Technical Information

Introduction

This bulletin provides basic information necessary for the safe handling of Viton™ fluoroelastomers as a class of materials and their associated chemicals and compounds. Information on cleanup after accidental burning is also included.

Individual polymers and chemicals, especially experimental and semi-commercial grades and proprietary precompounds, may differ in their safe handling requirements. These are covered by Safety Data Sheets (SDS), which you can obtain from your Chemours representative for all of our products.

The current SDS, furnished with your first shipment of Viton™, or when updated, should always be reviewed prior to experimental or production use of any Viton™ fluoroelastomer, precompound, or associated chemical. Further copies are available upon request.

As with the majority of polymer-based systems, the key to safe handling during processing is often the provision of adequate ventilation. Specific ventilation guidance is not given in this bulletin, but if needed, can be obtained from industry heating and ventilation experts.

Workplace concentration limits for air contaminants are governed by federal, state, and local regulations. This bulletin, and associated SDS, can indicate the likely emissions and quantities from a unit of polymer or compound; but, only the processor can assess conditions in a specific plant or operation.

Raw Materials

Viton™ Fluoroelastomers

Handling in Use

Using recommended handling procedures, raw un-precompounded Viton™ fluoroelastomers present no significant health hazards.

As with many polymers, minute quantities of potentially irritating gases may diffuse from the raw elastomer on storage, even at room temperature. All containers should be opened and used in well-ventilated areas.

Good practice dictates that impervious gloves be worn when handling raw polymer or chemicals. In case of eye contact, immediately flush the eyes for at least 15 min with water. If bare skin is contacted by Viton™, wash with water. Pelletized types of Viton™ may accumulate a static charge during handling and pouring from a bag. If polymer pellets are handled in the vicinity of flammable vapors, e.g., when making coatings or adhesives, efficient spark-proof ventilation should be provided. Equipment and personnel should be grounded to avoid hazards from a possible static electricity discharge. Refer to the National Fire Protection Association (NFPA) RP77 "Recommended Practice on Static Electricity" for guidelines in reducing the fire hazards associated with static electricity.

Disposal

In case reuse or recycling is not possible, incineration with energy recovery is the preferred method of disposal. The incinerator must be equipped with an appropriate scrubber to remove hydrogen fluoride. Local regulations must be followed. Disposal via landfill in accordance with local regulations is another option.

Accidental Burning

Necessary information for fire fighters and cleanup staff is given in the section entitled "Vulcanizates."

Curatives and Curing Agents

Handling in Use

The range of curatives and auxiliaries offered by Chemours differs markedly in chemical composition, depending upon the nature of the vulcanization system. **Table 1** summarizes compositions, LD50 values, and hazard ratings according to European Directive 67/548/EEC, as amended, and

Chemours™

2001/58/EC for mixtures. It is essential to consult the current individual SDS for each product prior to first use; but, certain basic principles for safe handling apply to all, i.e.:

- Contact with eyes, skin, and clothing should be avoided. Wear impervious gloves and a facemask when handling. Avoid breathing vapors. Use only with adequate ventilation.

- If skin contact occurs, flush the skin with water. In the event of eye contact, flush with water for at least 15 min and obtain qualified medical attention. Wash contaminated clothing before reuse.

- In the event of accidental exposure to vulcanization vapors or combustion fumes, move to fresh air immediately. If the exposed person is not breathing, give artificial respiration. If the exposed person has difficulty breathing, administer oxygen. Call a physician immediately.

Chemical Classes

Dihydroxyaromatic (Bisphenol) Systems

Three of the commercial curatives offered in this group are Viton™ Curatives No. 20, 30, and 40. They are masterbatches of chemicals in Viton™ fluoroelastomer. This reduces any potential hazards from exposure to dust in handling. The precautions for safe handling of raw Viton™ polymers and compounds also apply to these products.

A fourth curative, Viton™ Curative No. 50, is not a masterbatch, but rather a 100% active curing agent. Exposure to dust may be irritating to nose and throat. All four curatives are skin irritants to guinea pigs, but do not cause sensitization. Additional information on Viton™ curatives is contained in Chemours bulletin, "Viton™ Curative No. 50."

Polyfunctional Amine Systems

Diak™ No. 1 and No. 3 may cause irritation of eyes and skin and may also form flammable dust-air mixtures. They should be kept away from heat, sparks, and flame and only used where equipment is grounded.

If used in abnormally high concentrations, Diak™ No. 1 and No. 3 can promote substantial heat buildup in compounds of Viton™ during injection, compression, or transfer molding or extrusion (see Appendix 1).

Suggested maximum use limits are 2 phr for Diak™ No. 1 and 4 phr for Diak™ No. 3.

Note: Additional information on Diak™ curing agents is contained in Chemours bulletin, "Diak™ Curing Agents for Viton™ Fluoroelastomers." Diak™ No. 4 is a polyfunctional amine-based curative now sold only by the R.T. Vanderbilt Company and its agents. The supplier's SDS and product label information should be studied prior to use.

Peroxide-Based Systems

Chemours supplies Diak™ No. 7 and No. 8 for use as co-agents in the peroxide vulcanization of G-type Viton™ fluoroelastomer grades. Diak™ No. 7 may be either a liquid or crystalline solid at ambient temperatures. Diak™ No. 8 is a granular solid that may form flammable dust-air mixtures. It should be kept away from heat, sparks, and flame and only used where equipment is grounded.

Additional information on Diak™ No. 8 is contained in Chemours bulletin, "Diak™ No. 8, A Coagent for Peroxide-Cured Viton™."

Note: Chemours does not supply peroxides. Suppliers, SDS, product labels, and other safe handling information should be consulted prior to use.

Processing Aids

Three proprietary processing aids are available, designated VPA (Viton™ Processing Aids) No. 1, No. 2, and No. 3. Descriptions and (67/548/EEC classifications) of these products are given in Table 2.

Storage containers should be kept in a cool, dry place.

VPA No. 1 and No. 3 can cause irritation of eyes and skin. Handling precautions are essentially the same as those for Diak™ No. 1, No. 3, and No. 8, including treatment for accidental inhalation of dust or fumes and eye contamination.

VPA No. 2 has no toxicological hazards known to Chemours.

These products present no special disposal problems. Dispose of them in accordance with federal, state, and local regulations for sulfur chemicals and waxes.

Additional information may be found in individual SDS and Chemours bulletin, "Viton™ Processing Aids."

Table 1. Viton™ Fluoroelastomer Curatives and Auxiliaries: Nature and Hazard Ratings

Product	Composition	Active Ingredient Hazards[1]	Product Rating[2]
Dihydroxyaromatic (Bisphenol) Systems			
Viton™ Curative No. 20	33% benzyltriphenylphosphonium chloride, 67% Viton™ polymer	LD50 = 43	T[3]
Viton™ Curative No. 30	50% 2,2-bis-4-hydroxyphenylperfluoropropane (bisphenol AF), 50% Viton™ polymer	LC50 = <1 ALD = 3,400	Xi, N
Viton™ Curative No. 40	33% 2,4-dihydroxybenzophenone, 67% Viton™ polymer	LD50 = 6,100 LC50 = 4.6–10	Xi, N
Viton™ Curative No. 50	Bisphenol AF Benzyltriphenylphosphonium- Bisphenol AF salt	ALD = 3,400 LD50 = 4,385 LC50 = <1	Xi, N
Polyfunctional Amines			
Diak™ No. 1	100% hexamethylene diamine carbamate	LD50 = 2,875	Xi
Diak™ No. 3	100% N,N'-dicinnamylidene-1,6-hexanediamine	ALD = 6.2	Xi
Peroxide System Co-Agents			
Diak™ No. 7	100% triallyl isocyanurate	LD50 = 700	Xn
Diak™ No. 8	100% trimethallyl isocyanurate	LD50 = 3,376	Xn

[1]Human Health: Oral Rat, LD50 mg/kg; Toxicity to Fish: LC50 (96 hr) mg/L; Inhalation: ALD (4 hr rat) mg/L
[2]According to 67/548/EEC as amended and 2001/58/EC for mixtures
[3]Xn = Harmful, Xi = Irritant, N = Environmental Hazard, T = Toxic

Table 2. Chemours Process Aids: Nature and Hazard Ratings

Product	Composition	Active Ingredient Hazards Human Health: Oral Rat, LD50 mg/kg	Rating by 67/548/EEC, as Amended, and 2001/58/EC for Mixtures
VPA No. 1	66% aromatic sulfur compound in hydrocarbon wax	LD50 = 24,000[1]	Xi[2]
VPA No. 2	100% natural vegetable wax	—	—
VPA No. 3	Approximately 74% aliphatic sulfur compound on an inert silica carrier tetramethylene sulfone	LD50 = 2,400	Xn

[1]Dermal Mouse
[2]Xn = Harmful, Xi = Irritant

Other Compounding Ingredients

General

Compound ingredients for Viton™ from sources other than Chemours may pose hazards in handling and use. Before use, suppliers' SDS, label directions, and other safe handling advice should be consulted.

