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Primary Gas Toxicities and Smoke Particle Characteristics During a Two-Stage Combustion of Mine Conveyor Belts

Development of a Test Parameter

By Maria I. De Rosa and Charles D. Litton

BUREAU OF MINES



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	L/min	liter per minute
cm	centimeter	m	meter
cm ² /p	square centimeter per particle	min	minute
cm ² /(p•g)	square centimeter per particle per gram	pct	percent
ft	foot	p/cm ²	particle per square centimeter
g	gram	ppm	part per million
in	inch	ppm/g	part per million per gram
L	liter		

PRIMARY GAS TOXICITIES AND SMOKE PARTICLE CHARACTERISTICS DURING A TWO-STAGE COMBUSTION OF MINE CONVEYORS BELTS

Development of a Test Parameter

By Maria I. De Rosa¹ and Charles D. Litton²

ABSTRACT

The U.S. Bureau of Mines performed experiments to determine if the primary gas toxicities evolved during the early ($\sim 300^\circ\text{C}$) and later ($\geq 400^\circ\text{C}$) combustion stages of mine conveyor belts could be predicted by a smoke particle characteristic. The experiments were conducted in an approximately 20-L furnace at set furnace temperatures of 150° , 250° , and $1,000^\circ\text{C}$, with a furnace airflow of 10 L/min. The variables studied, as a function of time, included hydrogen chloride and carbon monoxide concentrations, the average smoke particle diameter (d_g) and number concentration (n_o), and the product of the average smoke particle diameter and concentration ($d_g n_o$). Other variables included the sample and furnace temperatures and the sample mass weight loss.

Results show that the inverse of the smoke particle diameter-concentration product ($1/d_g n_o$), correlates directly with the hydrogen chloride and carbon monoxide toxicities released in large quantities during the early and later stages of combustion.

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INTRODUCTION

In 1984, the U.S. Bureau of Mines, within its mission to create and maintain safety in the mines and, specifically, to assess the hazard of mine materials during fire, initiated a series of experiments to characterize smoke particles and primary gas toxicities evolved during the combustion of mine materials. The characterization may lead to the development of testing parameters to assess, simply and inexpensively, the toxic hazard of materials during fire, before they are brought into underground mines. It was found (1)³ that smoke particles produced by different combustibles differed in average diameter (d_p), average number concentration (n_o), and the product of average diameter and concentration ($d_p n_o$). Could a relationship be established between the smoke particle diameter-concentration product ($d_p n_o$), and the gas toxicities evolved from various combustibles during their thermal decomposition?

This relationship was established in subsequent studies (2-4) in which the inverse of the diameter-concentration product ($1/d_p n_o$) of smoke particles produced during the combustion of coal, wood, cotton, polyester fabric, burlap, and polyvinyl chloride brattices was found to correlate directly with toxicity data obtained with similar materials and reported in the literature by Anderson (5) (animal study) and Paciorek (6) (gas analyses).

In the present study, composed of two parts, the Bureau set out to establish correlations between the inverse of the smoke particle diameter-concentration product ($1/d_p n_o$), and the primary toxicities evolved during a two-stage

combustion of polyvinyl chloride (PVC), neoprene, and styrene-butadiene (SBR) mine conveyor belts. These correlations, as mentioned above, may lead to the development of a predictive test parameter useful in assessing the toxic hazard of mine conveyor belts during the early (approximately at 300° C) and later (at or above 400° C) stages of combustion.

Hydrogen chloride (HCl) with a short-term exposure limit (STEL) of 25 ppm and immediately dangerous to life and health (IDLH) at 100 ppm, was found by Paciorek (6) and confirmed by the Bureau to be the primary toxicity evolved in large quantities during the early stage of combustion for all three types of conveyor belts. Carbon monoxide (CO) concentrations were found to be insignificant at this stage (6). However, at higher temperatures (at or above 400° C), which in a fire can be reached in a matter of minutes, immediately following dehydrochlorination of the material, large quantities of carbon monoxide (STEL, 400 ppm; IDLH, 1,500 ppm) evolve. Therefore, in the first part of the study, the smoke particle characteristic $1/d_p n_o$ was correlated with the primary gas toxicity (hydrogen chloride) of early combustion, and in the second part of the study, the smoke particle characteristic $1/d_p n_o$ was correlated with the combined gas primary toxicities (hydrogen chloride and carbon monoxide) of a later stage of combustion. Hydrogen chloride has been found (7) to linger in the environment long after the combustion of PVC and chlorinated materials has ended.

BACKGROUND

Conveyor belts are made of complex mixtures of a variety of components. However, although the number of individual belt compositions is very large, the number of major pure components is comparatively small; the belts most widely used in mines contain either a halogenated base polymer (PVC and neoprene belts) or a halogenated additive (SBR belt) to impart fire resistance. Owing to economic considerations, PVC resin probably is the most widely used of the halogenated polymers. However, this polymer releases hydrogen chloride at temperatures as low as 180° C, and the reaction is accelerated in oxidizing atmospheres; for pure resin, hydrogen chloride is the only toxic product (approximately 90 pct) evolved at temperatures below 200° C (8-9). The gas is highly irritant to the mucous membranes of the eyes and respiratory tract (10-11). Its release depends on the chlorine or chlorinated additive content of the material, on material burning rates, on the amount of material present, and on the vicinity of the material to the fire source (12). Furthermore, PVC requires large quantities of plasticizers (phthalate esters), which, following dehydrochlorination, produce large

quantities of phthalic anhydride, unsaturated hydrocarbons, and above all carbon monoxide (6). Moreover, during PVC fires, only 13 to 30 pct carboxyhemoglobin (COHb) is considered an LC50 (lethal concentration at which 50 pct of the exposed laboratory animals die), compared with 85 pct for pure carbon monoxide (13). Phosgene (IDLH, 2 ppm), produced by passing carbon monoxide and chlorine (Cl_2) over activated charcoal, has also been reported as present in PVC fires (14). Inhalation of 2 to 5 ppm of phosgene causes irritation of the mucous membranes of the respiratory tract, causing acid damage to the lungs, followed by suffocating cough. Tables 1 and 2 (15-16) report human responses to various hydrogen chloride and carbon monoxide concentrations.

Neoprene, because of its chlorine content, exhibits flame-retardant characteristics. Although considered thermally stable up to 300° C, it has been found (6) to degrade at 180° C. Neoprene, like PVC, has hydrogen chloride as the major degradation toxic product during the early stage of combustion. At 250° C, hydrogen chloride accounts for 80 pct of the chlorine present. At higher

³Italic numbers in parentheses refer to items in the list of references at the end of this report.

temperatures, carbon monoxide is liberated in large quantities because of gross degradation of the material (6).

