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Aging Effects on Fire-Retardant Additives in Organic Materials for Nuclear Plant Applications

Roger L. Clough

This report documents part of the Qualification Testing Evaluation (QTE) Program being conducted by Sandia National Laboratories

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Albuquerque, New Mexico 87185
operated by
Sandia National Laboratories
for the
U. S. Department of Energy

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ABSTRACT

Inhibiting fire is a major concern of nuclear safety. One of the most widely used commercial fire-retardant additives incorporated into cable insulation and other organic materials to reduce their flammability has been the halocarbon (usually a chlorinated hydrocarbon), typically in combination with antimony oxide. Such materials may be installed for the design lifetime of a nuclear plant; this report describes an investigation of the long-term aging behavior of these fire-retardant additives in polymeric materials.

Extensive aging experiments on fire-retarded formulations of ethylene propylene rubber (EPR) and of chlorosulfonated polyethylene (CSPE) have been carried out, with chemical analysis of halogen and antimony content performed as a function of aging time and conditions. Oxygen index flammability measurements were also performed on selected samples. Significant fire-retardant losses (both chlorine (Cl) and antimony (Sb)) were found to occur in certain of the fire-retardant materials but not in others, depending on the molecular structure of the particular halogen-containing component. The Cl:Sb loss ratios indicate that a chemical reaction takes place under the aging conditions to form the volatile compound, antimony trichloride (SbCl_3). The EPR formulations showed a modestly increased flammability with fire-retardant loss on aging. CSPE materials exhibited a significant decrease in flammability on aging despite the loss of flame retardants. This appears to be correlated with the loss of flammable, volatile components from the formulation.

Using the activation energy of 34 kcal/mol derived from Arrhenius treatment of the antimony loss data for the EPR formulation having the most rapid loss rate, it is predicted that fire-retardant loss should become appreciable for this material only at substantially elevated temperatures or exceedingly long times. The data indicate that the loss of halogen- and antimony-based fire retardants appears to be insignificant under ambient conditions expected for nuclear plants.

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INTRODUCTION

Fire protection is a major concern in nuclear safety. Awareness in this area was much heightened following the fire in the nuclear plant at Brown's Ferry in March of 1975.¹⁻³ The NRC issued a Regulatory Guide on Fire Protection in June of 1976,⁴ and has been funding research in the area of fire testing,⁵ including an extensive series of cable tray fire tests performed by Klamerus at Sandia.⁶

Flammable materials in nuclear plants include a variety of organic polymers used in various applications, most notably as cable insulation materials. The flammability of organic polymers, many of which consist chiefly of carbon and hydrogen, is a problem of general concern to the polymer industry. Consequently, much work has been done on the study of polymer combustion properties. Reduction of the flammability of organic materials is achieved by the incorporation of fire-retardant additives into the polymer formulations. One of the most widely used types of fire-retardant additive has been the halogenated hydrocarbon, usually in combination with antimony oxide (Sb_2O_3).⁷ This halogen-antimony combination has been employed in conjunction with many different generic polymer types, and is used today in a variety of applications including (along with cable insulation materials) a host of commercial products made with rubbers, plastics, paints and textiles.

The halogenated hydrocarbon (the halogen is usually chlorine, but may be bromine) by itself can have a fire-retardant effect,⁹ while antimony oxide alone acts essentially as an inert filler and has little effect on the flammability properties of polymer materials.¹⁰⁻¹² In combination, the two additives work in a synergistic fashion. This is believed to occur by reaction under the high temperatures of the fire environment to give a volatile antimony halide. The overall chemical reaction is outlined in equations 1 and 2.^{7,8}



The antimony halide and/or its secondary breakdown products apparently serve as efficient free radical scavengers in the flame region above the burning material.^{7,8,10,13} The fire-retardant effect of these two additives has been seen in a variety of small-scale flammability tests which reflect the susceptibility of materials to combustion in the environment of a small ignition source.^{7,8}

Some types of polymers are intrinsically less flammable than others. For example, polymers containing chlorine substituents along the chain backbone such as polyvinyl chloride (PVC), chlorosulfonated polyethylene (Hypalon)*, and chloroprene (neoprene), have inherently reduced flammability.¹⁰ Depending on the degree of flame retardancy desired, these materials may be used either with or without added antimony oxide.^{14,15} The three chlorinated materials named above are used extensively as cable jacketing materials in the nuclear industry. Non-chlorinated polymer types can be fire retarded by inclusion of Sb_2O_3 along with a low molecular weight halogenated-hydrocarbon in the formulation.

Materials used in nuclear plant applications are expected to last for the design lifetime (typically 40 years). Recently there has been increased concern over qualifying critical components with respect to their ability to function after ambient aging. Because of this concern, extensive NRC-funded research has been carried out on organic polymers to investigate the effects of aging on their mechanical properties.¹⁶ The results have shown that dramatic differences can exist between aged and unaged materials, indicating that aging must be a major consideration in qualification testing with respect to mechanical and electrical performance.

Because of the concern for understanding the performance of aged materials, the question was raised of the long-term aging behavior of cable insulation materials with respect to potential loss of the fire-retardant additives and resulting loss of flammability-inhibiting properties. A literature search failed to bring to light any study on fire-retardant aging of halogen or halogen-antimony flame-retarded materials, despite the fact that this retardant system has had widespread use during the past several decades.⁷

This report describes the results of an extensive series of fire-retardant aging experiments on formulations of two material types of importance in present-day nuclear plant applications. One of these, Hypalon®, is a chlorinated material; the other, ethylene-propylene rubber (EPR) is a nonchlorinated material.

*Hypalon is a registered trademark of E. I. duPont de Nemours and Company.

EXPERIMENTAL

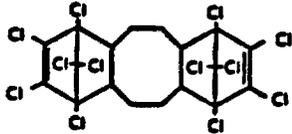
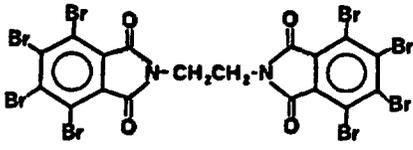
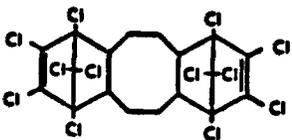
Samples made from two different EPR types (Table I) were used in the aging experiments. One of these (A) is typical of formulations currently used in certain cable material.^{17,18} The other (B) is similar to formulations used for certain structural applications. Five different variations with respect to fire-retardant additives were prepared. Four of these contained antimony oxide (Sb_2O_3) in combination with one of three different commercial halogenated-hydrocarbon flame-retarding agents. The halogenated-hydrocarbon additives are representative of compounds used as flame-retardant additives in recent years.^{8,9,19} One formulation prepared for the aging studies (EPR III) was intended as a control sample and not a realistic flame-retardant system; it contained only Sb_2O_3 in the absence of any chlorinated compound. The five flame retardant EPR formulations are summarized in Table II.