Lead-Containing Compounds

Lead, lead oxides (including litharge), and other lead compounds are regulated in the United States under the Occupational Safety and Health Act, 29 CFR 1910.1025, Subpart Z—Toxic and Hazardous Substances. The permissible exposure limit (PEL) is 50 µg/m³ of lead in air averaged over an 8-hr period. However, an action level of 25 µg/m³ of lead in air requires special procedures. See the OSHA Regulation cited previously. Before using lead compounds, local regulations on use and disposal, including scrap compounds and products, must be reviewed.

To avoid exposure to lead-containing powders, Chemours strongly advises the use of commercial dispersions of a suitable grade of, e.g., litharge in Viton™ fluoroelastomer. Local sales offices or technical service representatives can usually suggest potentially suitable products. See also Precautions section, "Finely Divided Metals and Metal Oxides."

Precautions Related to Compounds and Vulcanizates

Exothermic Decompositions

Three potential causes of sudden exothermic decomposition of the FKM class of elastomers, which includes Viton™, have been identified. Occurrence is rare, but conditions giving rise to the possibility should be understood.

Diesel Effect

This is manifested by a sudden and vigorous decomposition during processing, causing a rapid and noisy emission of charred material from the equipment. It is not related to any specific grade of Viton™ or form of compound and has been known to occur with other types of elastomers. Individual production incidents have been investigated and the phenomenon studied under laboratory conditions, as in **Appendix 1**.

All evidence suggests that this type of thermal decomposition arises from heat generated by adiabatic compression of air pockets in the compound during rapid compression. Thus, the phenomenon is usually observed with injection molding; although, examples from transfer or compression molding and extrusion have occurred. Predictably, high compound viscosity is a contributory factor.

Study of **Appendix 1** shows exothermic reaction of uncured compounds of Viton™ beginning at about 316 °C (601 °F), as determined by differential thermal analysis (DTA). Thermogravimetric analysis (TGA) indicates that 50% weight loss occurs at about 475–500 °C (887–932 °F), and that Viton™ is completely volatilized at 550 °C (1022 °F). Any operation that subjects a compound of Viton™ (or any other FKM-type fluoroelastomer) to temperatures above 316 °C (601 °F) can initiate rapid decomposition. Calculations show that a pocket of air can easily be heated to 500 °C (932 °F) if compression is rapid enough.

To minimize the possibility of exothermic decomposition of compounds of Viton™ from the diesel effect, we suggest:

- Use the lowest viscosity compound consistent with overall processing and end-use requirements.

- Incorporate an effective process aid, such as VPA Nos. 1, 2, or 3 or carnauba wax, in the compound.

- Avoid unnecessarily fast injection, transfer, or mold closing speeds.

- Ensure absence of unnecessarily tight constrictions in the flow path, e.g., dies, sprues, runners, and gates.

- Ensure that no scorched or cold material remains in injection systems that could increase back pressure.

- Ensure that machine location and guards minimize the risk of damage or injury, should an incident occur.

- Avoid contamination of processing equipment with other materials or cleansing compounds, especially any that might leave residual particles of aluminum or other metals (see subsection following).

Finely Divided Metals and Metal Oxides

Finely divided metals should not be used as compounding ingredients for Viton™ fluoroelastomers or allowed to contaminate compounds based on them. Stocks containing such powders, especially aluminum and magnesium, have been known to undergo vigorous exothermic decomposition at moderately elevated temperatures. Compounds containing bronze powder have been exposed to temperatures as high as 275 °C (527 °F) without incident, but their incorporation is not recommended.

Some metal oxides dispersed at high concentrations in fluoroelastomers, and other elastomers, such as natural rubber, SBR, polychloroprene, and ethylenepropylene copolymers, may undergo exothermic decomposition in the region of 200 °C (392 °F). For example, a masterbatch of lead oxide (litharge)/Viton™ 80/20 decomposed exothermically when heated above 200 °C (392 °F), yielding metallic lead as one of the by-products. This type of decomposition has also been observed in compounds of Viton™ containing excessively high levels (>15 phr) of metal oxide, such as magnesium oxide.

Accelerated rate calorimetry (ARC) tests were run on various combinations of magnesium oxide and fluoroelastomer that contained a bisphenol cure system. Four mixtures ranging from 9 to 40 phr magnesium oxide were tested in a calorimetric unit pressurized to 2.1 MPa with pure oxygen.

The ARC plots of "Self Heating Rate" versus Temperature show that, under conditions of very high oxygen concentration, once a reaction begins, it becomes a "runaway" reaction with a relatively large release of energy. At these very high oxygen concentrations (designed to ensure complete combustion in the calorimeter), the results can be used to establish the total oxidation potential of the system. The kinetics of the reaction that would take place in conventional rubber equipment are not well understood.

ARC measurements indicate that as the level of magnesium oxide increases in a fluoroelastomer

compound containing curing agents, the temperature at which exothermic reaction takes place decreases. At levels of magnesium oxide above 25 phr, the decrease in activation temperature is even more pronounced. The temperature predicted by the lower concentrations of magnesium oxide for the onset reaction at 40 phr of magnesium oxide is 140 °C (284 °F), but the actual measured onset was only 106 °C (223 °F).

Even in the absence of curing agents, exothermic decomposition reactions have been observed in instances in which very high levels of magnesium oxide were mixed into fluoroelastomer gum polymer. One known example was a case in which an exothermic reaction occurred in a production-scale internal mixer, in which a manufacturer attempted to incorporate 80 phr magnesium oxide into Viton™ A-100.

Reaction Onset Temperature
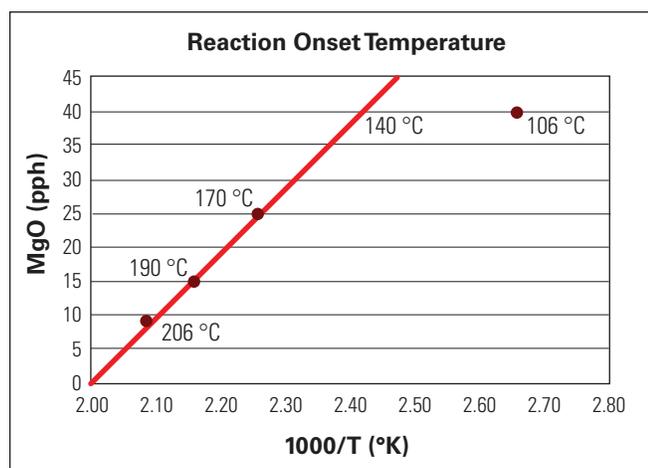
Additional information is given in the paper, "The Exothermic Decomposition of Litharge-Elastomer Dispersions," by M.B.M. Simpson, presented at the Rubber Division of the American Chemical Society, Atlanta, Georgia, March 26–29, 1979.

Oven Fires During Post-Cure

Press cured vulcanizates based upon Viton™ fluoroelastomers often require a subsequent air oven post-cure, typically for up to 24 hr at 200–250 °C (392–482 °F), to develop optimum properties. This operation is generally uneventful. Occasionally, fires have occurred during post-cure that appear to involve exothermic decomposition of the exposed vulcanizates. This would not be expected from the threshold temperature of approximately 316 °C (601 °F) for exothermic reactions in uncured compounds based upon Viton™, as shown in **Appendix 1**.

Studies under laboratory conditions indicated that:

- Commercial compounds containing MT carbon black or relatively high levels of iron oxide (a potential dehydrofluorinating agent) were thermally stable for at least 24 hr at 320 °C (608 °F) by differential scanning calorimetry (DSC) and even to 350 °C (662 °F) when heated in an adequate air stream.

- When tested by accelerating rate calorimetry (ARC) in a sealed system without air flow, initiation temperatures could be as low as 200 °C (392 °F) for compounds containing iron oxide and MT black and in the region of 110–140 °C (230–284 °F) for compounds containing iron oxide, MT, and ground anthracite fillers. Regardless of filler system, times in excess of 24 hr were required for the maximum rate of heat generation to be reached.

- Surface contamination with silica-containing materials might exert a catalytic effect.

- Based on this evidence and broad experience, we believe that oven fires during post-cure can be avoided to occur if recommended practice is followed, i.e.:

  - Ensure a rate of air flow to provide at least 10 complete changes per hour positively vented to atmosphere, preferably through a gas scrubber unit.

    Note: See **Appendices 2** and **3** for a discussion of vapor emissions from curing and post-curing.

  - Keep loading to a maximum 10% of the chamber volume.

