weights of 150-450 g. After milling, the batch is divided into 75-g batches. Each batch is pressed in an aluminum window mold (1/16 in. thick, 6 x 6 in.) and between two pieces of 5-mil-thick FEP* film, which has been cleaned with trichloroethylene. Pressing continues for 30 minutes at 150°C on a Dake Corporation Model 44-250 press. Samples that do not require press cure are pressed only long enough to obtain a 1/16-in. sheet approximately 5 minutes.

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*Du Pont tradename for a copolymer of tetrafluoroethylene and hexafluoropropylene.

The FEP film is removed and the samples are then postcured according to the following schedule:

30 min at 135°C
2 hr at 150°C
2 hr at 175°C
24 hr at 200°C.

Following postcure, sample sheets are removed from the oven and placed between two clean pieces of 5-mil-thick FEP. One hundred disks (11/16 in. dia x 1/16 in. thick) are then punched from the 6 x 6 in. sheet and the FEP peeled from each. Initially disks were degreased by rinsing with trichloroethylene, but this was stopped after formulation 16 when tests showed no change in sensitivity after washing. Finally, the disks are loaded into Aclar* bags for shipping to NASA-Marshall.

Several formulations were either specially prepared or given special after-treatments. Formulations 47-49 containing Diak 1 were prepared identically to corresponding formulations containing Diak 3; a lesser amount of Diak 1 was used because of its lower molecular weight, but equivalent molar amounts of diamine crosslinker were used with both Diak 3 and 1. Formulation 53 was fully formulated, and cut into disks, then extracted with three portions of ethyl acetate (reagent grade) for 6 hours at 25°C. Excess ethyl acetate was removed from the disks by heating in a vacuum oven at 100° and 10^{-3} torr for 12 hours.

Formulation 54, prepared in exactly the same way as 53, was coated on both surfaces with a thin film of pure Viton by dipping the postcured sheet in a 15% solution of Viton dissolved in methyl ethyl ketone. The sheet was dried in a circulating air oven at 100°C for 16 hours and cut

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*Allied Chemical Corporation tradename for fluorohalocarbon polymer.

into disks. The coating on each disk was estimated to be 3-5 Mils thick.

All impact tests were carried out at NASA-Marshall on 100 disks of each formulation using the ABMA impact tester and following the procedure outlined in MSFC-SPEC-106-B. Results were reported by NASA-Marshall in four categories: A flash on primary impact, a flash on rebound, an audible report on rebound, and a flash and audible report on rebound. However, the MSFC-SPEC-106-B criteria makes no distinction between primary and rebound reactions. No reactions of any kind in the first 20 samples impacted at 10 kg-m imput energy is considered acceptable; reaction in the initial 20 followed by no reactions in the next 40 impacts is also acceptable. Two reactions in the first 20 impacts leads to rejection.

We report only total reactions in 100 impacts, and in most cases we have no way of telling whether a formulation would have passed or failed since the sequence of reactions in 100 trials was not reported to us.

Results

Standard Components

Thirty-eight formulations were prepared using standard formulation components in most of the possible combinations. Several nonstandard formulations or treatments were also prepared. All the standard formulations are listed in Table I together with impact test results. To ensure that our formulation procedures and NASA's test procedure were reproducible, we prepared several formulations using the same components and cure cycles. These replicate samples are mostly grouped together in Table I. For example formulations 1, 25, 26, and 41 are all pure Viton stock. Formulation 1 was remarkably sensitive but the other three were insensitive as expected. The