SBR raw gum is flammable and requires large quantities of chlorinated additives, in addition to fillers, plasticizers, and sulfur organic activators; its final degradation products derive from all these constituents. The major toxic component, during the early stage of combustion, is again hydrogen chloride although in much smaller quantities than those generated from PVC and neoprene belts, at higher temperatures, the major toxic component is carbon monoxide (6).

TABLE 1.—Effects of inhaling hydrogen chloride on humans (15)

Hydrogen chloride concentration in air, ppm	Symptoms
1 to 5	Limit of detection by smelling.
5 to 10	Mild irritation of mucous membranes.
35	Irritation of throat on short exposure.
50 to 100	Barely tolerable.
1,000	Danger of lung edema after merely short exposure.

TABLE 2.—Human response to various concentrations of carboxyhemoglobin (16)

Blood saturation, pct carboxyhemoglobin	Response of healthy adult ¹
0.3 to 0.7 . .	Normal range due to endogenous carbon monoxide production.
1 to 5	Increase in cardiac output to compensate for reduction in oxygen-carrying capacity of blood.
5 to 9	Exercise tolerance reduced; visual light threshold increased.
16 to 20 . . .	Headache; visual evoked response abnormal.
20 to 30 . . .	Throbbing headache; nausea; fine manual dexterity abnormal.
30 to 40 . . .	Severe headache; nausea and vomiting; syncope.
50	Coma; convulsions.
67 to 70 . . .	Lethal if not treated.

¹Exposure to carbon monoxide in concentrations in excess of 50,000 ppm can result in fatal cardiac arrhythmia and death before venous carboxyhemoglobin saturation is significantly elevated.

EXPERIMENTAL SYSTEM

The system (fig. 1) consists of an approximately 20-L furnace whose temperature during experiments rises automatically from ambient (fig. 2) at a rate depending on the set temperature, which can range from 100° to 1,200° C. The experimental temperatures are monitored continuously with type K thermocouples connected to a strip chart recorder. A universal load cell, located under

the furnace floor and contacted by the sample cup, transmits voltages of sample mass weight loss, via a bridge amplifier, to another strip chart recorder. A vacuum pump draws ambient air continuously into the furnace (10 L/min), via an opening at the center of the furnace door, and sends combustion air to the carbon monoxide, carbon dioxide, and oxygen gas analyzers and to the

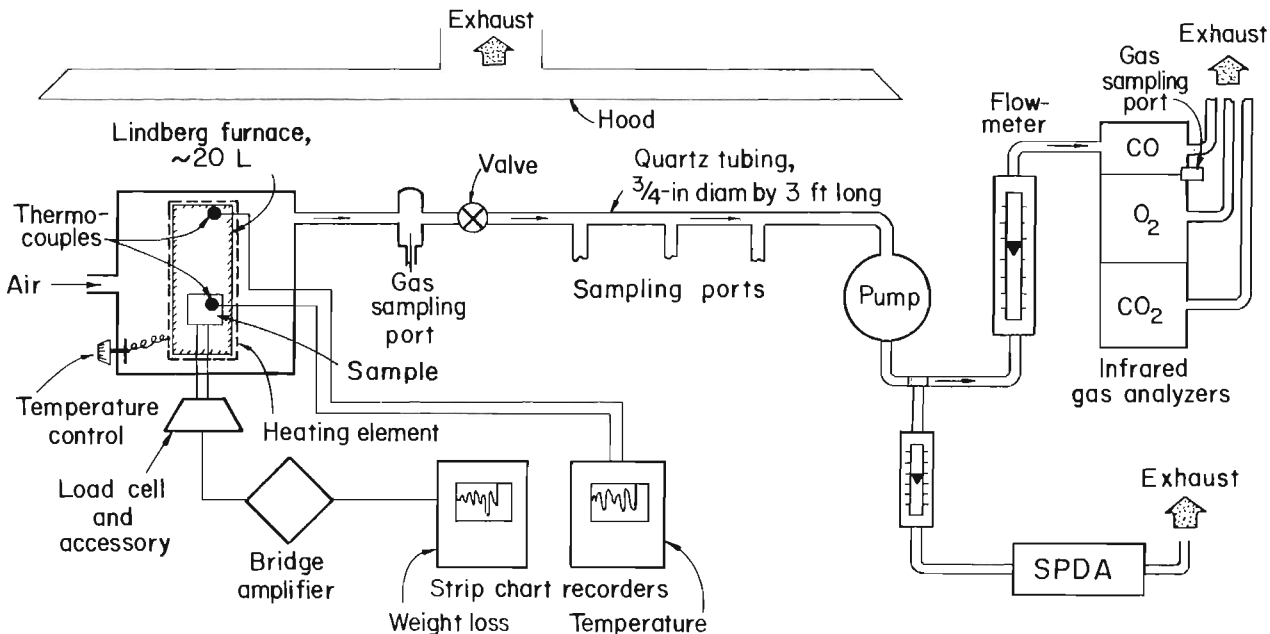


Figure 1.—Experimental system.