  - Load so that air can freely circulate around the parts being post-cured.

  - Ensure that post-cure ovens are fitted with high temperature cut-outs, checked between each cure cycle and set to a maximum 25 °C (77 °F) above the desired temperature.

More detailed information may be found in the paper, "An Investigation of Fluoroelastomer Post-Cure Oven Fires," by R.E. Tarney and E.W. Thomas, ACS Rubber Division Meeting, Fall 1991, Detroit.

Vapors From High Temperature Curing and Post-Curing

Evolution and Area Ventilation

As with all elastomers, vapors are evolved from compounds based upon Viton™ during cure or post-cure at suggested temperatures. Area and local ventilation in work areas should be controlled. Ventilation should be adequate to prevent exposure of personnel to such vapors at levels greater than are permitted by national

and local regulations. Anyone accidentally inhaling significant vulcanization vapors should be immediately moved to fresh air, given artificial respiration if indicated, and examined promptly by qualified medical personnel.

It is very difficult to provide direct correlations of work place concentrations of any vulcanization by-product gas to the possible evolution figures given in this bulletin, as many factors are involved (size and surface area of parts, processing temperatures, cycle times, size of room, efficiency of ventilation, etc). The processor must ensure that, under his/her unique conditions, atmospheric concentrations at a minimum comply with the requirements of local regulatory agencies.

Evolution of Hydrogen Fluoride

Regardless of the Viton™ type or the nature of the vulcanization system, cure or post-cure near or above 200 °C (392 °F) may liberate small quantities of hydrogen fluoride, which is toxic and can cause prolonged irritation to the respiratory tract. Hydrogen fluoride is regulated as an air contaminant in the United States under OSHA CFR Title 29 1910.1000, which sets the 8-hr time weighted average (TWA) exposure limit in any 8-hr work shift of a 40-hr work week at 3 ppm.

Values for the evolution of hydrogen fluoride during press and post-curing under laboratory conditions are given in Table 3 of Appendix 2 for bisphenol and amine-cured compounds and in Table 3 of Appendix 3 for peroxide-cured compositions. Note that the highest values obtained for any of the cure systems was 7 mg/kg compound for simulated press cure and 700 mg/kg compound for simulated post-cure.

Specific Cure System Derivatives

Reference to Table 5, Appendix 2, shows that significant amounts of bisphenol AF, the active ingredient in Viton™ Curative No. 30, and triphenylphosphine oxide may be evolved from conventional bisphenol cure systems. As noted in Table 1, bisphenol AF is a skin irritant and rated as Xi (by European Directive 67/548/EEC as amended). It may sublime and crystallize in ventilation ducting. Triphenylphosphine oxide with an ALD value (oral rat) of 1,500 mg/kg is rated T (toxic). Effective ventilation is necessary to remove it. Compounds containing Viton™ Curative No. 20 will also generate small amounts of benzene during vulcanization. The European Union classifies benzene as a Category 1 carcinogen, i.e., "a substance known to be carcinogenic to man." Occupational exposure is regulated via Member State legislation.

Please review local legislation for the occupational exposure levels in your country. Data in Appendix 2 indicates that the level of emission is likely low, with the majority released during post-cure.

Peroxide-curable fluoroelastomers typically contain either bromo- or iodo-substituted cure site monomers and/or iodine modification of polymer chain ends. This being the case, methyl halides may be liberated during cure. These include methyl bromide and/or methyl iodide. The SDS for the specific product to be used should be consulted. Both methyl bromide and methyl iodide are regulated as potentially hazardous air contaminants in the European Union, the U.S., and most industrialized nations. Information on methyl halide evolution from various types of peroxide-curable Viton™ may be found in Appendices 3 and 4.

Some peroxide-cured fluoroelastomer compounds can generate other potentially hazardous substances, such as formaldehyde, acetone, and carbon monoxide. Workplace exposure limits for these three peroxide-cure reaction by-products have been established by the American Conference of Governmental Industrial Hygienists (ACGIH) and government agencies, such as the Occupational Safety and Health Agency (OSHA). Exposure to these peroxide-cure reaction by-products can be managed with local ventilation, personal protective equipment, and administrative control. See the Chemours technical bulletin, "Proper Use of Local Exhaust Ventilation During Processing of Plastics," available on the Chemours website.

Vulcanizates

Dust From Grinding

As indicated in Table 3, fine dust from the grinding or abrading of raw Viton™ polymers or products made from them can generate toxic decomposition products if burned.

Smoking in areas in which these conditions occur should be prohibited, and operators should be cautioned not to contaminate smoking materials with the dust. They should be advised to wash their hands thoroughly before smoking anywhere.

To avoid inhalation of dust particles, a respirator should be worn and adequate ventilation provided. Safety goggles should be worn to prevent dust from coming in contact with the eyes.

Table 3. Combustion Products of Vulcanization of Viton™

Compound Formulation	Viton™ E-60C[a]		Viton™ B-910[b]	
Polymer	100		100	
Magnesium Oxide	3		3	
Calcium Hydroxide	6		3	
MT Carbon Black (N990)	30		30	
Cure: 10 min at 177 °C (351 °F), press 24 hr at 232 °C (450 °F), oven				
Combustion Products, mg/g Sample	Excess O_2	Deficiency O_2	Excess O_2	Deficiency O_2
Carbon Monoxide (CO)	—	121	—	96
Carbon Dioxide (CO_2)	1,836	1,514	1,927	2,000
Hydrogen Fluoride (HF)	251	161	250	88
Carbonyl Fluoride (COF_2)	—	63	—	23
Fluoroform (CHF_3)	—	15	—	10
Vinylidene Fluoride (H_2CCF_2)	—	Trace[c]	—	Trace
Hexafluoropropylene (C_3F_6)	—	Trace	—	Trace
Miscellaneous Low Molecular Weight				
Fluoropolymer Fragments	—	Trace	—	Trace

[a]A-type polymer containing O-ring levels of bisphenol-based curatives.
[b]B-type polymer containing O-ring levels of bisphenol-based curatives.
[c]Trace = <5 mg/g sample

Accidental Burning

As noted in the previous section, intentional burning of Viton™ or its vulcanizates is not advised, except in approved incinerators, owing to possible formation of toxic and corrosive combustion products.

In the event of an accidental fire, fire fighters and cleanup personnel should be aware of the likely formation of hazardous by-products. Data in Table 3 show that these may include hydrogen fluoride, carbonyl fluoride, carbon monoxide, and low molecular weight fluorocarbon fragments. Personnel fighting such a fire must wear facemasks and self-contained breathing apparatus. All unprotected personnel must leave the area immediately. Anyone exposed to fumes from the fire should be moved to fresh air at once and given qualified medical attention.

Cleanup

Personnel handling residues of Viton™ polymers, compounds, or parts made from them that have been involved in a fire must wear impervious acid-resistant gloves to protect the skin from these possibly highly corrosive residues. Gloves may be of neoprene or polyvinyl chloride (PVC) if temperatures are below the melting point of the glove. Any liquid residues should be assumed to be highly acidic.

All residues should be neutralized by treatment with copious amounts of lime (calcium hydroxide solution). Solid treated residues should be disposed of in the same manner as Viton™ polymers. Used gloves must be discarded.

Combustion Products of Vulcanization

Table 3 shows quantitative laboratory measurements of the combustion products of bisphenol-cured Viton™ E-60C and Viton™ B-910 under well-ventilated conditions (excess of oxygen) and poorly ventilated conditions (deficiency of oxygen). Because these data are from a one-time test under controlled conditions, they are not necessarily representative of an actual fire situation. They provide information on likely by-products of combustion of typical vulcanizates.

High Temperature Service (Above 275 °C [527 °F])

In most applications, parts made from Viton™ can be exposed to temperatures up to 275 °C (527 °F) without significant decomposition or health hazard. As shown in Table 3 of Appendix 2, traces of evolved hydrogen fluoride can be detected from compounds during vulcanization at temperatures close to 200 °C (392 °F), and vulcanizates must be expected to behave similarly. Even so, evolution

of significant levels of hydrogen fluoride from vulcanizates is unlikely, unless the vulcanizates are severely degraded.

Laboratory tests supporting this were conducted in air using very small quantities of test specimens prepared from a standard vulcanizate of Viton™ E-60C. The results may not be valid if other compounding ingredients are included in the vulcanizate formulation or during exposure to other environments, as the effect of additional ingredients on decomposition cannot be predicted.

Use or testing of vulcanizates of Viton™ at temperatures above 316 °C (601 °F) in air or in other media should be avoided. This temperature represents the approximate likely onset of exothermic decomposition for specific compositions, as shown in Appendix 1, Figure 1B.