Table I

EFFECT OF STANDARD FORMULATION COMPONENTS ON VITON-B IMPACT SENSITIVITY

Components (pph)[a]		Formulation Number																																			
		1	25	26	41	2	2R	3	3R	4	4R	30	28	29	27	5	5R	6	7	7R	8	9	10	11	11R	12	13	14	15	16	14u[b]	15u[b]	16u[b]	16R	17	18(pph)	19	36	52
Viton-B	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X(100)	X	X	X
Carbon	20	-	-	-	-	X	X	-	-	-	-	-	-	-	X	-	-	-	-	-	X	X	X	-	-	-	-	X	X	X	X	X	X	X	-	X (20)	X	X	X
Maglite Y	7	-	-	-	-	-	X	X	-	-	-	-	X	-	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	-	X (15)	X	X	X
PbO$_2$	7	-	-	-	-	-	-	-	-	X	X	-	X	X	X	-	-	-	-	-	-	-	-	X	X	X	X	X	X	X	X	X	X	X	-	-	X	X	X
Diak-3	4	-	-	-	-	-	-	-	-	-	-	X	-	X	-	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X (3)	X	X	X
Cure[c]		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	X	X	X	-	X	X	-	-	X	X	-	X	X	-	X	X	X	X	X	X	X	X
Postcure[d]		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	X	X	-	-	X	-	-	-	X	-	-	X	-	-	X	X	X	X	X	X	X
Flashes/primary impact		5	0	0	0	0	1	0	2	3	0	0	0	0	0	0	0	0	1	0	0	0	0	5	5	0	0	0	0	2	0	0	0	0	1	0	0	0	0
Flashes/rebound		5	1	1	1	5	5	6	18	6	5	14	4	22	2	3	13	3	5	4	2	1	2	9	0	2	3	3	1	1	2	3	1	0	2	2	0	5	17
Audible/rebound		10	0	0	0	5	0	3	7	3	2	3	1	5	3	6	5	0	0	0	5	2	2	27	14	5	1	1	2	2	1	2	2	5	2	0	5	0	0
Flash/audible/rebound		1	0	0	0	0	4	0	0	0	0	0	0	0	1	1	0	0	0	0	0	1	0	1	0	0	0	0	0	1	0	0	0	0	0	1	0	0	0
Total Positives/100 samples		21	1	1	1	10	10	9	27	12	7	17	5	27	7	10	18	3	6	4	7	4	4	42	19	7	4	4	3	6	3	5	3	5	5	2	5	5	17

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[a] Parts per hundred.

[b] Samples unwashed.

[c] 30 min at 150°C.

[d] Oven cure: 30 min at 135°C; 2 hr at 150°C; 2 hr at 175°C; 24 hr at 200°C.

general reproducibility of these tests on duplicated and replicate samples is about ±30% over the full range of sensitivity from samples such as 16 and 16R (4/100 and 6/100) to 11 and 11R (42/100 and 19/100).

To make cross comparisons among these formulations easier, we have listed in Table II a group of uncured formulations having at least one formulation component. Most of these samples have at least 10 incidents per 100 samples, which is considered quite sensitive; 11 is the most sensitive formulation prepared, with 42 incidents per 100 samples.

Although no one component or combination of components seems to especially sensitize Viton B, those containing Diak-3 may be somewhat more sensitive. There does appear to be a clear reduction in sensitivity when carbon is added to formulations (compare 5 or 5R and 8; and 11 or 11R and 14).

Another clear relation between sensitivity and composition emerges from comparisons of the effect of cure and postcure as shown in Table III.

Formulations 5, 6, and 7 constitute a group with identical component formulation but with different cure and postcure treatments. The uncured sample, 5, shows a higher sensitivity than the two other samples, which were cured or cured and postcured. Even more dramatic is the change in the set 11, 12, and 13 where postcure effects a reduction of 38 incidents per 100 samples.

Fully formulated but uncured Viton B is, as we have noted, markedly less sensitive than are samples partially formulated but without carbon. This reduced sensitivity is not further reduced on cure or postcure treatment; addition of carbon seems to be equivalent

Table II

EFFECTS OF COMPONENTS ON IMPACT SENSITIVITY OF UNCURED VITON-B FORMULATIONS[a]

Components (pph)[b]		Formulation Number														
		2	3	3R	4	4R	5	5R	8	30	28	27	29	11	11R	14
Viton-B	100	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Carbon	20	X							X			X				X
Maglite Y	7		X	X			X	X	X		X	X		X	X	X
PbO_2					X	X					X	X	X	X	X	X
Diak-3	4						X	X	X	X			X	X	X	X
Total Positives/ 100 samples		10	9	27	12	7	10	18	7	17	5	7	27	42	19	4

[a] Condensed from Table I.

[b] Parts per hundred.

Table III

EFFECT OF CURE AND POSTCURE ON IMPACT SENSITIVITY OF VITON B FORMULATIONS[a]

Components (pph)[b]		Formulation No.					
		5	6	7	11	12	13
Viton-B	100	X	X	X	X	X	X
Carbon	20						
Maglite Y	7	X	X	X	X	X	X
PbO_2	7				X	X	X
Diak-3	4	X	X	X	X	X	X
Cure			X	X		X	X
Postcure				X			X
Total Positives/ 100 samples		10	3	6	42	7	4

[a] Condensed from Table I.