TABLE I
EPR BASE FORMULATIONS

EPR A	(parts)	EPR B	(parts)
Nordel 2722	(90)	Vistalon 4608	(100)
Low Density PE	(20)	Zinc Oxide	(5)
Zinc Oxide	(5)	Stearic Acid	(1)
Paraffin Wax	(5)	HAF Black	(50)
Litharge	(5)	SRF Black	(50)
Zn Salt (ZMB)	(2)	MT Black	(50)
Aminox	(1)	Sunpar 2280	(40)
Treated Calcined Clay	(60)	Ethyl Tellurac	(0.5)
Vinyl Silane	(1)	MBT	(1.0)
SRF Black	(2)	Sulfur	(1.5)
Di-cup R	(3)		

Table II

FIRE RETARDANT COMPONENTS USED

DESIGNATION	BASE COMPOUND*	FIRE RETARDANTS	(parts)
EPR I	A		(33)
		Sb ₂ O ₃	(10)
EPR II	A		(33)
		Sb ₂ O ₃	(10)
EPR III	A	Sb ₂ O ₃	(10)
EPR IV	B		(20)
		Sb ₂ O ₃	(10)
EPR V	B	$x_2C-(CX_2)_nCX_2$ <p>X = H, Cl</p> <p>[Cl = 70%, by weight, of the cpd.]</p>	(20)
		Sb ₂ O ₃	(10)

*Refers to base formulations in Table I.

A chlorosulfonated polyethylene (Hypalon®) formulation, similar to that used in cable material applications¹⁸ (shown in Table III), was used in the aging experiments. Two hypalon variations were studied, namely with and without added Sb₂O₃ (HYP-I = no added Sb₂O₃; HYP-II = 7 parts added Sb₂O₃).

Samples of the compression-molded polymers were prepared by Burke Rubber Corporation; specimens having dimensions of 15.2 cm x .6 cm x .2 cm (6" x .22" x .07") were utilized in the aging experiments.

Thermal aging of polymer samples was carried out in chambers which were placed inside ovens. The chambers had carefully controlled air flow (giving the equivalent of two changes of atmosphere per hour) and temperature control to within $\pm 1^{\circ}\text{C}$.

TABLE III
CHLOROSULFONATED POLYETHYLENE FORMULATION*

HYP I	(parts)
Hypalon 40	(100)
LGB Clay	(75)
Philblack A	(15)
NBC	(2)
Kenaflex A	(10)
Sunolite 240	(2)
Sundex 790	(30)
Litharge Paste	(20)
MBT (Captex)	(1)
Tetrone A	(2)

*HYP II is identical to HYP I except that it contains an additional 7 parts Sb₂O₃

The wet chemical analysis for antimony (Sb) and chlorine (Cl) was carried out by Spang Microanalytical Laboratories of Eagle Harbor, Michigan. Chlorine was determined using a standard silver coulometric technique.^{20,21} Antimony was determined using atomic absorption spectroscopy.²² Wet chemical analytical data given throughout this report represent the average of at least two different determinations. The mean error in the data given for Cl is approximately ± 0.15 absolute percent in the case of the EPR samples. In the case of the Hypalon samples, it ranged from ± 0.2 to ± 0.5 absolute percent. The mean error for the antimony determinations was approximately ± 0.07 absolute percent in both materials.

Neutron activation analysis for Cl and Sb was performed on intact polymer specimens using 14 MeV neutrons.²³ The activation reactions used were: $^{37}\text{Cl}(\text{fn},\text{p})^{37}\text{S}$ and $^{123}\text{Sb}(\text{fn}, 2\text{n})^{122}\text{Sb}$. The activation reaction generally used for Sb analysis [$^{121}\text{Sb}(\text{fn}, 2\text{n})^{120}\text{Sb}$] was impractical with these polymer samples due to interference by other elements in the formulation including silicon and chlorine. Reference standards were established with NaCl-Sb₂O₃ - benzoin oxime mixtures. Activated samples were counted on a Ge(Li) detector coupled to a 4096-channel multichannel analyzer. The precision of the analysis for both Cl and Sb was on the order of $\pm 10\%$ relative.

Oxygen index flammability measurements were carried out by US Testing Corporation of Los Angeles, California, according to the ASTM standard.²⁴

RESULTS AND DISCUSSION

Fire-Retardant Loss From EPR Formulations

Of the EPR formulations studied, four of the five (EPR numbers I through IV) did not show appreciable changes in fire-retardant content after either 6 months at 120°C or 8 months at 110°C. In contrast to this are the results obtained with the formulation designated as EPR-V. Initial scoping experiments revealed significant fire-retardant losses in this material, and extensive aging tests were undertaken at a series of different temperatures. The temperature range (120°C-80°C) was chosen to include the lowest temperatures (based on the scoping experiments) expected to be practical for use in thermal aging experiments on a reasonable timescale. This experimental design was chosen to provide the optimum data to allow for extrapolation of the results on the most rapidly changing formulation examined (i.e., EPR-V) to lower temperature conditions which would be typical of ambient environments of interest.

Aging at 80°C gave rise to no measurable changes in the fire-retardant content during the timescale of the experiment (two years). Figs. 1 and 2 present the data for antimony content (as derived by atomic absorption) and for chlorine content (as derived by coulometry) as a function of aging time at the temperatures: 120°, 110°, 100° and 90°C. In order to provide independent verification of the aging-induced disappearance of these elements from the polymer matrix, a portion of the samples were analyzed by the neutron activation technique. This data is presented in Figs. 3 and 4. The trends seen with the two techniques are in agreement; significant losses of both chlorine and antimony are clearly seen.

Mechanistic Implications

Chlorine loss can conceivably occur by two mechanisms: 1) simple migration and evaporation of the chlorinated hydrocarbon out of the polymer matrix, and 2) degradation involving dehydrochlorination. Antimony oxide has a volatilization temperature of 1550°C,²⁵ so that any significant antimony loss at low temperatures must be preceded by chemical reaction to yield a more volatile species.