If, for any reason, controlled exposure to temperatures above 316 °C (601 °F) is required, or is possible through accident, the user should ensure that effective precautions are taken to protect personnel from exposure to fumes or condensates. Appropriate medical treatment should be available for hydrogen fluoride burns or other exposure from inhalation or contact with a decomposed part or condensate. As previously noted, all equipment, etc., suspected of contamination with decomposition by-products should be liberally treated with lime water. Neoprene or PVC gloves should be worn at all times when dismantling equipment or handling parts and then discarded.

It is the responsibility of the part manufacturer and end-user to determine that a specific application is safe, particularly at temperatures above 316 °C (601 °F).

Note: These comments only apply to parts made from FKM-type fluoroelastomers. They do not apply to Kalrez® perfluoroelastomer or Teflon™ fluoropolymer resin parts, which behave differently at high temperatures.

Appendix 1

Occasional Exothermic Decompositions During Processing of Viton™ Fluoroelastomer

Abstract

Occasional exothermic decompositions have been observed in the course of processing fluoroelastomer compounds. These exothermic events can be caused by various factors, including a diesel effect, the presence of finely divided metals, excessive thickness, and level of blowing agent employed in the manufacture of blown sponge, and attempting to incorporate excessively high levels of metal oxides into either gum fluoroelastomer or fluoroelastomer compounds containing curatives.

Based upon results from laboratory studies of factors conducive to exothermic decomposition, the following practices should be observed:

1. Amines or compounds that could serve as potential sources of amines should be avoided in formulations of Viton™ unless checked carefully. Diak™ curing agents based on amine carbamates (Diak™ No. 1, No. 3, and No. 4) should be used only at the recommended levels. Concentrations of Diak™ No. 1 exceeding 2 phr and Diak™ No. 3 above 4 phr may cause substantial heat buildup during compression molding. Such high levels are rarely, if ever, necessary.

2. Formulations of Viton™ containing N,N'-dinitrosopentamethylene-tetramine-type blowing agents should not be used for the manufacture of sponge exceeding 12.7 mm thickness. Temperatures during molding of such sponge compounds should not exceed 153 °C (307 °F). Chemours experience indicates azodicarbonamide can be used safely as a blowing agent for closed cell sponge of Viton™ at least up to 25.4 mm thickness and temperatures to 204 °C (399 °F). Additional compounding data on sponge of Viton™ may be obtained from your Chemours representative.

3. In extrusion, transfer, and injection molding, very stiff stocks of Viton™ should be avoided. Pre-warming will help prevent excessive frictional heat. For high viscosity compounds of Viton™ A-HV, minimum barrel and screw temperatures during extrusion are likely to be above 100 °C (212 °F); while for lower viscosity types, a temperature of 80 °C (176 °F) should suffice.

   Note: Owing to the diversity of extruder, screw, and die designs, these temperatures are only a guide.

4. Metal oxides, such as magnesium oxide (MgO) and calcium hydroxide, should not be used at concentrations greater than 15 phr in fluoroelastomer polymers and especially not in fluoroelastomer compounds containing curatives/cross-linking agents.

Experimental Studies

Solid compounds based upon Viton™ A containing graduated levels of Diak™ No. 1 and No. 3 amine carbamate curing agents used in these studies are shown in Table 1. A sponge compound blown with a typical dinitrosopentamethylene-tetramine blowing agent is shown in Table 2.

Table 1. Effects of Amines and Levels on Heat Build-Up in Solid Vulcanizates of Viton™

Compounds	1	2	3	4	5	6
Viton™ A	100	100	100	100	100	100
Low Activity Magnesia	15	15	15	15	15	15
N990 (MT) Black	20	20	20	20	20	20
Diak™ No. 3	3	6	12	—	—	—
Diak™ No. 1	—	—	—	1.5	3	6
Heat Build-Up						
Mold Temperature: 163 °C (325 °F)[a]						
Exotherm, °C[b]	3	28	>140	3	19	>140
Appearance	Okay	Okay	Charred	Okay	Okay	Charred
Mold Temperature: 210 °C (410 °F)						
Exotherm, °C	12	—	—	—	—	—
Appearance	Okay	—	—	—	—	—

[a]Mold was a steel ring, 28.7 mm ID, 25.4 mm height
[b]Difference between the stock and platen temperatures

Table 2. Heat Build-Up in Sponge Compounds of Viton™

Compound				
Viton™ A		100		
Low Activity Magnesia		15		
N990 (MT) Black		20		
Petroleum		3		
Activator Blend[a]		4		
Blowing Agent[b]		7.5		
Diak™ No. 1		1.25		
Heat Build-Up				
Mold Temperature, °C	128	145	153	163
Mold Height: 25.4 mm				
Exotherm, °C[c]	9	20	23	140
Appearance	Sponged	Sponged	Sponged	Charred
Mold Height: 12.7 mm				
Exotherm, °C			13	17
Appearance			Sponged	Sponged

[a]2 parts Darvan® MS (R.T. Vanderbilt Co.), 1 part modified urea.
[b]N,N'-dinitrosopentamethylene-tetramine. Opex® 42 was used.
[d]Difference between the stock and platen temperatures

Exothermic behavior was studied by two techniques:

Differential Thermal Analysis (DTA)

DTA outputs in millivolts versus temperature obtained from samples of raw Viton™ A, A-HV, and B are depicted in **Figure 1a**. Compounds 1, 2, and 3 in **Table 1** and the sponge recipe of **Table 2** are depicted in **Figure 1b**. A rise in the DTA curve indicates a positive temperature difference arising from an exothermic process. A decline results from an endothermic negative temperature difference. Sharp changes in the curve occur when the generation or consumption of heat is rapid.

Conclusions are:

- Curves in **Figure 1a** confirm the excellent heat stability of raw Viton™ polymers. For both Viton™ A and A-HV, exothermic decomposition starts at 440–450 °C (824–842 °F), reaching a peak at about 465 °C (869 °F). For Viton™ B copolymer, these temperatures rise to 475 and 493 °C (887 and 919 °F), respectively, confirming its known better heat resistance.

- The significant minimum temperatures for Viton™ A and B prior to exothermic decomposition suggest an endothermic process, probably evaporation of volatile material.

- Reference to Compound 1 in **Figure 1b** suggests that, at the "standard" 3.0 phr level of Diak™ No. 3, the onset of exothermic reaction begins at 316 °C (601 °F), although the temperature of maximum rate remains at 440–475 °C (824–887 °F). There is no sharp exothermic. The lower initiation of the exotherm probably results from the reaction of magnesium oxide with HF formed by dehydrofluorination of the polymer.

  Note: Some compounds of Viton™ may lose up to 5% of their weight, presumably at least partly through decomposition, in 7 days at 275 °C (527 °F).

- In contrast to compound 1 in which the curing reaction proceeds smoothly without gross heat generation, compounds 2 and 3, containing 6 and 12 parts Diak™ No. 3 respectively, experience strong exothermic reactions at temperatures as low as 325 °C (617 °F). Similar exothermic patterns emerge when excess amounts of Diak™ No. 1 are added, as indicated in **Table 1**.

- Similarly, the sponge compound from **Table 2** which contains a normal level of 1.25 phr Diak™ No. 1 produces a strong exotherm in the 300–325 °C (572–617 °F) region. The blowing agent is known to decompose to yield hexamethylenetetramine

and nitrogen. Hence, it can be concluded that the by-product amine accelerates cure and generates excessive heat at relatively moderate temperatures.

- An industrial exothermic decomposition incident, in which a large excess of Diak™ No. 3 was inadvertently used, confirmed the possible effect of excess amines. It is advisable to expect excesses of any active curative to have the same potential.

Heat Build-Up in Simulated Molding

DTA studies employ small samples and generated heat dissipates rapidly. However, in industrial practice, heat dissipation is slow and temperature buildup is an important factor. To approach actual processing conditions, larger samples were studied. This involved molding 12.7- and 25.4-mm cross-section materials.

Table 1 illustrates the effects on exotherm generation of normal and excessive levels of Diak™ No. 3 and No. 1 in Viton™ A when molded into 25.4 mm thick sections. **Table 2** compares the behavior of the sponge compound molded at thicknesses of 25.4 and 12.7 mm, respectively. Internal stock temperatures were measured by probe thermocouples.

Conclusions are:

- Compound No. 1, which contains the standard 3 phr level of Diak™ No. 3 and was molded into 25.4 mm thick section, exhibits only a small temperature rise at a mold temperature as high as 210 °C (410 °F) (a similar result was obtained at 260 °C [500 °F]).

- At the same thickness, excess levels of Diak™ No. 3 and No. 1 induced highly exothermic reactions at 163 °C (325 °F).

- At 25.4 mm thickness, the sponge compound in **Table 2** exhibited a significant exotherm at temperatures as low as 145 °C (293 °F) and an uncontrolled reaction at 163 °C (325 °F).