[b] Parts per hundred

to curing Viton formulations insofar as reduction in sensitivity is concerned. Table IV brings together a group of formulations that illustrates this point. Addition of carbon to formulation 11 reduces its sensitivity to 4 per 100, which is nearly the same as found for 12 and 13, which are cured and postcured versions of 11; on curing or post curing formulation 14 to give 15 or 16, sensitivity is not further reduced.

Table IV

EFFECT OF CARBON AND CURE ON IMPACT SENSITIVITY OF VITON B FORMULATIONS[a]

Components (pph)[a]		Formulation No.					
		11	12	13	14	15	16
Viton B	100	X	X	X	X	X	X
Carbon	20				X	X	X
Maglite	7	X	X	X	X	X	X
PbO_2	7	X	X	X	X	X	X
Diak-3	4	X	X	X	X	X	X
Cure			X	X		X	X
Postcure				X			X
Total Positives/100		42	7	4	4	3	6

[a] Condensed from Table I.

[b] Parts per hundred.

Carbon Black as a Variable in LOX Sensitivity of Viton B

The results in Table IV show clearly that carbon black is an effective desensitizing component in Viton B formulations, and at 20 pph it is the chief component of standard formulations. Therefore, the effect of carbon black on sensitivity is of special interest, related perhaps to its chemical and physical properties as well as to the level of loading.

For these reasons we prepared four samples (31, 32, 33, and 34) of uncured Viton-B plus carbon black in which the following properties of the carbon black filler were varied: loading, particle size, and volatiles. The effect of loading on sensitivity was examined by doubling the amount of Sterling NS. Particle size was varied in one formulation by using a carbon black that has small particles (Regal 330). Volatiles were studied using Mogul special, a carbon black that also possesses a smaller particle size and lower pH than Sterling NS. The formulations, the pertinent properties of these carbon black fillers, and the resultant impact sensitivities obtained are shown in Table V along with results obtained with the Viton-B carbon black mixture used in our standard formulation (2 and 2R). The results appear to indicate that the loading and the particle size of carbon have little, if any, effect on the impact sensitivity.

The formulation containing Mogul Special (34) exhibited more primary positive impacts than the standard formulations (2 and 2R), but the total number of positives was somewhat reduced. This suggests that, if volatiles in carbon have an effect on sensitivity, it is not a large one.

This study was completed before all the results on multiple component formulations were available. Perhaps a study similar to this one but using a complete formulation such as 14 might give different results.

Organic Sensitizers: Diaks and Their Products

Although no clearcut sensitization by Diak 3 was shown in the results in Table I, there is a trend in that direction. The desensitization effected by carbon and by curing can be explained by a common mechanism, namely, that Diak 3 hydrolyses to give cinnamaldehyde and hexanediamine and that cinnamaldehyde in particular (which is easily oxidized and therefore sensitizes) is removed by carbon or by volatilization during curing. In preliminary experiments in which formulations were extracted before and after curing, formulations were found by gas

Table V

COMPOSITION AND IMPACT SENSITIVITIES OF VITON-CARBON FORMULATIONS

Components	(pph)[a]	Formulation Number						Carbon[b] Chemical and Physical Properties			
		Standard		Variations							
		2	2R	31	32	33	34	Nitrogen Surface Area (m^2/g)	Particle Size $(m\mu)$	Volatile Content (%)	pH
Viton-B	100	X	X	X	X	X	X				
Sterling NS	20	X	X					27	90[c]	1.0	--
Sterling NS	40			X				27	90[c]	1.0	--
Sterling MT-FF	20				X			8	250	0.5	9.5
Regal 330	20					X		86	25	1.0	7.5
Mogul Special	20						X	24	24	13.0	3.5
Flashes/primary		0	1	2	0	0	3				
Flashes/rebound		5	5	3	6	2	4				
Audible/rebound		5	0	3	1	3	1				
Flash/audible/rebound		0	4	1	0	0	0				
Total positives/100 samples		10	10	9	7	5	8				

[a] Parts per hundred.

[b] These data obtained from technical information brochures suppl

[c] Calculated from surface area information by assuming spherical

chromatographic analysis to have more cinnamaldehyde after curing but this amount decreased during postcuring.