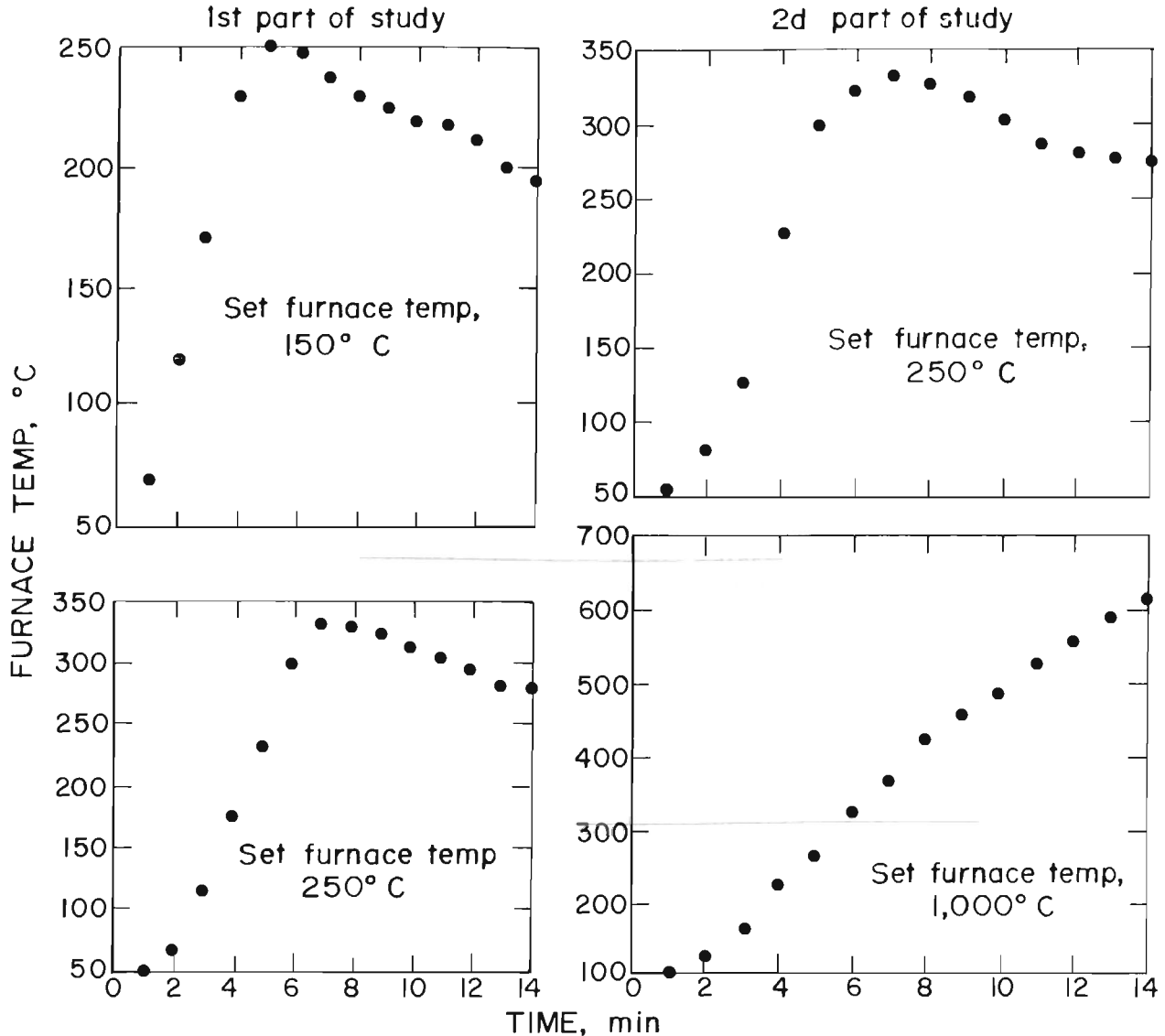


Figure 2.—Furnace temperature versus time at set furnace temperatures of 150° and 250° C (left) and 250° and 1,000° C (right).

submicrometer particle detector-analyzer (SPDA) (at 1.6 L/min) (17). Flowmeters, installed between the pump outlet and the gas and particle analyzers, provide visual flow indication.

In the first part of the study, real-time SPDA voltages were acquired for the manual computation of the average smoke particle diameter-concentration product. In the

second part of the study, a data acquisition system was installed. Data of sample and furnace temperatures, sample weight loss, and the SPDA voltages were continuously acquired, mathematically treated, logged, filed, and displayed by means of a miniframe computer, via a laboratory-based real-time data acquisition system. Subsequently, the data were transferred into a data bank and plotted.

EXPERIMENTAL PROCEDURE

FIRST PART OF STUDY

The first set of experiments (eight experiments in the set; each experiment repeated three items) was performed

at a set furnace temperature of 250° C (fig. 2) for a 14-min duration with 1-g samples of PVC (P1 and P2), neoprene (N1 and N2), and SBR (S1 and S2) mine conveyor belts. A list of the materials, which were the same belt

materials used by Paciorek (6), is reported in table 3. A 1-g sample was placed in a 2.5-cm-diameter sample cup, and the furnace was set at the desired temperature with a furnace airflow of 10 L/min, 1.6 L/min of which was directed into the SPDA; the remainder of the combustion air was directed into the gas analyzers and into the exhaust hood. At 250° C, hydrogen chloride concentrations were measured by short-term exposure tubes (Bureau hydrogen chloride measured values agree comfortably with the hydrogen chloride values measured by Paciorek (6) with a different methodology). The chlorine content of the material was determined by the oxygen-bomb-combustion, selective-electrode method. Syringe grab samples, stored in sealed containers, were analyzed for carbon monoxide, carbon dioxide, and oxygen by the gas chromatography method. Other variables measured, as a function of time, were the sample and furnace temperatures, sample mass weight loss, and the SPDA initial (without smoke) and experimental (with smoke) voltages. At 150° C and 14 min duration, only materials weight changes were observed.

SECOND PART OF STUDY

Two sets of experiments (five experiments per set; each experiment repeated three times) were performed at set furnace temperatures of 250° and 1,000° C (fig. 2) for a 14-min duration with 1-g samples of PVC (P1a and P2a), neoprene (N1a), and SBR (S1a and S2a) mine conveyor belts. A list of the materials is reported in table 3. At 250° C, measurements of hydrogen chloride, carbon monoxide, carbon dioxide, and oxygen concentrations, and

analyses of the chlorine content of the materials were done in the same manner as described previously. At 1,000° C, only the rates of carbon monoxide evolution and material weight loss were observed.

TABLE 3.—Materials Investigated

Conveyor belt materials	Description	Chlorine, pct
1ST PART OF STUDY		
PVC:		
P1	Polymer component is PVC resin with fillers.	18
P2 do	16
Neoprene:		
N1	Polymer component is neoprene rubber with fillers.	20
N2 do	13.2
SBR:		
S1	Polystyrene-butadiene rubber with chlorinated additives.	2.3
S2 do	15
2D PART OF STUDY		
PVC:		
P1a	Polymer component is PVC resin with fillers.	23
P2a do	21
Neoprene:		
N1a	Polymer component is neoprene rubber with fillers.	11
SBR:		
S1a	Polystyrene-butadiene rubber with chlorinated additives.	5
S2a do19

DATA REDUCTION AND ANALYSES

At 250° C set furnace temperature and 14-min duration, representing the early stage of combustion at which most of the hydrogen chloride evolves with no gross degradation of the sample, hydrogen chloride and carbon monoxide were measured in parts per million. The hydrogen chloride and carbon monoxide concentrations observed at 0.1 g of sample weight loss, adjusted to 1 g of weight loss, yielded the hydrogen chloride and carbon monoxide load values in parts per million per gram. The load values, derived at a specific time and airflow, are important toxicological parameters, because they established a priori the total concentrations of each gas expected to evolve. Hydrogen chloride evolves in large quantities (approaching load values) during the early stage of combustion (approximately at 300° C), because of the early and fast dehydrochlorination process; carbon monoxide evolves in large quantities (approaching load values) during a later stage of combustion (at or above 400° C), because of gross degradation of the sample. Therefore, the hydrogen chloride load values are predictive of the toxic hazard that PVC and chlorinated belts pose during the early stage of combustion (carbon monoxide concentrations are minimal at this stage), and hydrogen chloride load values combined with carbon monoxide load values are predictive of the toxic

hazard that belts pose during the later stage of combustion.