- At 12.7 mm thickness, 163 °C (325 °F), the sponge compound exhibited only a moderate exotherm. Thus, size and shape of moldings are significant factors, and the likelihood of uncontrolled exothermic decomposition increases with part thickness.

Summary

The results are consistent and indicate that to avoid the risk of uncontrolled exothermic reactions in the molding of compounds based upon Viton™, excessive amounts of active amines or functional additives that generate active amines at molding temperatures should be avoided. The

same precaution should be applied to all other curing agents and auxiliaries. Exothermic effects, if present, are likely to be magnified as section thickness increases.

Exothermic decomposition of standard compounds of Viton™ during extrusion or molding is most likely due to localized temperature rise from adiabatic compression of air pockets or frictional heat. Thermogravimetric analysis (TGA) shows no significant weight changes (gas evolution) or other signs of more eruptive decompositions until the 475–500 °C (887–932 °F) zone is reached. This is possible during the adiabatic compression of air pockets.

DTA studies on uncured compounds indicate that limited exothermic decomposition can occur once stock temperatures reach 290–316 °C (554–601 °F). This may impair vulcanizate properties without other obvious manifestations.

The risk of localized or general excessive frictional heat generation may obviously be reduced by avoiding the use of unnecessarily stiff stocks. In injection or transfer molding, flow paths should be designed to minimize back pressure. The presence of scorched or cold material in injection molding or extrusion systems will also contribute to pressure buildup.

Although good compounding and processing practice will minimize the small risk of exothermic decomposition of compounds based upon Viton™, the processor should carefully consider the desirability of additional precautions arising from exceptional specific circumstances. These include the deliberate incorporation of abnormally high levels of any active curative. Also, attention is drawn to the section entitled "Oven Fires During Post-Cure."

Figure 1. DTA Curves of Polymers and Compounds of Viton™

Reference Table 1 and Table 2 for the formulations.
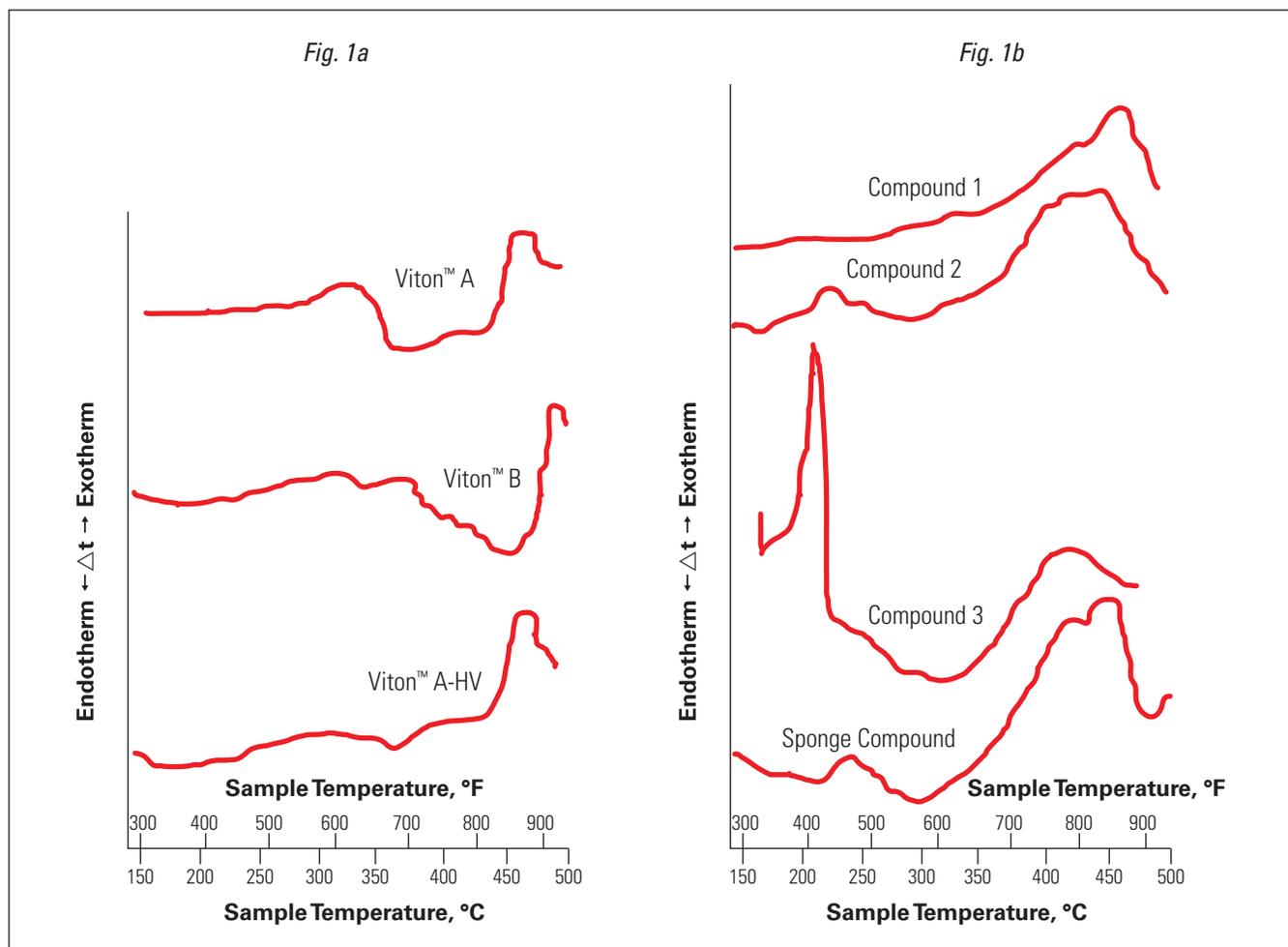
DTA studies on Viton™ A-HV have also been reported by K.L. Paciorek, W.J. Lajilness, and C.T. Lenk, J. Polymer Sci. 60 (1962), 141

Appendix 2

The Volatile Products Evolved From Bisphenol and Diamine Curable Fluoroelastomer Compounds

Abstract

Little information has been reported regarding the volatile components evolved during curing of fluoroelastomers. It is important to know qualitatively and quantitatively which materials, such as hydrogen fluoride and fluoroolefins, are emitted. Previous work[1,2] concerned the identification of the pyrolysis products evolved from cured vulcanizates. The purpose of the study described here was to identify and determine quantitatively the volatile products evolved during curing of typical fluoroelastomer formulations. The study did not cover all potential compounding variations. It was intended only to provide general information.

Procedures

Four typical fluoroelastomer compounds (Table 1) were chosen to represent systems curable by bisphenol (Compound A) and diamine (Compounds B, C, and D). The compounds were prepared by mill mixing.

Fluoroelastomers generally require two curing steps: (1) press cure, which typically consists of heating in a mold for 10 min at 190 °C (374 °F), followed by (2) the post-cure, which is accomplished by heating, usually 24 hr at 232 °C (450 °F), in a circulating air oven.

Separate thermogravimetric analysis of the fluoroelastomers, carbon black, and metal oxides up to 250 °C (482 °F) showed that the total weight loss from these components together contributed less than 0.2% to the total weight loss reported. This indicates that the volatiles lost from the compounds likely consist of water generated by the curing reaction.

Five complementary techniques were used in the analysis: (1) measurement of the gross weight loss in the press and/or in the oven; (2) determination of the hydrogen fluoride evolved; (3) analysis of the low-boiling volatile fraction by quantitative mass spectrometry; (4) identification by gas chromatography-mass-spectrometry and determination of the high boiling volatile fraction by gas chromatography; and (5) determination of the total weight of the high-boiling component mixture evolved during the post-cure, as well as Karl Fischer water analysis of this fraction.

Table 1. Fluoroelastomer Compounds

	A	B	C	D
Viton™ E-60C[a]	100	—	—	—
Viton™ A[b]	—	100	—	—
Viton™ B[c]	—	—	100	100
MT Black	30	20	20	20
Calcium Hydroxide	6	—	—	—
Magnesium Oxide	3[d]	15[e]	15[5]	15[5]
HMDAC[f]	—	1.25	—	—
DCHD[g]	—	—	3	—
Amine Salt[h]	—	—	—	1.8

[a]Viton™ E-60C is a fluoroelastomer containing bisphenol curing agents.
[b]Viton™ A is a copolymer of vinylidene fluoride and hexafluoropropene.
[c]Viton™ B is a copolymer of vinylidene fluoride, hexafluoropropene, and tetrafluoroethylene.
[d]High-activity, high-surface area
[e]Low-activity, low-surface area
[f]Hexamethylenediamine carbamate (Diak™ No. 1, Chemours).
[g]N,N'-dicinnamylidene-1,6-hexanediamine (Diak™ No. 3, Chemours).
[h]An alicyclic amine salt (Diak™ No. 4, Chemours).