Whether or not it is correct, this line of thinking prompted two studies on the possible role of cinnamaldehyde as a sensitizer. First, several formulations were prepared in which Diak 3 was replaced with an equivalent amount of Diak-1 (the carbamate ester of hexanediamine), which in hydrolysis can give only alcohol, carbon dioxide, and diamine. Second, one standard, cured formulation containing Diak 3 was extracted with ethyl acetate, an effective swelling solvent for Viton B, to remove residual amounts of non polymeric organic compounds including cinnamaldehyde. Small weight losses of ~0.5% indicate that extraction was removing soluble organic material; no dimensional changes in the discs were noted.

Results with Diak-1, Nos. 42-49, may be compared with their Diak-3 analogs, Nos. 11-16, where the initial three samples in each series were formulated without carbon and the later three samples were complete formulations. A marked reduction in sensitivity is found for the uncured formulation containing Diak-1 (no carbon) compared to the formulation containing Diak-3 (no carbon), that is No. 42 versus No. 11. The difference disappears on addition of carbon or on curing. In fact, the cured complete Diak-1 formulations are slightly more sensitive than those containing Diak-3. We are suspicious of the results in Nos. 47-49 because of the very high sensitivity of a standard formulation, No. 52, prepared at the same time (see Table VII).

No. 53 in Table VI was a standard formulation extracted to remove unbound organic material. Its sensitivity is also very high for a completely formulated material; either extraction in some way actually sensitized the sample by creating interstitial voids or this series of formulations (nos. 47-54) were adventitiously sensitized in some unknown way. The result for formulation No. 54 is therefore puzzling since it shows a low sensitivity comparable to that of other fully formulated samples such as Nos. 16 or 16u. Its unexceptional sensitivity may reflect an exceptional reduction in sensitivity over its uncoated counterpart, No. 52 (4/100 versus 17/100).

Table VI

EFFECT OF DIAK 1, EXTRACTION, AND COATING ON IMPACT SENSITIVITY OF FORMULATED VITON B

Components (pph)[a]		Formulation No.							
		42	43	44	47	48	49	53[b]	54[c]
Viton B	100	X	X	X	X	X	X	X	X
Carbon	20				X	X	X	X	X
Maglite Y	7	X	X	X	X	X	X	X	X
PbO_2	7	X	X	X	X	X	X	X	X
Diak-3	4							X	X
Diak-1	1.5	X	X	X	X	X	X		
Cure			X	X		X	X	X	X
Postcure				X			X	X	X
Flashes/primary		0	1	0	0	2	0	0	0
Flashes/rebound		2	5	8	4	6	3	5	4
Audible/rebound		1	0	0	4	1	0	9	0
Flash/audible/rebound		0	0	0	0	0	0	0	0
Total positives/100 samples		3	6	8	8	9	3	14	4

[a] Parts per hundred.

[b] Extracted with EtOAc at 25°.

[c] Coated with 3-5 mil unformulated Viton stock.

EFFECT OF FIRE RETARDANTS ON IMPACT SENSITIVITY

The successful use of fire retardants in plastics in ambient atmospheres suggests that they might be effective in reducing the impact sensitivity of Viton in LOX. The most commonly used retardants contain bromine, chlorine, phosphorus, antimony, or boron, or combinations of these elements. The work described in this section used all of these classes of retardants.

Procedures

The following fire retardants were selected for incorporation into Viton-B formulations because they are effective fire retardants in polymers and are stable at 200°C, the postcure temperature for Viton-B.

Retardant	Chemical Formula	Source
Tricresyl phosphate	$[C_6H_4(CH_3)O]_3PO$	Stauffer Chemicals
Tris(2,3-dichloropropyl)phosphate	$[CH_2ClCHClCH_2O]_3PO$	Stauffer Chemicals
Tris(2,3-dibromopropyl)phosphate	$[CH_2BrCHBrCH_2O]_3PO$	Stauffer Chemicals
Antimony oxide	Sb_2O_3	Fisher Scientific
Antimony oxychloride	SbOCl	K & K Laboratories
Dechlorane Plus 515	proprietary (65% Cl)	Hooker Chemical Co.

Elastomers were formulated with retardants by milling in the amount of retardant needed to give 1 wt % phosphorus, 10 wt % Sb_2O_3, 14.5 wt % Dechlorane, and 3-25 wt % SbOCl after all other formulation components were added.

The elastomers containing tricresyl phosphate, tris(2,3-dichloropropyl)phosphate, antimony oxide, antimony oxychloride, and Dechlorane Plus were prepared successfully. While both the tris-phosphates exuded some retardant on press and postcuring, only the tris-(2,3-dibromopropyl)phosphate foamed; it has been reported that decomposition of tris(2,3-dichloropropyl)phosphate occurs at ~200°C.[6] One sample was prepared with carbon coated with 0.03% boric acid.