Under these conditions, the average smoke particle diameter (d_g) was measured in micrometers, the average number concentration (n_o) in particles per cubic centimeter, and the product of the average smoke particle and concentration ($d_g n_o$) in particles per square centimeter. The $d_g n_o$ is obtained from the ratio of the SPDA experimental and initial current output (I_e/I_o) following the relationship in equation 1. See also figure 3.

$$I_e/I_o = 1/(K d_g n_o) (1 - \exp(-K d_g n_o)) \quad (1)$$

where K = charging constant ($k = 0.012 \text{ cm}^2/p$).

Once $d_g n_o$ is determined, d_g can be obtained from equation 2.

$$d_g = (e\alpha I_e/d_g n_o - 1)/(I_e), \quad (2)$$

where I_e = SPDA charged particle current;

and α = constant.

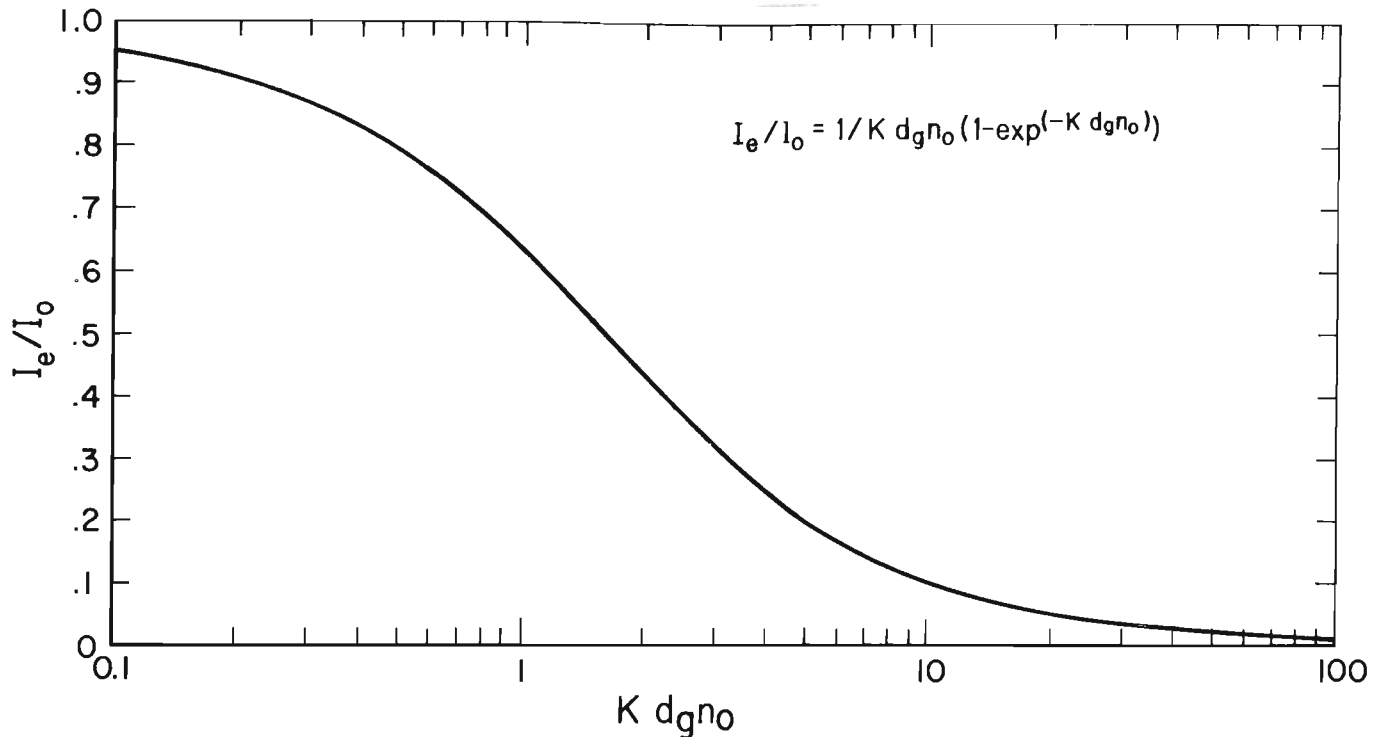


Figure 3.—SPDA current ratio (I_e/I_o) as function of smoke particle diameter-concentration product ($d_g n_o$).

The inverse of $d_g n_o$ values, observed during each experiment for each sample, was correlated with the hydrogen chloride concentrations.

The total $d_g n_o$ values, observed during each experiment for each sample, adjusted to 1 g of sample mass weight loss, yielded the $d_g n_o$ load values in particles per square centimeter per gram. The inverse $1/d_g n_o$ load values were correlated with the hydrogen chloride load values, and with the combined hydrogen chloride and carbon monoxide load values. The carbon monoxide load values were previously normalized to hydrogen chloride values by scaling them down by a factor of 15, because carbon monoxide is at least 15 times less toxic than hydrogen

chloride. The $1/d_g n_o$ load values were also correlated with the combined hydrogen chloride and carbon monoxide load values scaled to their STEL and IDLH values.

At 150° C set furnace temperature and 14-min duration, sample weight changes (increases) were observed. At 1,000° C set furnace temperature and 14-min duration, carbon monoxide, carbon dioxide, and oxygen concentrations, sample weight loss, and sample and furnace temperatures were observed. These observations enabled comparisons between the expected carbon monoxide concentrations, as predicted by the carbon monoxide load values derived at 250° C, and the actual carbon monoxide values evolved.

RESULTS AND DISCUSSION

FIRST PART OF STUDY

At 250° C, the PVC belts, followed by the neoprene belts, released the highest hydrogen chloride concentrations at 10 pct sample weight loss, yielding the highest toxic loads at the earliest time, at the fastest rates (fig. 4), because of their high chlorine content (fig. 5), and early, rapid weight loss (fig. 6). Furthermore, because of large weight loss, belts of the same type, but with a lower toxic load, released even higher hydrogen chloride concentrations, at an earlier time. The PVC belts also yielded

the highest $1/d_g n_o$ values (fig. 7). Evidently, the higher and more rapid the hydrogen chloride release, the lower the number of solid particles available to the SPDA. The majority of particles, in the liquid state as hydrochloric acid, are not registered by the SPDA. By contrast, the SBR belts released the lowest hydrogen chloride concentrations, yielding the lowest toxic loads at the latest time, because of a low content of chlorinated additives and late, small weight loss. Because of this last property, the SBR belt whose hydrogen chloride load value approached that observed for neoprene belts released much lower hydrogen