Gross Weight Loss During Curing

Samples of compounded stocks, ca. 60 g, were cured as slabs for 10 min at 193 °C (379 °F), either in a rubber press or oven. The total weight losses are expressed in g/100 g of the total fluoroelastomer compound, designated as wt%. The purpose of heating in an oven under press-cure conditions was to establish a base for later analytical studies in which a press could not be used. Once press or oven cured, the cumulative weight losses were measured after further heating for 12, 24, and 36 hr at 232 °C (450 °F), as in normal post-cures. These data established the total amount of volatile material evolved during curing.

Oven curing was accomplished in a circulating air oven maintained at the appropriate temperature, ±5 °C (±9 °F), by a calibrated iron-constantan thermocouple.

Determination of the Hydrogen Fluoride Evolved During Curing

Samples of the fluoroelastomer compounds, ca. 6 g, cut into strips (2 x 2 x 120 mm), were placed in a platinum boat, which was weighed, inserted into a nickel tube, and heated in a furnace. The temperature was maintained with an Electronic Control Systems, Inc., temperature controller to ±5 °C (±41 °F). Dry air, 50 cm^3/min, was passed over the sample and then bubbled through 100 cm^3 of stirred 0.1 N KOH solution in a polyethylene bottle. The fluoride ion absorbed in this solution was measured with an Orion fluoride-ion electrode calibrated to detect 0.2 ppm ±1%. This corresponds to 0.0004 wt% of the fluoroelastomer compound. The fluoride found is expressed as wt% of the fluoroelastomer compound. A control experiment confirmed that HF was not reacting with the apparatus: KHF_2 (Technical) was decomposed isothermally at 350 °C (662 °F) for about 16 hr; the expected amounts of fluoride were found in both the KF residue and KOH solution used to trap the HF.

Analysis of the Low-Boiling Components Evolved During Curing

The low-boiling components, defined to include products with boiling points lower than that of water, were identified and measured with a calibrated mass spectrometer. Quantitative analysis by calibrated mass spectrometry gave the weight of the volatile component in the gas mixture directly.

Sample strips, ca. 1 g, of the fluoroelastomer compounds were suspended on glass rods and heated in partially evacuated, sealed tubes (200 cm^3) containing approximately 4 kPa air pressure. After simulated press cure and oven post-cure, the total pressure of the gas mixture was measured and an aliquot introduced into the mass spectrometer for analysis.

Analysis of the High-Boiling Components Evolved During Curing

High-boiling components were defined to include water and the components with boiling points higher than that of water.

Quantitative gas chromatographic analysis was performed with a Chromalytics MP 3 multipurpose thermal analyzer, equipped with thermal-conductivity detector and temperature programming. A two-step procedure was used with the instrument: (1) Cure simulation was accomplished by heating the sample, ca. 0.1 g, in a 6.35 mm OD Pyrex® tube, swept with helium at ca. 30 cm/min, in a programmable micro-furnace. Samples were heated at 40 °C (104 °F)/min to the desired temperature for the specified periods of time. The volatile components were collected in a 460 mm long, 3.1 mm OD integral dry-ice-cooled, U-shaped trap packed with Porapak® Q. (2) Gas-chromatographic separation was attained by rapidly heating (<2 min) the trap to 200 °C (392 °F) and back-eluting the adsorbed components onto a 3 m long, 3.1 mm OD 3% Dexsil® 300 GC on Chromosorb® W (80/100 mesh) stainless steel column. Temperature programming of the chromatographic column from 25–300 °C (77–572 °F) at a rate of 16 °C (61 °F)/min was used.

During the gas chromatographic analysis of the high-boiling components from a particular compound, it was assumed that peaks with equal retention times corresponded to the same component. The area of each component reported was measured by triangulation. In the absence of calibration, the areas are assumed to represent relative percentages of the weight loss. Area calibration for a few of the known components confirmed the approximate validity of this assumption.

Identification of each component was accomplished by gas-chromatography-mass-spectrometry. The volatile components were collected on a smaller (15 cm) dry-ice-cooled Tenax® TA trap. The trap was attached in front of the gas chromatographic column, and the components were back-eluted onto the column under the conditions specified for the gas-chromatographic separation above.

Weight Determination and Karl Fischer Water Analysis

The analysis of the high-boiling mixture evolved during the cure was accomplished by isothermally heating a sample of the fluoroelastomer compound, ca. 20 g, for 24 hr as described above, and collecting the high-boiling components. Dry nitrogen, 30 cm^3/min, was passed over the samples and then through a tared, dry-ice-cooled, nitrogen-blanketed trap. The trap was allowed to warm to room temperature under nitrogen before being reweighed. The weight gain of the trap divided by the weight loss of the sample represents the contribution of the high-boiling components to the total weight loss.

The weighed high-boiling component mixture was analyzed for its water content by the Karl Fischer method. The results are expressed as wt% of the high-boiling component mixture collected.

Results and Discussion

A variety of cross-linking agents and accelerators are used with fluoroelastomers, among them are diamines, protected diamines (e.g., hexamethylenediamine carbamate), and a combination of bisphenols and "onium" salts (e.g., 1,4-dihydroxybenzene with tetraphenylphosphonium chloride).

Weight Loss During Curing

Table 2 shows that approximately twice as much weight is lost during initial heating in an air oven as during the same heat exposure in a closed mold in the press. This occurs because the volatile components escape from the sample less easily when it is confined in a mold, as in actual factory operations. Thus, the amounts of volatile components evolved during commercial press-cure operations will be less than those reported here for the simulated cure.

During the regular curing conditions (Table 2), the greatest weight loss occurs during the first 12 hr of the post-cure. After this, the rate decreases considerably.

Composition of the Volatile Components

Hydrogen Fluoride

Because hydrogen fluoride[7,8] has a very low threshold limit value[9] (3 ppm), a study to detect it at very low levels was undertaken. The results in Table 3 show that only very small amounts of HF are evolved during simulated cure.

Low-Boiling Materials

It was not possible to determine accurately the relative amounts of low- and high-boiling materials evolved during

Table 2. Cumulative Weight Loss

Compound (see Table 1)	Cumulative Loss, wt%			
	A	B	C	D
Regular Cure				
Press, 10 min at 193 °C (379 °F)	0.32	0.28	0.26	0.27
Oven at 232 °C (450 °F)				
12 hr total	1.38	1.51	2.16	1.32
24 hr total	1.54	1.83	2.48	1.56
36 hr total	1.64	2.06	2.67	1.71
Simulated Cure				
Oven, 10 min at 193 °C (379 °F)	0.69	0.78	0.81	0.68
Oven at 232 °C (450 °F)				
12 hr total	1.28	1.47	1.85	1.23
24 hr total	1.42	1.75	2.15	1.43
36 hr total	1.50	1.94	2.33	1.56

Table 3. Hydrogen Fluoride Evolved

Compound (see Table 1)	HF Found, mg/kg Compound			
	A	B	C	D
Press, 10 min at 193 °C (379 °F)	7	4	4	<4
Oven 24 hr at 232 °C (450 °F)	80	140	620	260

press cure. However, the quantity of the low-boiling materials evolved during the post-cure was estimated by subtracting the weight of high-boiling material from the total weight loss (Table 4).

Quantitative mass spectral analysis of the low-boiling material evolved during the press cure indicated large amounts of carbon dioxide (CO_2) are formed. Thus, much of the weight loss during press cure undoubtedly is due to this component. Carbon dioxide was the only low-boiling component emitted during the post-cure as detected by quantitative mass spectrometry, except that trace amounts of ethanol and CO were observed for Compound A. No fluorocarbon breakdown products were detected.

The quantities of CO_2 determined by mass spectrometry were much higher than the quantity of low-boiling materials calculated as discussed above. It was concluded that a portion of the CO_2 detected during the post-cure was generated from the reaction of atmospheric oxygen originally introduced in the sample tubes with the fluoroelastomer compound. The oxygen content of the tubes was not affected by the 10-min heating at 193 °C (379 °F). However, the oxygen was completely consumed during the heating at 232 °C (450 °F). Consequently, the mass spectral data were used only to identify the low-boiling components, rather than to determine them quantitatively. The limiting detectability for the mass spectrometer in these experiments was approximately 0.1%.

High-Boiling Materials

Table 4 shows that the high-boiling material represents the major portion of the weight loss, 80–97%. Because the trapping procedure of the two experimental techniques 4 and 5 was similar, it was assumed that the material collected in the gas chromatographic trap also accounted for the major portion of the weight loss.