All samples were impact tested at NASA/Marshall in the usual way.

Results

Impact test results indicate that at the retardant levels tested, tricresyl phosphate and Sb_2O_3 sensitized Viton, but dichloropropyl phosphate, Dechlorane Plus, Sb_2O_3, and boric acid had no real effect. These results are summarized in Table VII.

On the other hand, results with SbOCl shown in Table VIII were initially quite encouraging. Results for three samples containing SbOCl, two at 34 pph and one at 17 pph (25 and 12.5 wt %) indicated that the effect of SbOCl on reducing sensitivity seems quite pronounced. Later results at lower loadings, Nos. 50 and 51, showed little effect of SbOCl on sensitivity but duplicates Nos. 50R and 51R, exhibit very low sensitivities more in agreement with our earlier experiments.

But here again we must view the results at low loadings of SbOCl with some caution owing to the great sensitivities of the standard samples No. 52 and 52R. If we accept the results in Table VIII at face value, however, they indicate that SbOCl is an effective inhibitor even down to the 4.3 pph level where its effect on physical properties should be minimal. Earlier results with 17 and 34 pph clearly show a decrease in sensitivity compared with standards such as Nos. 16 or 16u.

Table VII

EFFECT OF RETARDANTS ON IMPACT SENSITIVITY OF VITON B

Component	pph[a]	Formulation Number									
		19	20	21	22	23	24	38	39	40	35
Standard Viton components		X	X	X	X	X	X	X	X	X	X
Tricresyl phosphate	16.4		X								
Tris(2,3-dibromopropyl)[b] phosphate	13.3			X							
Tris(2,3-dichloropropyl) phosphate	19.2				X						
Antimony oxide (Sb_2O_3)	13.8					X					
Dechlorane Plus 515	20							X	X	X	
Sb_2O_3	10								X		
Sb_2O_3	18									X	
Boric acid[c]											X
Flashes/primary impact		0	2	--	0	2	0	0	0	0	0
Flashes/rebound		0	0	--	2	3	0	9	3	5	1
Audible report/rebound		5	10	--	1	4	0	9	4	7	2
Flashes and audible report/ rebound		0	0	--	0	0	0	0	0	0	2
Total Positives/100		5	12	--	3	9		18	7	12	5

[a] Parts per hundred.

[b] Exudes retardant on cure, foams on postcure; not tested.

[c] Precipitated on carbon black, 0.03 wt %.

Table VIII

EFFECT OF SbOCl ON IMPACT SENSITIVITY OF CURED VITON B

Components	pph[a]	Formulation Number								
		24	24R	37	50	50R	51	51R	52	52R
Standard Viton B formulation (cured and postcured)		X	X	X					X	X
SbOCl	34.4	X	X							
SbOCl	17.2			X						
SbOCl	8.6				X	X				
SbOCl	4.3						X	X		
Flashes/primary		0	0	0	0	0	0	0	0	0
Flashes/rebound		0	4	2	7	2	7	1	17	7
Audible/rebound		0	0	0	2	1	11	2	0	4
Flash/audible/rebound		0	4	2	9	3	18	3	17	11
Total Positives/100 Samples		0	4	2	9	3	18	3	17	11

[a] Parts per hundred.

MICROANALYSES

CHF microanalyses were completed on all Viton samples. Fluorine analyses were done by combusting an appropriate weight of the sample followed by thorium nitrate titration of the fluoride ion in the hydrolyzed products. Carbon and hydrogen were determined using a Hewlett-Packard Model 185 CHN analyzer. The percentages of fluorine, carbon, and hydrogen found are given in Table IX.

Values for residue were measured for the first 29 samples only and generally seemed to be too high when we made the reasonable assumption that MgO and mixed lead oxides were the main constituents. Moreover, comparisons of residue, initial composition, cure state, and sensitivity show no clear relationships among these factors; samples containing either carbon or MgO or both gave no more residue on the average than those without either carbon or MgO. The two most sensitive samples had the least and the most residues (1 and 2 respectively). For these reasons residue analyses were discontinued and are not shown in the table.

X-ray analysis of a residue from the CHN analyzer combustion* of sample 16 showed the residue to be about 60% MgO, 30% Mg_2SiO_4, and 10% an unknown compound. Silicate residue resulting from etching of the combustion flask would account for part of the high residue percentages. The absence of MgF_2 indicates that probably only a small fraction of MgO reacts with HF to form MgF_2. Moreover, formation of any significant

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*Combustion was performed in a platinum boat in a quartz tube at 1160°C with extra-high purity O_2 for 20 minutes.