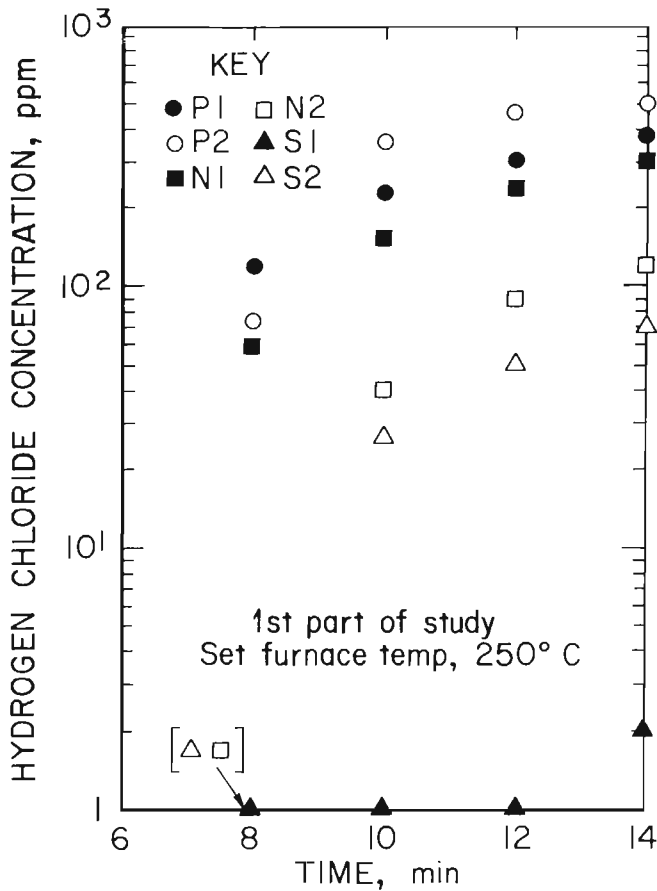


Figure 4.—Hydrogen chloride concentration versus time (first part of study) at 250° C.

chloride concentrations than expected. Could an optimum content of chlorinated additives be derived experimentally, which would impart fire-resistant properties to this type of belt and at the same time release the lowest possible hydrogen chloride concentration?

Correlations were established ($r > 0.78$) between the $1/d_g n_o$ values and the hydrogen chloride concentration (fig. 8); correlations were also established between the $1/d_g n_o$ load and the hydrogen chloride load (fig. 9). Results are shown in table 4. The table shows that PVC belt P1, with a chlorine content of 18 pct, released the largest hydrogen chloride concentration at 10 pct mass weight loss, yielding the highest toxic load, which contained approximately 50 times the STEL value and at least 10 times the IDLH concentration. Belt P1 also yielded the highest $1/d_g n_o$ value. By contrast, PVC belt P2, with a

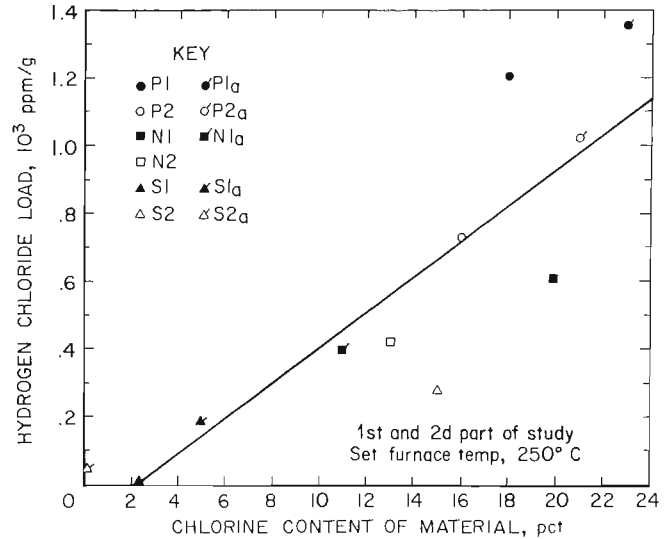


Figure 5.—Hydrogen chloride load (first and second parts of study) versus chlorine content of material at 250° C.

chlorine content of 16 pct, released a lower hydrogen chloride concentration at 10 pct of weight loss; however, the belt experienced a much larger total weight loss, releasing its toxic load faster, at an earlier time. Finally, SBR belt S1, with a chlorine content of only 2.3 pct, released a very low hydrogen chloride concentration, yielding a very low toxic load, at the latest time. These properties are of extreme importance during the early, critical stage of combustion.

At 150° C, all belts experienced only weight increase, owing to material oxidation and/or expansion. It appears that the belts experiencing the highest increase experienced the highest weight loss. Evidently, at higher temperatures, oxidation renders heat penetration possible, thus facilitating the combustion of the materials.

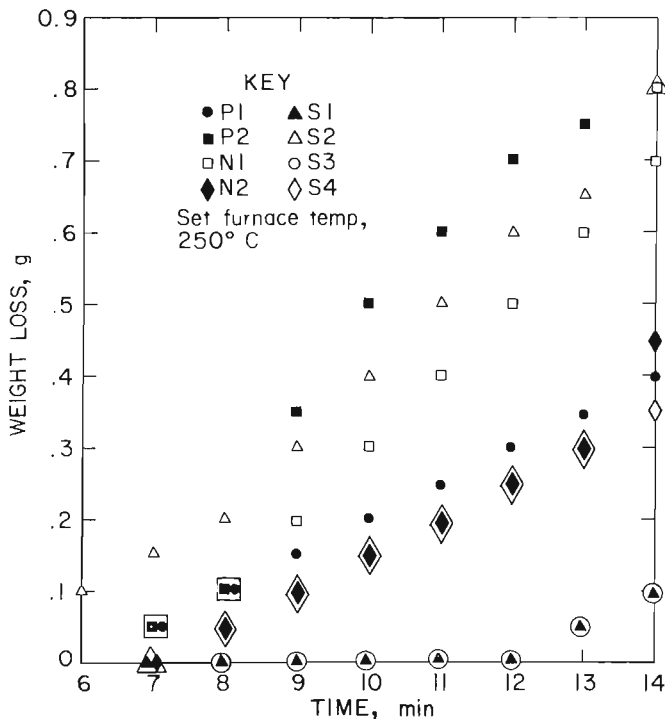


Figure 6.-Weight loss versus time (first part of study) at 250° C.