Karl Fischer water analysis on the collected high-boiling component mixture indicated that it was mainly water (approximately 94–98%). The high levels of water found are in good agreement with the gas chromatographic values in Table 5 and confirm previous observations by other workers[3,4,5].

Table 5 contains the tabulated results of the gas chromatographic data for each fluoroelastomer compound. Water is the only major high-boiling component evolved from each fluoroelastomer compound during each curing step. The content of the other components generally diminishes with time.

Four additional components were detected from Compound A, with the major portion of the organo-phosphine oxide evolved during the post-cure. Only one high-boiling component, hexamethylenediamine, was detected from Compound B, and it diminishes significantly after the post-cure. Four high-boiling components were detected from Compound C, and each diminishes with time. Two high-boiling components were detected from Compound D, and they also diminish with time.

A rather complete picture of the major products evolved during curing was obtained by combining the data presented. Because the low-boiling components are mainly CO_2, the only components of concern are the high-boiling components. The percentage of a particular high-boiling component evolved from a fluoroelastomer compound during the press plus 24 hr post-cure can be estimated by:

Equation (5)—Component (wt%) = A x B x C x 10^{-4}

where A is the total weight loss obtained from Table 2, B the percent of the component of interest obtained from the gas chromatographic data in Table 5, and C the percent of the weight loss collected as high-boiling material obtained from Table 4. For example, from 100 g of Compound A, a total of 1.45 g of water and 0.04 g of R3PO would be evolved after 10 min at 193 °C (379 °F), followed by 24 hr at 232 °C (450 °F) (Table 6).

Calibration of the gas chromatograph for selected high-boiling components was accomplished by injecting known quantities. It was found that the quantities of the calibrated component determined in this way agreed roughly with the amounts calculated by Equation (5).

A variety of other factors not studied here can affect the nature and quality of the evolved components. Important factors are: (a) the curing temperature, (b) the type and amount of filler and curatives, and (c) the impurities in these components.

Evolution of Benzene

It is known that bisphenol-cured fluoroelastomer compounds accelerated with benzyl triphenyl phosphonium chloride and similar agents can liberate small amounts of benzene during vulcanization. A separate study utilizing capillary gas chromatography/mass spectroscopy (head-space technique) indicated that an average of 5 mg benzene per kilograms of compound (0.0005%) may be evolved under simulated vulcanization conditions, the majority during post-cure.

Table 4. High-Boiling Material Collected

Compound (see Table 1)	A	B	C	D
High-Boiling Components[a], wt%	93–97	80–83	80–81	80–89
Low-Boiling Components[b], wt%	3–7	17–20	19–20	11–20
Water Content of High Boilers[c], %	94–96	96–97	97–98	94–97

[a]Weight of high-boiling components collected, during the press and 240-hr post-cure, in a dry-ice trap, divided by the total weight loss of the sample (see Experimental, Technique 5)
[b]By difference
[c]Water found as wt% of the high-boiling component mixture

Table 5. High-Boiling Compounds Evolved

Compound (see Table 1)	A		B		C		D	
Time	10 min	24 hr	10 min	24 hr	10 min	24 hr	10 min	24 hr
Temperature, °C	193	232[a]	193	232[a]	193	232[a]	193	232[a]
H_2O	98.6	96.6	93.5	98.1	69.4	83.6	85.1	90.0
$C_6H_5CH_3$	0.1	0.1	0.0	0.0	1.2	0.5	0.0	0.0
HO-Ar-OH[b]	0.5	0.4	0.0	0.0	0.0	0.0	0.0	0.0
R3P[c]	0.2	0.1	0.0	0.0	0.0	0.0	0.0	0.0
R3PO[d]	0.4	2.7	0.0	0.0	0.0	0.0	0.0	0.0
$H_2N(CH_2)_6NH_2$	0.0	0.0	6.1	1.8	0.0	0.0	0.0	0.0
C_6H_5CHO	0.0	0.0	0.0	0.0	7.9	4.1	0.0	0.0
$C_6H_5CH = CHCHO$	0.0	0.0	0.0	0.0	18.5	8.9	0.0	0.0
C11, HgN[e]	0.0	0.0	0.0	0.0	2.9	2.1	0.0	0.0
Alicyclic Diamine[f]	0.0	0.0	0.0	0.0	0.0	0.0	13.9	6.9
Alicyclic Amine Fragment[g]	0.0	0.0	0.0	0.0	0.0	0.0	0.1	2.0
Other[h]	0.2	0.1	0.4	0.1	0.1	0.8	0.9	1.1

[a]After 10 min at 193 °C (379 °F)
[b]A bisphenol cross-linking agent of the type HO-Ar-X-Ar-OH
[c]An organo-phosphine accelerator fragment
[d]An organo-phosphine oxide accelerator fragment
[e]An unidentified fragment from the cross-linking agent
[f]A diamine cross-linking agent liberated from the alicyclic amine salt
[g]An unidentified fragment from the diamine reported above
[h]A series of unknown components

Table 6. Summary of the Volatile Products Evolved During Curing*

Compound (see Table 1)	A	B	C	D
Total Volatiles, wt%	1.5	1.8	2.5	1.6
H_2O, wt% of Volatiles	93	80	67	76
HF, wt% of Volatiles	1	1	2	2
CO_2, wt% of Volatiles	3	17	18	14
Curative Products, wt% of Volatiles	3	2	13	8

*10 min at 193 °C (379 °F) in the press plus 24 hr at 232 °C (450 °F) post-cure

Conclusions

The data show that hydrogen fluoride is not a major component of the gases evolved during any stage of the cure. During the press cure, the major components are carbon dioxide and water. Temperature and mold openings can have a significant effect on the weight loss during press cure. During the post-cure, the major components are water and carbon dioxide, while the rest of the components result primarily from the curing agents. No fluorocarbon breakdown products were detected.

A variety of factors can affect the nature of the products evolved from fluoroelastomer compounds during curing. Because the physiological effects of many of these compounds are not known, it is recommended that adequate ventilation always be used when curing fluoroelastomers.

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Appendix 3

Volatile Product Evolution from Non-APA Types of Peroxide-Cured Fluoroelastomer Compounds

Abstract

Volatile product evolution from non-APA types of peroxide-cured commercial grades of Viton™ under simulated press and post-cure conditions is reported, together with vulcanizate combustion products. Vulcanization by-products quantitatively reported include hydrogen fluoride, water, methyl bromide and miscellaneous organic components. Results from a laboratory air monitoring exercise for methyl bromide are also given.

Compounds

Compounds used for the reported evaluations, based respectively upon Viton™ GF and Viton™ GBL 900, are shown in **Table 1**. These two polymers are similar in composition, except that Viton™ GF is a high fluorine grade for maximum hydrocarbon and chemical resistance, whereas Viton™ GBL 900 is analogous to a typical B-type copolymer. The reported results are representative of what could be expected for similar compounds, based on the following polymers: Viton™ GBL-900, GF, GFLT, GLT, and ETP-900. All these types of Viton™ utilize a cure site monomer containing bromine to effect peroxide curing.

Outline Procedures

Hydrogen Fluoride Evolved in Curing

For simulated press cure, raw compound samples were heated for 10 min at 190 °C (374 °F) swept by air, which was then passed through 0.005N sodium hydroxide. Fluoride content of the resulting solutions was determined using a selective electrode and ion analyzer. For simulated post-cure, samples were first press cured 5 min at 190 °C (374 °F) and then heated in the air stream for 24 hr at 232 °C (450 °F).

Table 1. Peroxide-Curable Compounds of Viton™

Compound	Viton™ GF	Viton™ GBL 900
Polymer	100	100
MT Black (N908)	30	30
Sublimed Litharge	3	3
Diak™ No. 7	3	3
Luperco® 101-XL*	3	3

*50% active 2,5-dimethyl-2,5-di(butyl peroxy)hexane. Varox is similar.

Water Evolved in Curing

For simulated press cure, samples were heated for 10 min at 190 °C (374 °F) swept by dry nitrogen. Water content of the used nitrogen was monitored in a Karl Fischer titration vessel.

To simulate post-cure, samples press cured 5 min at 190 °C (374 °F) were heated for 24 hr at 232 °C (450 °F) in sealed combustion tubes. Upon completion, tubes and residues were swept with dry nitrogen for 30 min at 150 °C (302 °F), and water pickup monitored as before. Empty tubes were used as method blanks.

Organic Compounds Evolved in Simulated Press Curing (Viton™ GF Only)

Uncured samples were heated in helium from ambient at 10 °C (50 °F) per min and then held for 10 min at 190 °C (374 °F) in thermogravimetric apparatus to simulate press cure conditions. Analysis was performed by gas chromatography and mass spectroscopy.