Table IX

FLUORINE, CARBON, AND HYDROGEN ANALYSES OF VITON FORMULATIONS

Formulation Number	Fluorine (%)	Carbon (%)	Hydrogen (%)
1	64.24%	30.58%	1.63%
2	53.93	41.46	1.62
2R	57.50	41.20	1.47
3	59.71	28.63	1.58
3R	63.20	28.62	1.51
4	59.61	28.57	1.51
4R	62.10	28.71	1.48
5	58.84	30.41	1.74
5R	59.60	30.67	1.70
6	55.98	32.43	2.61
7	57.74	30.29	1.94
8	45.97	40.44	1.52
9	48.30	40.64	1.70
10	43.34	40.57	1.51
11	49.92	28.68	2.03
11R	53.40	28.80	1.60
12	53.10	29.10	2.14
13	57.50	28.33	1.78
14	48.23	38.67	1.70
14u	51.10	38.85	1.44
15	47.32	38.72	1.62
15u	49.90	38.78	2.29

Table IX (Continued)

FLUORINE, CARBON, AND HYDROGEN ANALYSES OF VITON FORMULATIONS

Formulation Number	Fluorine (%)	Carbon (%)	Hydrogen (%)
16	48.12	38.11	1.50
16u	44.58	38.31	1.60
17	57.43	33.23	1.77
18	42.27	38.87	1.79
19	49.50	38.55	1.32
20	53.30	38.70	1.38
21	-----	-----	----
22	50.60	37.75	1.38
23	47.70	34.75	1.18
24	38.80	30.65	1.10
24R	39.71	30.65	1.01
25	66.10	30.60	1.55
26	66.80	30.68	1.54
27	46.50	37.44	1.31
28	55.60	27.02	1.50
29	58.30	30.63	1.67
30	63.90	32.57	1.84
31	48.70	49.70	1.37
32	56.10	42.11	1.45
33	56.10	41.90	1.48
34	58.40	39.61	1.52
35	47.55	38.39	1.21

Table IX (Concluded)

FLUORINE, CARBON, AND HYDROGEN ANALYSES OF VITON FORMULATIONS

Formulation Number	Fluorine (%)	Carbon (%)	Hydrogen (%)
36	50.70	38.58	1.25
37	40.48	33.96	1.24
38	38.22	37.60	1.34
39	40.12	35.33	1.29
40	35.70	33.70	1.21
41	66.50	30.55	1.51
42	53.96	27.39	1.44
43	50.30	27.35	1.44
44	53.20	27.36	1.35
45	-----	-----	----
46	-----	-----	----
47	46.85	37.81	1.33
48	49.15	37.91	1.32
49	47.12	37.73	1.26
50	40.38	36.19	1.22
51	45.29	37.34	1.26
52	47.86	38.41	1.27
53	48.38	38.47	1.31
54	46.41	38.71	1.39

amount of HF and MgF_2 during curing would produce significant losses of analyzable fluorine. The experimental error in CHF analyses is large enough to obscure any small trends associated with the curing process.

We also performed a microanalysis of Diak 3 to check its purity. Comparison of the CHN analyses with the theoretical values based on the empirical formula $C_{24}H_{28}N_2$ (N,N'-dicinnamyladine-1,6-hexanediamine) indicates that Diak 3 is relatively pure as shown below.

	Theory	Experimental
Carbon	83.68%	83.20%
Hydrogen	8.19	8.15
Nitrogen	8.13	7.98

DISCUSSION AND CONCLUSIONS

A major part of this study has been devoted to the separate and combined effects of formulation components on the LOX impact sensitivity of Viton B. We have approached this complex subject from the point of view that sensitivity is dependent on a host of independent and interrelated chemical and physical properties and that formulation components may sensitize the elastomer by altering these properties.

We have deliberately avoided placing emphasis on the differences between primary and rebound positives in the impact tests as there appears to be no quantitative way to treat these differences. Many but not all of the formulations showing positive primaries also show a significant number of positive rebounds, but many formulations with significant numbers of rebound positives show no primary positives. Although it is tempting to conclude from the test results in Table I that the most sensitive materials are those with some primary and many rebound positives, the main consideration for our purposes is whether a particular combination of components or a specific treatment changed the total number of positives and not their distribution.