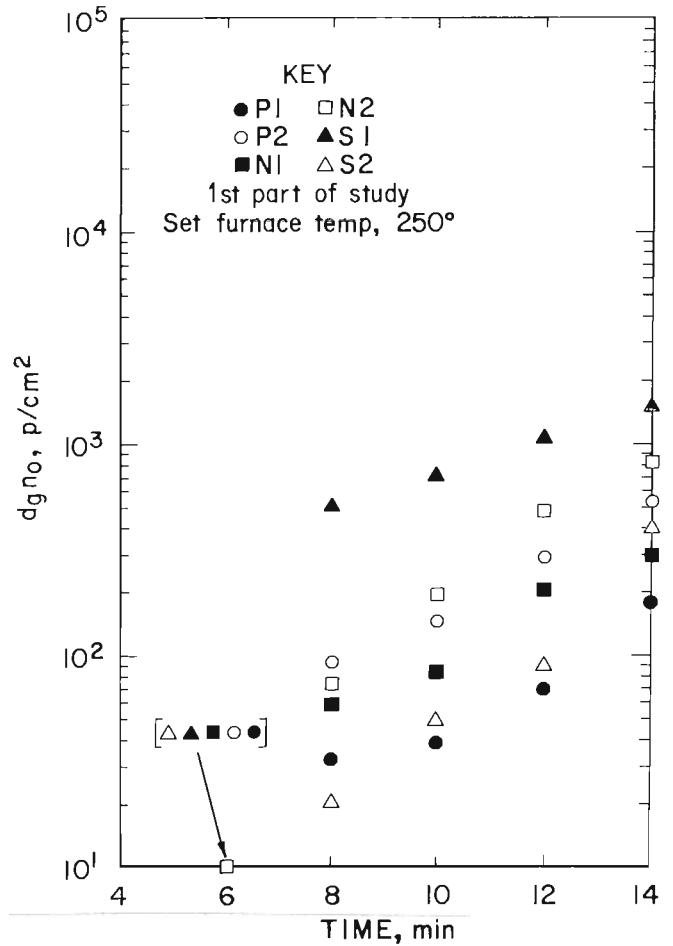


Figure 7.-Smoke particle diameter-concentration product ($d_g n_o$) versus time (first part of study) at 250° C.

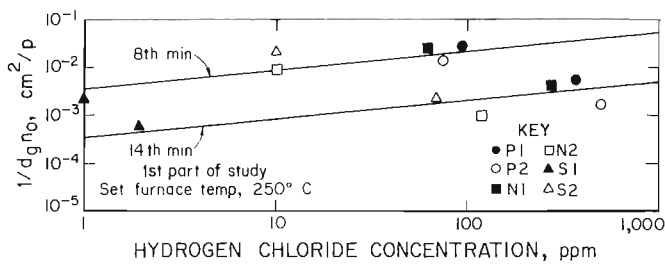


Figure 8.-Inverse of smoke particle diameter-concentration product ($1/d_g n_o$) versus hydrogen chloride concentration (first part of study) at 250° C.

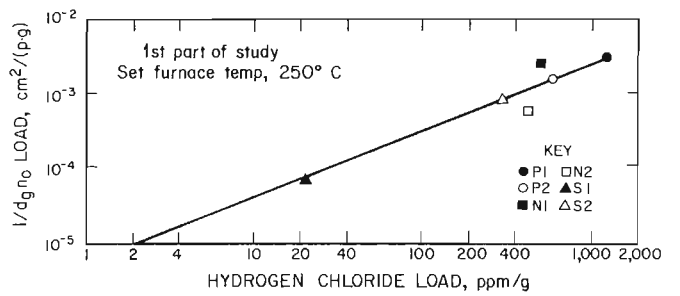


Figure 9.-Inverse of smoke particle diameter-concentration product ($1/d_g n_o$) load versus hydrogen chloride load (first part of study) at 250° C.

TABLE 4.—Oxidative thermal degradation data during first part of study at 250° C

(Furnace airflow, 10 L/min)

Conveyor belt material ¹	HCl, ppm	WL, g	Time, min	Total WL, g	Loads			
					HCl, ² ppm/g	HCl, STEL ³	HCl, IDLH ⁴	1/d _g n _o , ⁵ cm ² /(p•g)
PVC:								
P1, 18 pct Cl ₂	120	0.1	8	0.4	1,200	48	12	0.0023
P2, 16 pct Cl ₂	73	.1	8	.8	730	29	7.3	.0015
Neoprene:								
N1, 20 pct Cl ₂	62	.1	8	.7	620	25	6.2	.0023
N2, 13.2 pct Cl ₂	42	.1	10	.36	420	17	4.2	.0005
SBR:								
S1, 2.3 pct Cl ₂	2	.1	14	.1	20	.8	.2	.00007
S2, 15 pct Cl ₂	28	.1	10	.35	280	11.3	2.8	.0004

IDLH Immediately dangerous to life and health (100 ppm).

STEL Short-term exposure limit (25 ppm).

WL Weight loss.

¹1-g sample.²Derived from concentration observed at 0.1 g of sample weight loss per gram of weight loss, at a specific time and dilution air.³Number of STEL values contained in hydrogen chloride load.⁴Number of IDLH values contained in hydrogen chloride load.⁵Inverse of d_gn_o load is derived from total d_gn_o values per gram of sample weight loss.

SECOND PART OF STUDY

At 250° C, the PVC belts, followed by the neoprene belts, released the highest hydrogen chloride concentrations at 10 pct sample weight loss, yielding the highest toxic loads; these belts also yielded the highest 1/d_gn_o values. By contrast, the lowest hydrogen chloride concentrations were released by the SBR belts, yielding the lowest toxic loads; these belts also yielded the lowest 1/d_gn_o values. Furthermore, all SBR samples underwent very little physical change, while the PVC samples melted, yielding a viscous liquid. At 250° C, modest carbon monoxide concentrations were released by all types of belts, although the neoprene belts, followed by the PVC belts, released somewhat higher concentrations. At 1,000° C, however, all of the belts underwent extensive thermal decomposition accompanied by the evolution of large carbon monoxide concentrations (fig. 10), comparable to the toxic loads derived at 250° C, and large quantities of soot filaments.

Correlations ($r = 0.80$) were established between the smoke particle characteristic 1/d_gn_o load, the hydrogen chloride load, and the combined hydrogen chloride and

carbon monoxide loads (fig. 11); correlations were also established between 1/d_gn_o single loads (error of the mean < 8 pct) and the combined toxic loads (fig. 12). Results are shown in tables 5 and 6.

Table 5 shows that PVC belt P1a, with a chlorine content of 23 pct, released the highest hydrogen chloride concentration at 10 pct weight loss, yielding the highest toxic load, which contained 50 times the STEL value and 15 times the IDLH concentration; by contrast, the carbon monoxide load contained only 5 times its STEL value and only once the IDLH concentration. Belt P1a also yielded the highest 1/d_gn_o values.

Table 5 also shows that SBR belt S2a, with a chlorine content of only 0.2 pct, released an extremely low hydrogen chloride concentration; furthermore, it underwent extremely low weight loss; evidently, other types of fire-retardant additives may have been used. Finally, table 6 shows that, at 1,000° C, PVC belts underwent the highest weight loss, releasing the highest carbon monoxide concentrations. High carbon monoxide concentrations were also released by the neoprene belt, although it underwent lower weight loss than those observed for PVC belts.