Two antimony species, SbOCl and SbCl_3 , have been discussed in the past as playing key roles in the synergistic fire retardancy of the antimony oxide - halocarbon combination.^{26,27} Evidence that the principle species in the vapor phase in the flame environment was SbCl_3 has been previously obtained by mass spectrometry.⁷ However, it had been thought that HCl reacted with Sb_2O_3 to generate SbOCl , and that the production of SbCl_3 depended upon a series of endothermic disproportionation reactions of SbOCl which have been shown by differential thermal analysis to take place only at very high temperatures.^{7,28} The fact that the antimony oxide - halocarbon combination makes such a good flame-retardant agent had been discussed in terms of the fact that the decomposition temperature of SbOCl matched

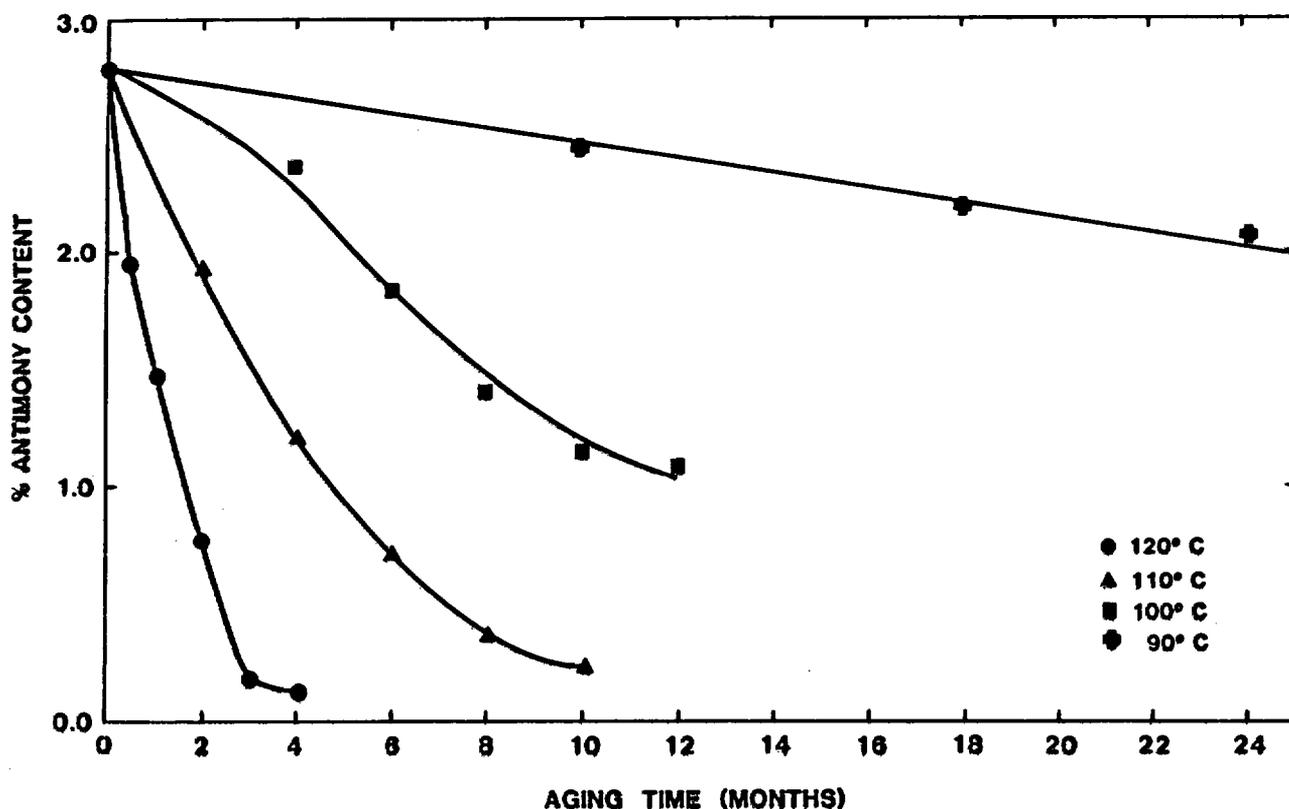


Figure 1. Antimony content (weight percent) as determined by atomic absorption spectroscopy on fire-retarded EPR (formulation EPR-V) as a function of thermal aging.

very well with the decomposition temperatures of typical polymeric materials with which it is used¹ (the so-called "right place at the right time" theory of flame retardancy).

Recently, a laser pyrolysis - mass spectrometry study has demonstrated that, in fact, when either the pyrolysis products of a PVC formulation or HCl from a cylinder were passed over unheated Sb_2O_3 , evidence could be obtained for the introduction of $SbCl_3$ into the gas phase.²⁹ These results indicated that $SbCl_3$ production was possible by reaction of HCl with Sb_2O_3 without involving the high temperature disproportionation reactions of intermediate $SbOCl$. Subsequent mass spectral studies in which mixtures containing Sb_2O_3 and polyvinylidene chloride were pyrolyzed together similarly revealed $SbCl_3$ volatilization at temperatures around $170^\circ C$, and also revealed Sb_4O_6 volatilization at temperatures around $300^\circ C$.^{30,31} The species Sb_4 was also detected, and its appearance was closely correlated to the appearance of $SbCl_3$ and of Sb_4O_6 .

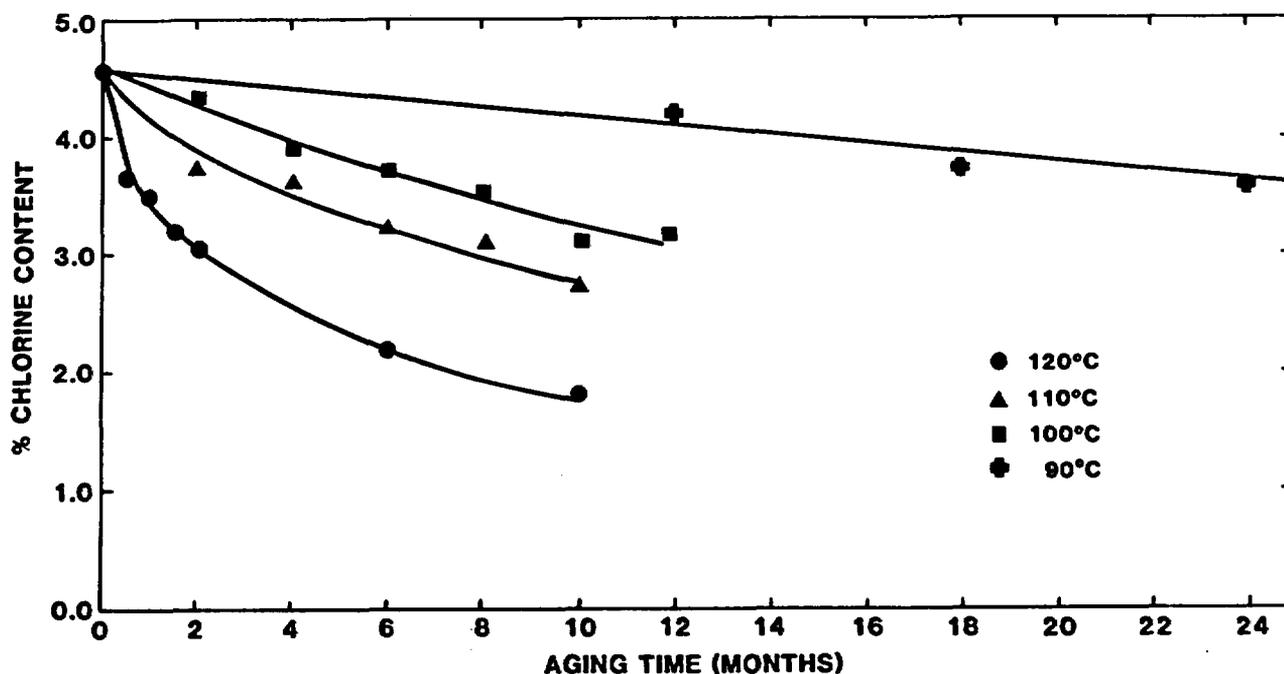


Figure 2. Chlorine content (weight percent) as determined by silver coulometry on fire-retarded EPR (formulation EPR-V) as a function of thermal aging.