The cumulative experience of testing a variety of formulations, many in duplicate or replicate, indicates that the simple error in reproducibility of the impact test is close to ±50% for total positives across the range of sensitivity from formulations like 16 and 16R to 11 and 11R. More sophisticated statistical treatment of the data hardly seems justified with the limited number of samples available for most formulations, and the following discussion and conclusions are based on the semiquantitative evaluation of the impact test results.

For example, the results in Table I seem to show rather clearly that insensitive Viton stock is readily sensitized by any one of the formulation components and by several combinations but that overall sensitivity is only markedly increased by certain combinations such as 29 or 11, both of which have PbO_2 and Diak-3, a potent oxidation-reduction mixture in its own right.

Some materials such as carbon and MgO may sensitize by providing many more point sources for conversion of kinetic energy into heat energy. Others such as Diak-3 or its hydrolysis product cinnimaldehyde, may sensitize mainly by providing a source of fuel that is ignitable at temperatures lower than the ignition temperature of the bulk polymer. Moderation of extreme sensitivity, as found in formulation 11 by addition of either carbon or by curing, suggests that Diak-3 or cinnimaldehyde is responsible for the special sensitivity found here. This conclusion is supported by the observation that substitution of Diak-1 for Diak-3 (No. 42) gives a formulation almost as insensitive as any we have prepared. The function of both carbon and curing may be similar in that they both can remove cinnimaldehyde from the formulation, one by absorption, the other by volatilization and/or oxidation. Thus carbon alone produces a noticeably sensitive elastomer (No. 2), whereas carbon moderates the sensitivity of another more sensitive formulation such as No. 11. But in both cases the final formulation is more sensitive than pure Viton.

Although similar analyses might be applied to other combinations of formulation components, the result seems to be the same for most compositions, namely, that curing reduces sensitivity but never to the level found for the pure elastomer. This incremental sensitivity may result from some combination of physical effects, such as creation of point sources for ignition such as hard particles and microbubbles, and chemical effects, such as formation of easily ignited organic fuels such as aldehyde. To test this latter idea, we extracted a standard formulation (No. 53) with ester to remove volatile organics, but the result was disappointingly ambiguous as noted in the results section.

Another approach to desensitization of Viton formulation was the simple expedient of removing ignition point sources and volatile fuel from direct contact with oxygen by thinly coating the formulated Viton surface with pure Viton. The value of this concept is arguable on the basis that many of the formulations display no positive reactions on initial impact but are very sensitive to impact on rebound after the sample has been broken into small pieces with large amounts of fresh surface. Despite this serious objection, coated sample 54 was only one-fourth as sensitive as the standard, 53, although this standard was exceptionally sensitive for unknown reasons. This approach appears to have some promise and deserves further investigation.

If we can regard the first part of this investigation as one in which we examined and manipulated those factors responsible for ignition of Viton formulations, then the second part using fire retardants can be thought of as an effort to interfere with the propagation of combustion in a polymer-oxygen system. This distinction is important and useful because we need better methods for selecting model systems such as polymer combustion as guides for choosing effective retardants. However, our results using polymer fire retardants suggest that burning polymers may be poor models for impact ignition.

Most of the retardants tried are effective to one degree or another with hydrocarbon polymers but, with one exception, are of little or no value for reducing impact sensitivity in Viton. The one exception, SbOCl, appears to be effective at loadings of 4.3 pph. A closely related retardant system, used extensively in polymers for fire retardance, is Sb_2O_3 and

Dechlorane Plus; trials with this mixture showed it to be ineffective in Viton. Studies at SRI[10] suggest that both SbOCl and Sb_2O_3 and Dechlorane Plus react in situ to form $SbCl_3$, a volatile and effective retardant for polymer combustion. The failure of one system and the success of a closely related one in reducing impact sensitivity of Viton formulations suggests that, little or no $SbCl_3$ is formed from Sb_2O_3 and Dechlorane Plus during the short time of impact burning but that the less complicated conversion of SbOCl to $SbCl_3$ proceeds fast enough under these conditions to be effective.

Another and possibly important difference between SbCl and Sb_2O_3 systems is that the oxychloride melts too low (170°C) for it to be an effective point source for ignition, whereas the oxide melts above 600°C and might well serve as an ignition source, thus off setting any positive effect of $SbCl_3$ were it formed. The data also suggest that Dechlorane itself may also sensitize Viton.