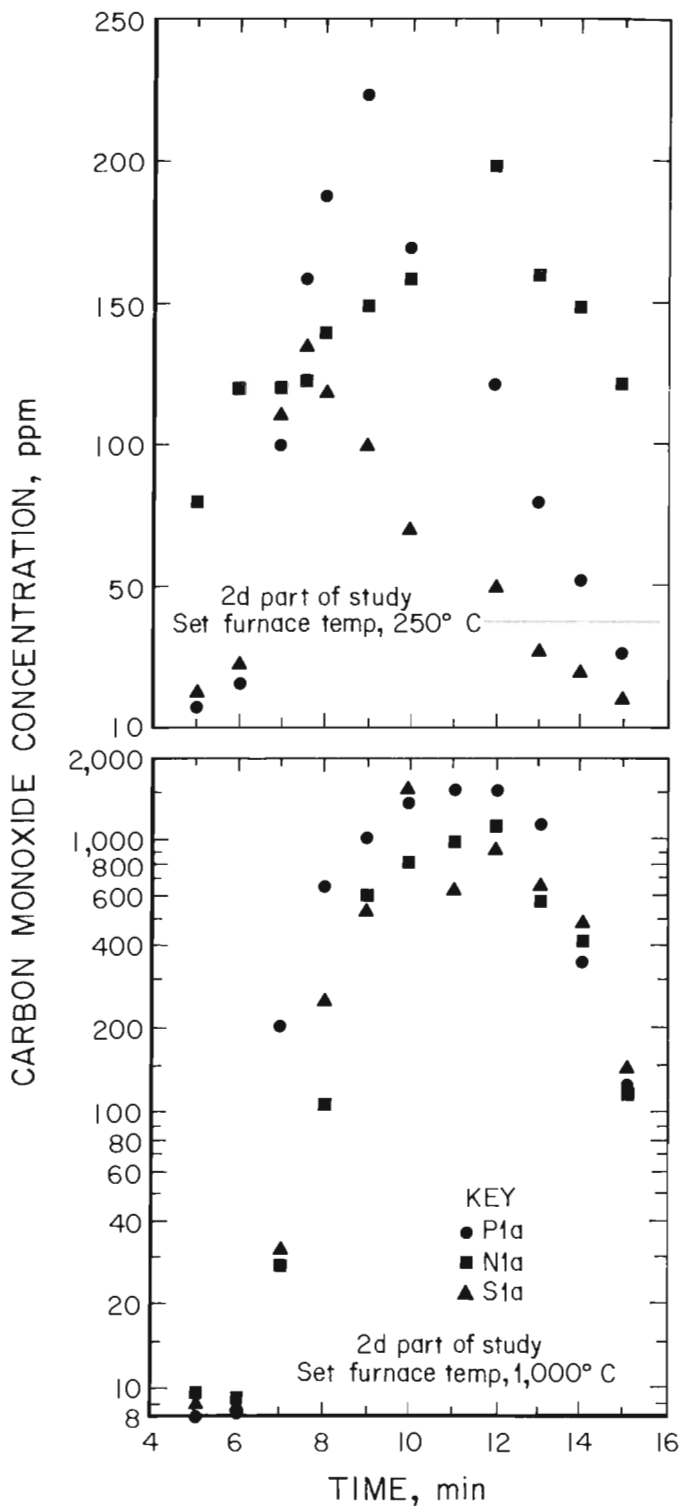


Figure 10.-Carbon monoxide concentration versus time (second part of study) at 250° and 1,000° C.

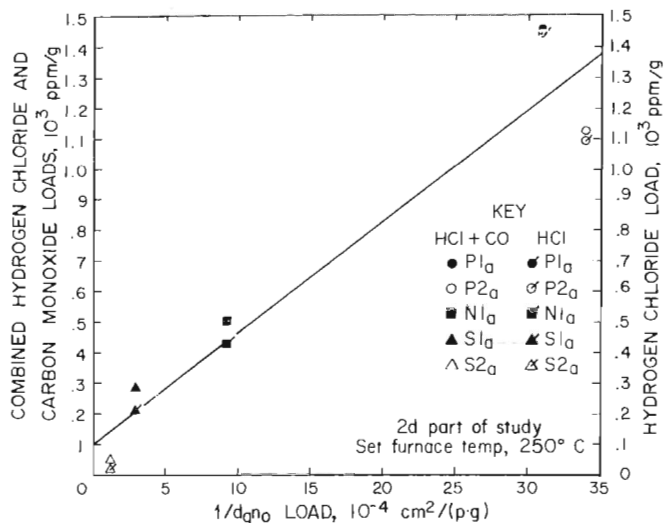


Figure 11.-Inverse of smoke particle diameter-concentration product ($1/d_{gn}$) load versus combined hydrogen chloride and carbon monoxide loads versus hydrogen chloride load (second part of study) at 250° C.

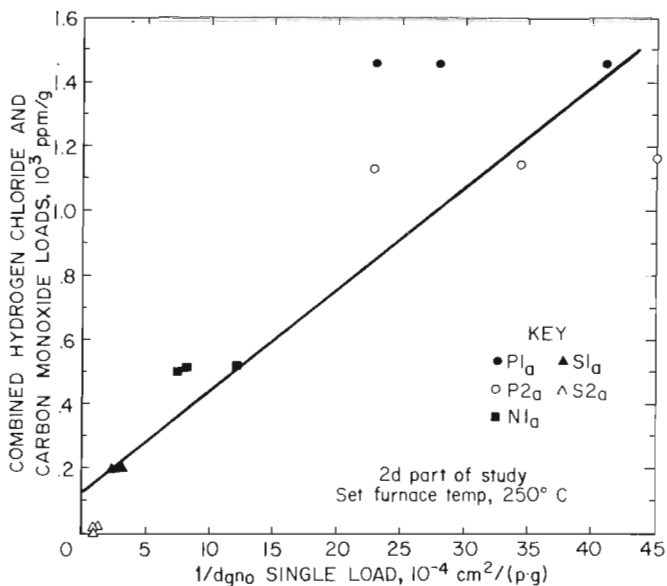


Figure 12.-Inverse of smoke particle diameter-concentration product ($1/d_{gn}$) single load versus combined toxic loads (second part of study) at 250° C.