From the data on the loss rates at the various aging temperatures and time periods obtained by us (Figs. 1 and 2), it can be calculated that the average molar ratio for the loss of these two elements is approximately 3:1 Cl:Sb. (There is a fair amount of experimental scatter in the data, along with indications of somewhat higher Cl:Sb ratios at the lowest temperature of 90°C). The data are consistent with a picture of the aging-induced antimony volatilization proceeding through the same chemical reactions (Eqs. 1 and 2) by which

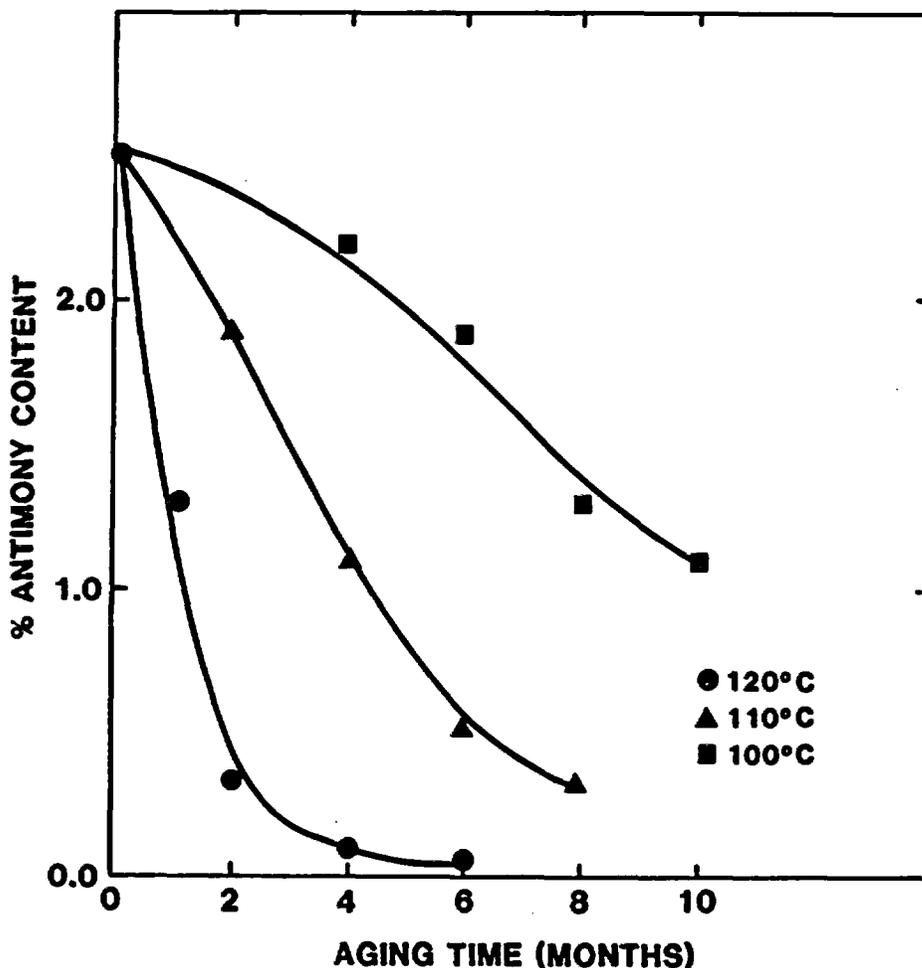


Figure 3. Antimony content (weight percent) as determined by 14 MeV neutron activation analysis for fire-retarded EPR (formulation EPR-V) as a function of thermal aging.

the two additives are believed to react in the fire environment to produce the flame-retarding effect. The stoichiometry indicates that the principle species through which the antimony volatilized from the polymer on aging is SbCl_3 (which has a boiling point of 283°C).²⁵ The antimony loss found in this work is consistent with the recent mass spectral evidence that SbCl_3 can be generated at low temperatures. Moreover, it demonstrates that very significant amounts of antimony volatilization (indeed, apparently total antimony loss) can occur from Sb_2O_3 -halocarbon fire-retarded polymer formulations at temperatures far below those required for thermal degradation and volatilization of the polymer itself. A large part of the chlorine lost on aging apparently involves decomposition of the chlorinated hydrocarbon, with evolution of HCl (which then reacts with the Sb_2O_3).

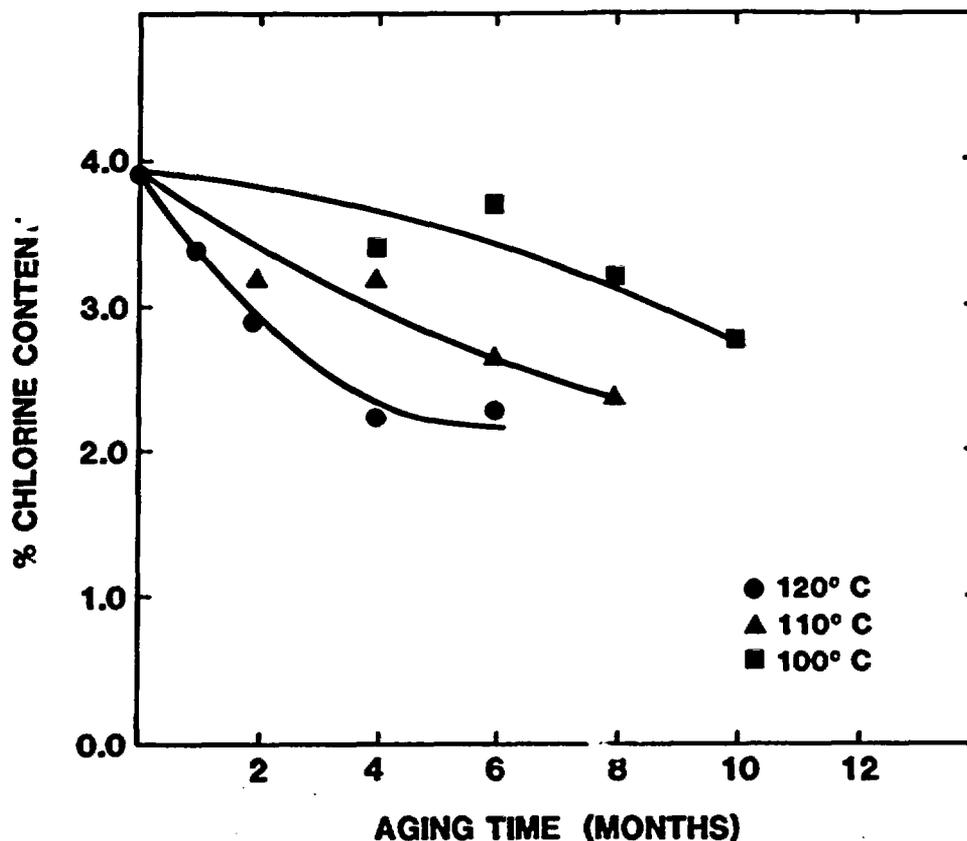


Figure 4. Chlorine content (weight percent) as determined by 14 MeV neutron activation analysis for fire-retarded EPR (formulation EPR-V) as a function of thermal aging.