We do not know why the other fire retardants tried were not effective or only slightly so. For example the phosphate esters are liquids and should not introduce complications in the ignition mechanism. However, there is no evidence that phosphates are particularly effective as fire retardants with fluorinated materials. The single experiment with boric acid absorbed on carbon is really not a fair trial for borates. Several more Viton formulations containing boric acid or borate ester should be examined at much higher loadings of borate.

Additional trials using SbOCl (at 4 and 8 pph) should be carried out as we believe there is enough evidence to justify a more careful study with this material. Additional studies on the effect of various loadings of SbOCl on the physical properties of Viton formulations are also needed; the one series of measurements at 34 pph was encouraging but too limited to evaluate the practical value of incorporating SbOCl into Viton.

Another approach is needed to formulating Viton with bromine compounds, which are ordinarily too unstable to survive the curing cycle. The effectiveness of bromine retardants depends in part on their rapid conversion to bromine atoms[1] by simple thermal reactions. Our earlier experience[4] in effectively desensitizing benzene to LOX impact ignition by adding methylene bromide argues strongly that bromine compounds can be effective under the special ignition and propagation conditions found in LOX impact.

Just as we found that formulation components affect sensitivity by a variety of mechanisms our results with retardants or desensitizers suggest that they act by a combination of physical and chemical modifications of the system; some modifications may affect ignition and others may affect propagation.

All our retardant results were based on one formulation. The same retardant may act differently with different formulations and there are few reliable characteristics that can be used as a guide in choosing an effective desensitizer. It seems almost certain that the most effective agents will be those that require the fewest chemical steps to convert them to a form active in retarding combustion propagation. Antimony oxychlorides appear to fit the requirements and bromine compounds should, providing they do not otherwise improve ignition efficiency.

The principal conclusion that emerges from this study is that the residual and variable impact sensitivity of fully formulated Viton is not due to any one formulation component or physical factor. Therefore future efforts to reliably desensitize Viton and other fluoroelastomers should concentrate on general techniques such as coating or addition of desensitizing materials. Our intitial experiments using this approach have given some encouraging results, and we believe that further studies could lead to a formulation that would be significantly and reliably less sensitive than those now available, without any significant sacrifice of physical properties.

LITERATURE REVIEW

Two comprehensive literature reviews covering the period January 1962 to June 1972 were run by NASA's Scientific and Technical Information Division, selecting on the key words LOX, GOX, impact sensitivity, and flammability. Several reports of possible interest selected from this search list were obtained and reviewed for information useful to this work.

Generally we found little information in these reports that has any direct bearing on the present investigation of Viton impact sensitivity. Fragmentary information found in three reports does seem worth noting. Hilz, Fenton, and Dolan[8] in reporting results of an impact sensitivity study on heat shield elastomers found several materials that, when incorporated into the silicone elastomer shielding, markedly increased sensitivity. Among these were micro quartz and carbon and graphite fibers. They suggested that fibers with high modulus gave the most increase in sensitivity owing to poor energy attenuation. Considering the complex systems they used and the limited trials and combinations, we have to view the conclusion with interest but with skepticism even though it is consistent with our ideas concerning the mechanism of initiation by means of hot spot formation.

Two reports on factors affecting impact sensitivity examine the effect of inert components. One by Key and Gayle[9] on addition of liquid nitrogen (LN) to LOX shows that addition of 8% LN to LOX decreases sensitivity of several materials by 1 kg/cm. For most materials, however, large amounts of LN (generally over 60%) are needed for significant desensitization. At 20:80 LOX:LN most materials are insensitive. The important point here seems to be that small amounts of LN can exert a significant effect on the threshold sensitivity even though from a safety standpoint mixtures are still hazardous. Either heat transfer from the sample to the LOX-LN mixture is very much faster than with LOX alone (which seems unlikely) or sustained ignition is a strong function of the oxygen concentration, a situation not unlike that found in flammability tests.

The third paper, by Blackstone,[10] deals mainly with a new way to measure sensitivity but does note that highly sensitive liquids do not sensitize inert ones unless present in significant quantities, like 50%. As with LOX-LN mixtures, dilution markedly reduces sensitivity, and in liquid systems sensitization by small amounts of added liquid is not observed. Blackstone implies, wrongly, that sensitization is not important in a general sense: Viton B is a good example of an inert material sensitized by added materials.

During the course of this investigation current issues of NASA's STAR were examined for listings under "oxygen," "liquid oxygen," "impact test," and "impact sensitivity." No relevant listings were found.

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