TABLE 5.—Oxidative thermal degradation data during second part of study at 250° C

(Furnace airflow, 10 L/min)

Conveyor belt material ¹	HCl, ppm	CO, ppm	WL, g	Time, min	Loads										
					HCl, ² ppm/g	HCl, STEL ³	HCl, IDLH ⁴	CO, ² ppm/g	CO, STEL ³	CO, IDLH ⁴	1/d _g n _o ⁵ cm ² /(p•g)	Combined HCl and CO ⁶			
												ppm/g	STEL ³	IDLH ⁴	
PVC:															
P1a, 23 pct Cl ₂ . . .	135	158	0.1	8	1,350	54	14	1,580	4	1	0.0031	1,455	58	15	
P2a, 21 pct Cl ₂ . . .	102	133	.1	8	1,020	41	10	1,333	3	1	.0034	1,130	60	12	
Neoprene:															
N1a, 11 pct Cl ₂ . . .	40	150	.1	9	400	16	4	1,500	4	1	.00092	500	20	5	
SBR:															
S1a, 5 pct Cl ₂	20	128	.1	9	200	8	2	1,250	3	1	.00029	283	11.3	3	
S2a, 0.19 pct Cl ₂ . .	<5	43	.04	10	50	2	.5	1,070	3	1	.00005	120	4.8	1.2	

IDLH Immediately dangerous to life and health (100 ppm).

STEL Short-term exposure limit (25 ppm).

WL Weight loss.

¹1-g sample.

²Derived from concentration observed at 0.1 g of sample weight loss per gram of weight loss, at a specific time and dilution air.

³Number of STEL values contained in each load.

⁴Number of IDLH values contained in each load.

⁵Inverse of d_gn_o load. Each d_gn_o load is derived from total d_gn_o values per gram of sample weight loss.

⁶Derived from combined hydrogen chloride and carbon monoxide load values. Each carbon monoxide load value has been normalized to hydrogen chloride values by scaling it down by a factor of 15, as carbon monoxide is at least 15 times less toxic than hydrogen chloride.

⁷Sample weight loss observed throughout the experiment. Hydrogen chloride and carbon monoxide concentrations observed at 0.04 g of weight loss, adjusted to 1 g of weight loss, yielded hydrogen chloride and carbon monoxide loads.

TABLE 6.—Comparison of oxidative thermal degradation data during second part of study
at 250° and 1,000° C

(Furnace airflow, 10 L/min)

Conveyor belt material ¹	250° C						1,000° C						
	CO, ppm	Time, min	O ₂ , pct	CO ₂ , ppm	Total WL, g	Temp, ² °C	CO, ppm	Time, min	O ₂ , pct	CO ₂ , ppm	Total WL, g	Temp, ² °C	
PVC:													
P1a	15	6	20.7	650	0.38	{	264	6	6	20.86	630	{	264
	157	8	20.8	780			319	617	8	20.7	1,300		363
	227	10	20.8	820			309	1,370	10	20.57	2,300		447
	123	12	20.8	800			294	1,480	12	20.52	2,700		522
	50	14	20.8	800			283	340	14	20.63	2,300		588
P2a	10	6	20.7	640	.36	{	264	23	6	20.93	840	{	264
	28	8	20.8	760			319	504	8	20.9	690		363
	133	10	20.8	820			309	1,900	10	20.75	9,000		447
	54	12	20.8	800			294	1,640	12	20.7	1,400		522
	11	14	20.78	800			283	532	14	20.8	1,100		588
Neoprene:													
N1a	118	6	20.7	1,200	.18	{	264	7	6	20.83	540	{	264
	120	8	20.8	1,500			319	106	8	20.76	980		363
	150	10	20.75	1,800			309	486	10	20.60	1,840		447
	199	12	20.8	2,000			294	1,030	12	20.50	2,470		522
	150	14	20.85	2,300			283	403	14	20.55	2,600		588
SBR:													
S1a	20	6	20.65	1,000	.14	{	264	1	6	20.83	620	{	264
	134	8	20.7	1,200			319	254	8	20.74	800		363
	100	10	20.7	1,300			309	1,470	10	20.46	1,820		447
	50	12	20.8	1,500			294	1,000	12	20.45	2,810		522
	20	14	20.75	1,200			283	453	14	20.56	2,570		588
S2a	10	6	20.8	900	.04	{	264	10	6	20.92	850	{	264
	14	8	20.8	1,100			319	34	8	20.92	680		363
	16	10	20.8	1,200			309	1,050	10	19.7	9,000		447
	10	12	20.8	1,600			294	86	12	20.77	1,500		522
	10	14	20.8	1,200			283	92	14	20.77	1,000		588

WL Weight loss.

¹1-g sample.

²Furnace.

CONCLUSIONS

According to these findings, the inverse of the smoke particle diameter-concentration product ($1/d_p n_o$) correlates directly and significantly with the primary gas toxicities evolved during a two-stage combustion of mine conveyor belts. The higher the toxicities, the larger the $1/d_p n_o$ values. Hydrogen chloride is the primary toxicity evolved in large quantities during the early stages of combustion (approximately at 300° C) because of the early dehydrochlorination process. The PVC belts, followed by the neoprene belts, released the largest hydrogen chloride concentrations, yielding the highest toxic loads at the earliest time, at the fastest rates, because of the high chlorine content in the materials and the early, fast, and large weight loss. Carbon monoxide concentrations were insignificant at this stage. The halogenated base polymer contained in the PVC and neoprene belts does not make the belts fire resistant. During early thermal decomposition, extremely large amounts of hydrogen chloride are released, making the belts extremely toxic.

By contrast, the SBR belts released the lowest hydrogen chloride concentrations, yielding the lowest toxic loads at the latest time, because of the low content of chlorinated additives in the materials and late weight loss; carbon monoxide concentrations were insignificant at this stage. An optimum content of chlorinated additives could be derived experimentally and required for this type of belt,

which would impart fire-resistant properties and at the same time yield the lowest possible hydrogen chloride concentrations during the early, critical stage of combustion.

The smoke particle characteristic $1/d_p n_o$ load correlates, also directly and significantly, with the combined hydrogen chloride and carbon monoxide toxicities. Carbon monoxide is the primary toxicity evolved in large quantities, because of the gross decomposition of the sample, during a later stage of combustion (at or above 400° C), which during a fire can develop in a matter of minutes, with neoprene and PVC belts releasing the largest concentrations.

In conclusion, belts' primary toxic loads and belts' ease of thermal decomposition determine the time at which dangerous concentrations of hydrogen chloride and carbon monoxide are reached in the environment; this "time" determines the degree of belts' toxic hazard during fire: the shorter the time, the more hazardous is the material.

The excellent correlation of the inverse of the smoke particle diameter-concentration product ($1/d_p n_o$) with the primary gas toxicities during a two-stage combustion of mine conveyor belts suggests its development and use as a test parameter for a simpler and less expensive method of assessing the toxic hazard of mine conveyor belts during fire, before they are brought underground.

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