Loss Rates

Figure 5 shows a plot of the log of the time required for disappearance of 25% of the antimony initially present, as a function of inverse aging temperature. The antimony loss is seen to exhibit linear Arrhenius behavior over this temperature range. Similar plots for 12.5% loss and for 50% loss also exhibit relatively linear Arrhenius behavior. The chlorine data covers a more limited range of relative total loss, and also has a larger relative error. Arrhenius plots exhibit more scatter, but also appear reasonably linear; Figure 6 is a plot of the log of the time required for disappearance of 25% of the initial chlorine content as a function of inverse temperature.

From the data in Figures 5 and 6, it is possible to estimate an apparent activation energy (E_a) for loss of the two fire-retardant components. The antimony loss gives an E_a of 34 ± 3 kcal/mole; chlorine loss has an E_a of about 31 ± 4 kcal/mole. The activation energies obtained for chlorine and antimony are very similar, and may in fact be the same within experimental error. The halogen-bearing component used in this formulation (EPR-V, Table I) is a chlorinated paraffin wax. The E_a values are similar to the apparent activation energies reported by Madorsky³² for the thermal dehydrochlorination of three different polyvinyl chloride specimens (26, 30 and 32 kcal/mol) obtained at higher temperatures (235-260°C).

Using the activation energy calculated for antimony loss, it is possible to extrapolate the loss rate to lower temperatures. The accuracy of such extrapolation depends, of course, on the overall process retaining linear Arrhenius behavior at the lower temperatures. Table IV presents data for the observed time for loss of 25% of the initial antimony content, while Table V shows calculated values of time for loss of 25% of initial antimony content at lower temperatures. The extrapolated data indicate that for EPR formulation V, antimony loss in sufficient amount to cause an appreciable effect on flammability properties during timescales of practical importance would only occur for material applications at significantly elevated temperatures (i.e., above 70°C).

The temperature of an operating high voltage cable will be below 50°C, and in most cases will fall in the range of 30-40°C;³³ low and medium voltage cables generate less heat than the high voltage cables. The ambient temperature of

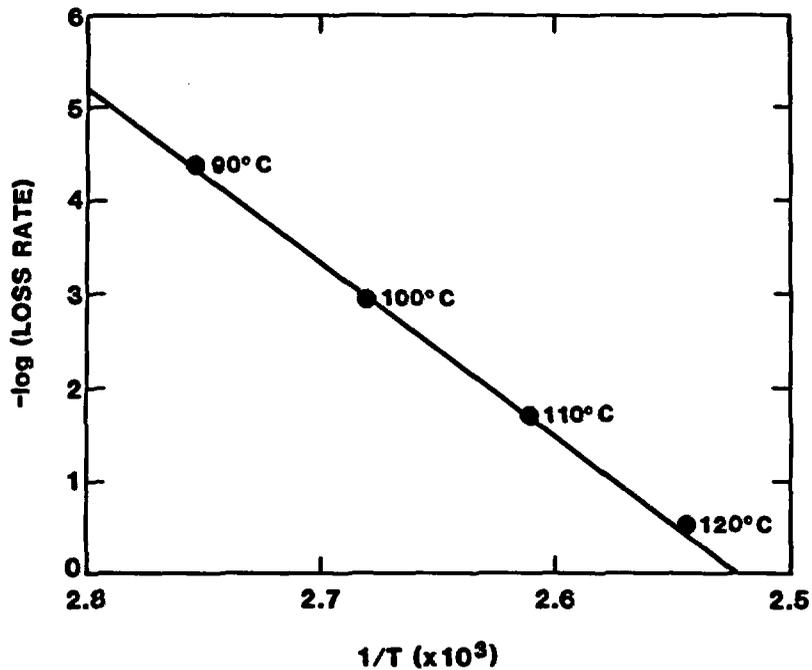


Figure 5. Arrhenius plot for 25% antimony loss rate [-log (.25/time in months)] from EPR-V as a function of inverse temperature.

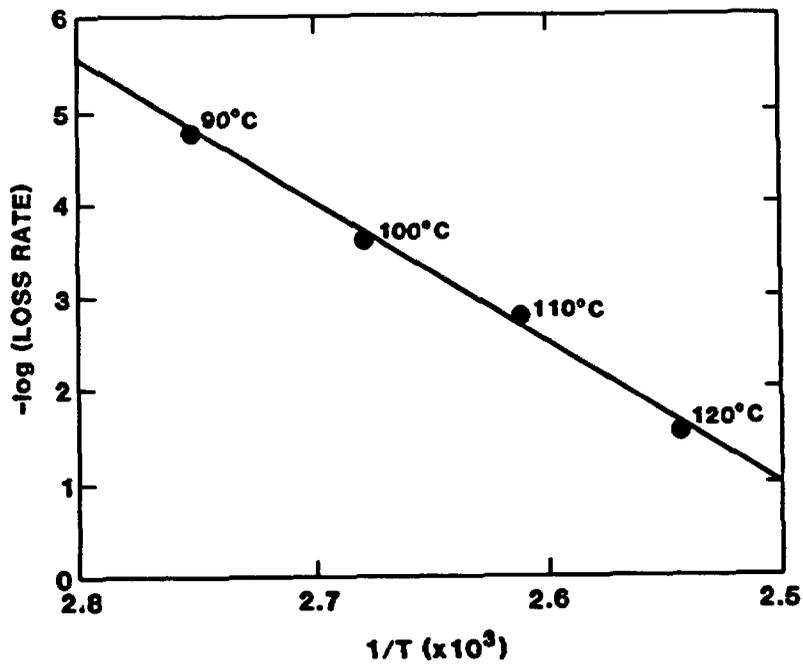


Figure 6. Arrhenius plot for 25% chlorine loss rate [-log (.25/time in months)] from EPR-V as a function of inverse temperature.