Vulcanizate Combustion Products

These were determined under good (excess oxygen) and poor (deficient oxygen) combustion conditions, as follows:

- Excess Oxygen

  A 15 mg sample was heated for 10 min at 900–1,000 °C (1,652–1,832 °F) in 500 mL air, i.e., a several-fold excess of oxygen. Under these conditions, all carbon in the samples was converted to CO_2. Qualitative and quantitative analysis of the combustion products was accomplished by infrared spectrophotometry.

- Deficient Oxygen

  The same apparatus was used, but with differing air supply and heating arrangements; the sample being heated as rapidly as possible. A number of samples spontaneously ignited. All burned faster than the supply of air, hence, in the oxygen-deficient environment, partial combustion products were formed. Carbon and other sublimates and distillates were subsequently "reburned." Thus, the IR cell finally contained all the combustion products that were gases or low-boiling liquid, high-boiling liquids having been "reburned."

Air Monitoring for Methyl Bromide

Appropriate method for air sampling for methyl bromide in the manufacturing environment is adsorption onto charcoal-filled tubes or use of proprietary Pro-tek® badges. The same desorption and gas chromatography conditions for analysis apply in both cases. Results of these studies are summarized in **Tables** 3 to **5**.

Exposure TWA and STEL Values

Values adopted by the American Conference of Governmental Industrial Hygienists (ACGIH) for 2004 for the by-products specifically discussed are given in **Table 2**. Limits in other countries are similar. The TWA value for methyl iodide is included for completeness.

Summary

The available data suggest that evolution of tightly controlled workplace concentration volatiles, such as hydrogen fluoride and methyl bromide, is low when adequate exhaust ventilation is provided. This was checked under laboratory conditions by molding test slabs (150 x 100 x 2.0 mm) based on Viton™ GF, six at a time for 5 min at 190 °C (374 °F), continuously for 6 hr. Results from air monitoring for hydrogen fluoride and methyl bromide versus TWA limits are given in **Table 5**.

All processors are advised to monitor air quality at the start of regular production and on a scheduled basis.

Table 2[a]

	TWA, ppm	STEL, ppm
Acetone	500	750
t-Butanol	100	—
Carbon Dioxide	5,000	30,000
Carbonyl Fluoride	2	5
Hydrogen Fluoride	—	3[b]
Methanol	200	250
Methyl Bromide	1	—
Methyl Iodide	2	—

[a]ACGIH TLV values from 2004
[b]This is a ceiling value

Table 3. Volatile Components, mg/kg Compound[1]

	Viton™ GF		Viton™ GBL 900	
	190 °C (374 °F)/10 min	232 °C (450 °F)/24 hr	190 °C (374 °F)/10 min	232 °C (450 °F)/24 hr
Evaluations 1 and 2				
Hydrogen Fluoride	0.2	700	0.3	170
Water	900	800	800	700
The organics evolved are quantified in Evaluation 3 shown below. Only simulated press-cured Viton™ GF was studied.				
Evaluation 3				
Methyl Bromide [2,3]	19			
Acetone	2,846			
i-Butene	56			
Methanol	96			
t-Butanol	297			
wt% Loss	1.3			

[1]Peaks for the components shown in Evaluation 3 were not fully resolved; hence, the quantitative accuracy may be questionable.
[2]A later study in a different laboratory indicated that up to 600 mg/kg of methyl bromide may be generated.
[3]As advised, methyl iodide is not normally emitted from compounds based upon non-APA grades of peroxide-cured Viton™ during vulcanization. Any exceptions will be advised in SDS for specific products.

Table 4. Combustion Products of Vulcanization of Viton™

	Viton™ GF		Viton™ GBL-900	
Combustion Products, mg/g Compound	Excess O_2	Deficiency O_2	Excess O_2	Deficiency O_2
Evaluation 4—Combustion Products of Vulcanizates of Peroxide-Cured Viton™[a]				
Carbon Monoxide (CO)	15	22	19	27
Carbon Dioxide (CO_2)	1,600	1,500	1,500	1,700
Hydrogen Fluoride (HF)[b]	514	516	508	503
Carbonyl Fluoride (COF_2)	15	—	—	—
Hexafluoroethane (C_2F_6)	9	9	—	5
Tetrafluoromethane (CF_4)	—	7	—	4

[a]Compounds press-cured 5 min/190 °C (374 °F) and post-cured 24 hr/232 °C (450 °F).
[b]Calculated assuming all unaccounted for fluoride forms hydrogen fluoride.

Table 5

	Measured, mg/m³	TWA, mg/m³	ppm
Evaluation 5			
Hydrogen Fluoride	0.03	0.5–2.5	1.8–3.0
Methyl Bromide	<2 detection limit	3.8*	1*

*United States

Appendix 4

Air Monitoring for Methyl Iodide During Vulcanization of Iodine-Containing, Peroxide Cure Types of Viton™

Abstract

The results of tests to evaluate airborne concentrations of methyl iodide during the vulcanization of iodine-containing peroxide cure types of Viton™ are reported.

APA types of peroxide cure Viton™ polymers contain iodine in the form of cure site monomer and as polymer chain end modifier. Types of Viton™ polymer that have iodine-based cure systems are designated by an "S" at the end of their name.

Procedures

The air monitoring was conducted at the Chemours laboratory in Stow, Ohio, by American Analytical Laboratories, Inc., over a four-hour time period, during which time 33 heats of compound #1964A08-01* were cured in a Wabash Press. Approximately 400 grams of the compound were in each of the 33 heats. Each heat molded six 102 x 152 x 1.0 mm ASTM test slabs in a six-cavity compression mold.

Formulation on last page of Appendix 4

The air monitoring consisted of the collection of one personal and three area air samples. The personal air sample (Sample 005A) was obtained from the breathing zone of the press operator who was responsible for the loading and unloading of the press and mold. The area air samples were collected from inside the fume hood that was over the press (Sample 002A), a position directly outside of the fume hood (Sample 003A), and a workbench that was 3 m (10 ft) away from the press (Sample 004A).

The air monitoring was conducted using Gilian model LFS-113D personal air monitoring pumps. These pumps were pre- and post-calibrated against a National Institute of Standards and Testing (NIST) traceable primary standard.

The samples collected to evaluate airborne concentrations of methyl iodide were shipped to Clayton Group Services in Novi, Michigan, for analysis. Table 1 below lists the contaminant evaluated and the corresponding National Institute of Occupational Safety and Health (NIOSH) analytical method.

Table 1

Contaminant	Analytical Method
Methyl Iodide	NIOSH 1014

OSHA Exposure Limits

The Occupational Safety and Health Administration (OSHA) currently has established the following permissible exposure limit (PEL) shown in Table 2.

Table 2

Contaminant	Permissible Exposure Limit
Methyl Iodide	5 ppm

The PEL is the legally enforceable level that OSHA has set for the implementation of engineering controls and the need for personal protective equipment. The OSHA PELs are evaluated as 8-hr time weighted averages. The calculated 8-hr time weighted average exposure for the press operator assumes that he/she did not have any exposure to methyl iodide for the remainder of the work shift.

Personal air samples were collected to evaluate the employees' exposures and compare those exposures to the PEL. Area samples were collected to evaluate the airborne concentration in the area where the samples are collected. These airborne concentrations do not represent personal exposures, but can be used to make initial determinations of personal protective equipment.

Results

The results of the air monitoring samples for methyl iodide are as follows:

Sample Description	Sample No.	Results, ppm	Calculated 8 hr TWA	OSHA PEL
Personal Sample	005A	0.14	0.07 ppm	5 ppm
Inside Fume Hood	002A	0.55	—	5 ppm
Outside Fume Hood	003A	0.11	—	5 ppm
3 meters From Press	004A	<0.036	—	5 ppm

Details of the air monitoring tests for methyl iodide are listed below.

Sample No.	Sample ID	Air Volume, L	Mel, µg	mg/m^3	ppm
001A	Field Blank	(0)	<1.0	—	—
002A	Inside Fume Hood	23.6	76	3.2	0.55
003A	Outside Fume Hood	48.9	30	0.62	0.11
004A	3 meters From Hood	48.2	<10	<0.21	<0.036
005A	Personal Sample	47.2	38	0.81	0.14

General Notes: < = Less than the indicated reporting limit   — = Information not available or applicable

Conclusions

Analysis of the personal and area air samples collected to evaluate methyl iodide reported that the airborne concentrations were well below the OSHA PEL of 5 ppm. Adequate ventilation is recommended to ensure that hazardous quantities of volatiles do not build up.

Formulation of Appendix 4 Compound 1964A08-01

	1964A08-01
Viton™ GBL-600S*	100.0
Diak™ No. 7	3.0
Varox DBPH-50	2.5
Zinc Oxide	3.0
MT (N990) Carbon Black	30.0
Armeen 18D	0.5
Struktol WS280	0.5

* Formerly designated as VTR-8650