TABLE IV
 EXPERIMENTALLY DETERMINED TIMES FOR LOSS OF 25%
 OF INITIAL ANTIMONY CONTENT
 (EPR-V)

<u>TEMP.</u>	<u>TIME</u>
120°C	2 wk
110°C	1.4 mo
100°C	4.8 mo
90°C	21 mo

TABLE V
 EXTRAPOLATED TIMES FOR LOSS OF 25%
 OF INITIAL ANTIMONY CONTENT
 (EPR-V)

<u>TEMP.</u>	<u>TIME</u>
80°C	7 yr
70°C	28 yr
60°C	120 yr
50°C	600 yr
40°C	3×10^3 yr
30°C	2×10^4 yr

A nuclear plant may contribute to raising the absolute temperature of the cable somewhat, depending on specific plant location. It appears that even for the material (EPR-V) which has the most rapid loss rate of the formulations tested, the fire-retardant loss should not be significant in the temperature range and timescale important for nuclear plants.

The data would, however, indicate the volatilization of fractional percentages of antimony at temperatures near ambient. The generation of antimony trichloride (SbCl_3) in applications having large quantities of fire-retardant materials in confined areas could have significant implications, since SbCl_3 has both corrosive and toxic properties.³⁴

Formulation Differences

The EPR formulations examined showed major differences in fire-retardant aging characteristics; only one formulation showed appreciable loss of fire-retardant additives under the thermal aging conditions studied. A major factor behind the differences between the EPR formulations examined is most likely the ease with which the particular halogenated hydrocarbon can break down to yield HCl (or HBr), which serves as the first step leading to the eventual loss of SbCl_3 (or SbBr_3).

Of the three halocarbon fire-retardant additives examined in this study (see Table II), the partially chlorinated paraffin used in EPR-V stands alone as being able to readily undergo an intramolecular dehydrohalogenation. (The bromine substituents in the halocarbon of EPR-II have no adjacent hydrogen substituent. The loss of adjacent H and Cl atoms from the halocarbon of EPR-I and EPR-IV would result in the formation of a double bond connecting two bridgehead positions - a situation of extremely unfavorable geometry [Bredt's rule].³⁵) It has been pointed out before⁹ that thermal degradation of halogenated flame-retardant additives during polymer processing can be a concern and that substantial differences exist in the thermal stability of various halogenated flame retardants at polyolefin processing temperatures (which can typically fall in the approximate range of 235°C - 250°C).⁹ Other differences in individual formulations could conceivably play a contributing role in determining rates of fire-retardant loss on aging.

Radiation-Thermal Aging

For the majority of cable insulation in a nuclear plant, probably only thermal aging will be important. Some of the cable, however, which is in the containment area may experience a significant amount of radiation. Figs. 7 and 8 show data for samples of EPR-V aged at 100° and at 110°C under conditions of simultaneous γ -irradiation at approximately 5 krad/hr. Comparison with Figs. 1 and 2 leads to the conclusion that the added radiation did not appreciably affect the fire retardant loss rate. Other irradiation experiments were performed on EPR-I at 110°C and 100°C, using a dose rate of approximately 5 krad/hr to a total dose of about 30 Mrad. As with the oven-aging experiments, no measurable change in chlorine or antimony content was detected. These results would tend to indicate that unlike aging-induced changes in tensile properties, where radiation exerts a predominant influence, the radiation aging of EPR with respect to the loss of fire-retardant additives is relatively less significant compared with the effects of thermal aging.

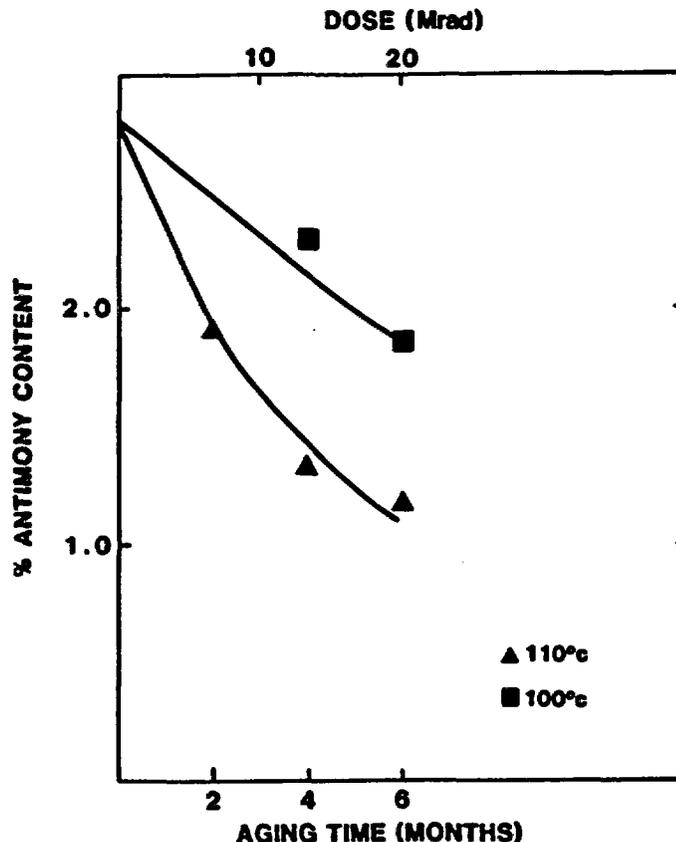


Figure 7. Antimony content (weight percent) as determined by atomic absorption spectroscopy on fire-retarded EPR (EPR-V) as a function of thermal aging with simultaneous γ -irradiation at 5 krad/hr.

This conclusion is consistent with a related observation reported previously. A value for the radiation yield of HCl loss from γ -irradiated PVC near room temperature was determined as $G(-\text{HCl}) = 13.36$. A similar radiation yield for the chlorinated hydrocarbon in EPR-V would lead to the expectation that only a small fraction of the total chlorine present would be lost after exposure to the radiation doses used in this study. By way of contrast, radiation effects show up strongly in terms of tensile property changes because only very small changes in chain scission or crosslinking are needed to produce noticeable macroscopic effects.

EPR Flammability Measurements

Material flammability can be discussed in terms of two general testing categories. The most commonly used type of combustion test evaluates flammability in the presence of a small-scale ignition source, and gives information on the propensity of materials to ignite and burn under low-level fire-initiating conditions (as was the case with the Brown's

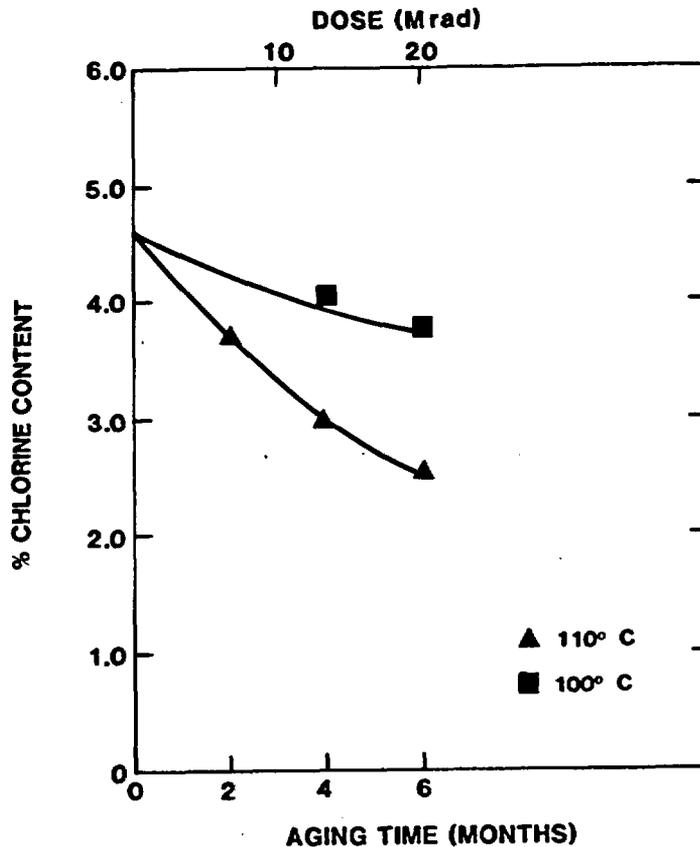


Figure 8. Chlorine content (weight percent) as determined by silver coulometry on fire-retarded EPR (EPR-V) as a function of thermal aging with simultaneous γ -irradiation at 5 krad/hr.

Ferry fire, which was set off by a candle used by an employee).^{1,3} There are numerous ASTM tests designed to fulfill this function. Such small-scale combustion results are strongly dependent on fire-retardant additives.^{8,9} A second type of fire test focuses on material flammability characteristics in the environment of an already existing, large-scale fire.³⁷

For the purposes of this study, we employed one of the most widely used of the small-scale ASTM flammability tests, the Limiting Oxygen Index Method,²⁴ for testing of selected samples from the aging experiments for comparison with the fire retardant loss data. The limiting oxygen index is defined as the minimum concentration of oxygen, in volume percent of a mixture of nitrogen and oxygen, that will support combustion.

$$LOI = \frac{(O_2)}{(O_2) + (N_2)}$$

Data from Oxygen Index Flammability Tests performed on several aged EPR samples having substantial fire retardant loss are given in Table VI. Changes in oxygen index are not large; the aged samples exhibit moderately increased flammability.

TABLE VI
OXYGEN INDEX DATA ON AGED SAMPLES OF
FIRE RETARDED EPR FORMULATION EPR-V

<u>AGING CONDITION</u>	<u>OXYGEN INDEX</u>
Unaged	28.0
12 months at 100°C	27.0
8 months at 110°C	26.5
4 months at 120°C	26.0

Fire-Retardant Loss From Chlorosulfonated Polyethylene

The second polymer type included in this work was chlorosulfonated polyethylene (Hypalon®). The formulation studied is characteristic of that used in cable jacketing material.¹⁸ Hypalon contains chlorine substituents distributed along the backbone of the polymer chain. Chlorination in the range of 35% is typical.³⁸ (Chlorosulphonyl groups initially present in low concentration in the resin react during curing as a part of the crosslinking process.)

Figs. 9 and 10 present data for chlorine and antimony content as determined by coulometry and atomic absorption, respectively, for HYP-II as a function of aging. Significant losses of both elements are found. Fig. 11 presents data for chlorine content (determined by coulometry) for CSPE formulation HYP-I which contains no Sb_2O_3 . Again, significant aging-induced chlorine loss is seen.

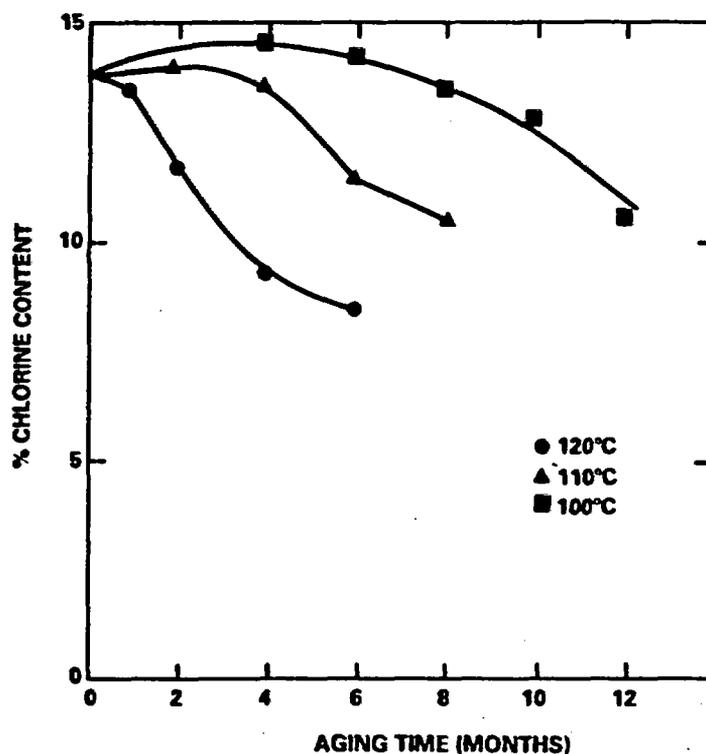


Figure 9. Chlorine content (weight percent) as determined by silver coulometry on HYP-II as a function of thermal aging.

Interestingly, the curves for antimony and chlorine loss exhibit a level phase or even an upward trend during the early stages. This behavior can be explained in terms of the loss of other volatile components from the formulations: Table VII shows weight loss for HYP-II as a function of aging time at 110°C.

Arrhenius treatment of the data is complicated by the rapid loss of volatile components proceeding simultaneously with the fire-retardant loss (the two processes could be expected to have different activation energies). A straightforward treatment of the data does not appear to yield suitably linear Arrhenius behavior, so that activation energies for the fire-retardant loss were not obtained. However, the chlorine and antimony losses are of the same general magnitude as those observed with the EPR-V over this temperature range. The fact that the hypalon formulations lose antimony and chlorine on aging must result from the fact that chlorosulfonated polyethylene, with its random distribution of chlorine substituents along the polymer backbone, can readily undergo intramolecular dehydrochlorination (as was the case with the chlorinated additive used in EPR-V).

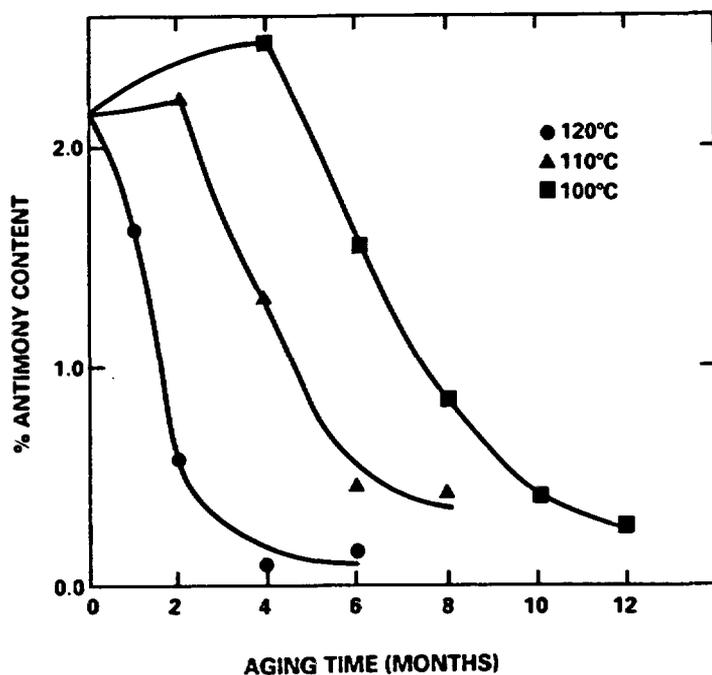


Figure 10. Antimony content (weight percent) as determined by atomic absorption spectroscopy on HYP-II as a function of thermal aging.

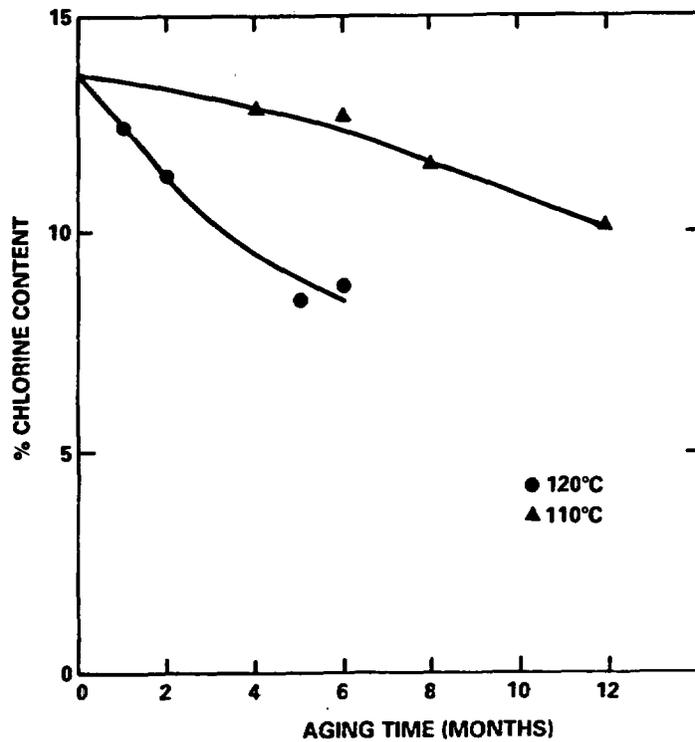


Figure 11. Chlorine content (weight percent) as determined by silver coulometry on HYP-I as a function of thermal aging.

TABLE VII
TOTAL WEIGHT LOSS FROM HYP - II
AGED AT 110°C

<u>AGING TIME</u>	<u>% WEIGHT LOSS</u>
2 wk	2.4%
4 wk	4.3%
8 wk	5.4%
12 wk	6.5%

Chlorosulfonated Polyethylene Flammability Measurements

Oxygen index measurements indicated very large changes between aged and unaged CSPE samples, with the material becoming less flammable after aging. The effect is seen with both HYP-I and with HYP-II (see Table VIII). This decreased flammability results despite the loss of both chlorine and antimony on aging.

The principle explanation for this observation most likely results from the loss of low molecular weight organic components from the formulation. These low molecular weight additives are relatively volatile and are nonchlorinated, and hence should be substantially more flammable than the highly chlorinated base polymer resin. Thermogravimetric analysis confirms a progressive decrease in the amount of weight loss during the early stages of the thermolysis of the CSPE samples, as a function of the extent of aging: Integrated weight loss data for samples heated from ambient to 425°C at 10°/min is tabulated in Table IX. Even assuming that a part of the species volatilized in the TGA experiment represents chlorine and antimony, the TGA differences between aged and unaged samples are substantially larger than can be accounted for by the differences in Cl and Sb content of the samples. The TGA analysis is probably a good indication of the relative amounts of volatile components released from these samples under combustion-initiating conditions of small-scale flammability tests.

Large changes in the flammability of chlorinated polymers as a function of additives has been noted before. For example plasticized PVC has much reduced flame retardancy compared with the unplasticized material.¹⁵ Apparently, in the case under consideration in the present study, the effect of the loss of chlorine and antimony on the oxygen index value is overridden by the effect of the loss of volatile organic additives.

TABLE VIII
 OXYGEN INDEX DATA ON
 SAMPLES OF CHLOROSULFONATED POLYETHYLENE
 AGED AT 110°C

<u>FORMULATION</u>	<u>AGING TIME</u>	<u>OXYGEN INDEX</u>
HYP-I	Unaged	35
	4 mo	46
	8 mo	46
HYP-II	Unaged	39
	4 mo	43
	8 mo	50

TABLE IX
 TGA* DATA SHOWING INTEGRATED WEIGHT LOSS
 TO 425°C FOR HYP - II SAMPLES
 PREAGED AT 110°C

<u>PREAGING TIME</u>	<u>% VOLATILIZED ON HEATING TO 425°C</u>
Unaged	25%
2 mo	22.4%
4 mo	16.5%
8 mo	15.1%

*TGA performed at 10°C/min heating rate in air.

CONCLUSIONS

Polymers containing halocarbon or halocarbon-antimony oxide based fire retardants can lose appreciable amounts of both halogen and antimony through volatilization during thermal aging. This is seen to hold where the halogen is contained in a low molecular weight additive in the formulation (as with EPR) as well as for the case where the halogen is a part of the base polymer resin (as with hypalon). Fire-retardant loss appears to be strongly dependent upon the molecular structure of the halocarbon in terms of its ability to undergo intramolecular loss of HCl. The HCl generated can react readily with Sb_2O_3 to produce the volatile $SbCl_3$.

Oxygen index flammability tests indicated modest increases in flammability of EPR with fire-retardant loss on aging. Hypalon formulations actually became markedly less flammable on aging; this behavior appeared to be associated with the loss of flammable, volatile additives from the polymer on aging.

Using the loss-rate data on the EPR formulation which lost fire retardants most rapidly, Arrhenius extrapolation indicated that the fire-retardant loss from this formulation should be important only at very significantly elevated temperatures; for example, loss of 25% of the initial antimony content should require some 120 years at 60°C and some 3,000 years at 40°C. The hypalon aging data was not amenable to an Arrhenius treatment, though fire-retardant loss rates under the accelerated laboratory conditions employed in this study were on the same order as those of the EPR formulation mentioned above.

The data generated in this work indicate that the loss of antimony-halocarbon fire retardants due to aging under the ambient conditions expected in nuclear plants should not be significant over the timescales of interest. There is nothing in the results that would be inconsistent with a supposition that the specification and testing of flammability and fire-retardant properties in terms of the unaged polymer materials is appropriate for indicating behavior throughout an estimated 40 year nuclear plant lifetime.

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