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Coal Mine Combustion Products: Conveyor Belts

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Coal Mine Combustion Products: Conveyor Belts

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COAL MINE COMBUSTION PRODUCTS: CONVEYOR BELTS

by

Arthur M. Hartstein[1] and David R. Forshey[2]

ABSTRACT

The Federal Bureau of Mines, under a contract with Ultrasystems, Inc., investigated the thermal oxidative degradation characteristics of conveyor belts used in underground mines. This included the determination of smoke evolution, glow characteristics, char yields, and the identification and quantification of all volatile decomposition products in the form of gram of specific product formed per gram of belt sample tested. In addition to these investigations, degradation studies were conducted on some pure ingredients used in conveyor-belt formulations.

Three basic classes of belts were investigated: neoprene, polyvinyl chloride, and styrene-butadiene rubber compositions. The studies indicate that styrene-butadiene-based belts exhibit good flame resistance and are the least hazardous in regard to overall formation of toxic decomposition products.

Under this program, thermogravimetric analysis was definitely established as a method of material differentiation.

INTRODUCTION

Past investigations by Ultrasystems, Inc.,[3] showed that all organic materials used in underground mining form toxic products upon thermal oxidative degradation. The relative quantity on a gram-per-gram basis and the nature, or toxicity, of the individual products formed was strongly

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[3]Hartstein, A. M., and D. R. Forshey. Coal Mine Combustion Products, Identification and Analysis. BuMines RI 7872, 1974, 12 pp.

Hartstein, A. M., and D. R. Forshey. Coal Mine Combustion Products: Neoprenes, Polyvinyl Chloride Compositions, Urethane Foam, and Wood. BuMines RI 7977, 1974, 25 pp.

Paciorek, K. L., R. H. Kratzer, J. Kaufman, and J. N. Nakahara. Coal Mine Combustion Products, Identification and Analysis. Annual Report No. 2, BuMines Contract No. H0133009, August 1974, 149 pp.; available for examination at the Office of the Assistant Director--Mining, Washington, D.C.

dependent on the particular composition tested. It was also found that the hazards of flammability and toxic-product formation varied widely for similarly used articles, such as conveyor belts, as well as for the various individual materials. Thus, a systematic study was initiated to (1) establish quantitatively the potential for toxic-product formation for a given class of articles, (2) correlate the formation of toxic products, by both type and quantity, with the presence of specific ingredients, (3) determine whether it is realistic to assume that an item such as a conveyor belt can be simultaneously flame resistant, exhibit good mechanical and wear characteristics, be priced economically, and evolve only small quantities of toxic products when subjected to oxidative thermal degradation, (4) translate the findings into guidelines for manufacturers, miner operators, and mine inspectors, and (5) use the data as a basis for meaningful regulations.

The present study was aimed primarily at conveyor belts because they are installed in considerable quantities along relatively long horizontal distances, often on the air-intake side of a ventilation system. In addition, there is the likelihood of overheating in use through friction at a stuck pulley or by contact with ignition sources.

EXPERIMENTAL WORK

All methods and procedures employed are presented in full detail in previous reports.[4] The test samples were decomposed in a sealed system, and all products volatile in vacuo at room temperature were identified and quantitated on the basis of gram of product per gram of test sample. The actual analyses of these volatiles were performed using a gas chromatograph attached to a double-focusing mass spectrometer coupled to a data acquisition and processing system with library search capability. To determine smoke formation, char yields, and glow characteristics, the stagnation-burner system described in previous publications[5] was utilized.

RESULTS AND DISCUSSION

Fifteen belt samples and four pure ingredients were subjected to thermal oxidative degradation. The belts tested and the pure ingredients studied are listed in tables 1 and 2, respectively. The results of the stagnation-burner experiments and thermogravimetric analyses will be discussed first, followed by the presentation of the data obtained in the sealed-system experiments. The investigation of the pure ingredients is described last; this work is being continued at present.

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[4]Work cited in footnote 3.
[5]Work cited in footnote 3.

TABLE 1. - Conveyor belt samples received from the Bureau of Mines

Sample	Description
E-1	Neoprene-Fire Resistant, manufactured by B. F. Goodrich Co. Contains polychloroprene, zinc oxide, magnesium oxide, polyethylene lubricant, carbon black, chlorinated hydrocarbons, phosphorus, fatty acid, phthalate plasticizer.
E-2	PVC-Fire Resistant, manufactured by B. F. Goodrich Co. Contains polyvinyl chloride, antimony oxide stabilizer, calcium oxide, plasticizers, thickener, coloring agent.
E-3	SBR-Fire Resistant, manufactured by B. F. Goodrich Co. Contains polystyrene-butadiene, zinc oxide, antimony oxide, chlorinated hydrocarbons, tackifying resins, polyethylene lubricant, carbon black, mineral pigments, antiozonant, phosphorous, antioxidant, fatty acid.
E-4	Grade 2-NR/SBR Non-Fire Resistant, manufactured by B. F. Goodrich Co. Contains polystyrene-butadiene, zinc oxide, tackifying agents, fatty acid, antiozonant, antioxidant, carbon black, processing oil (petroleum base).
E-5	USBM-SBR, manufactured by Goodyear Tire and Rubber Co. Composition confidential at the request of the manufacturer.
F-1	BFG KOR/NY/PVC 28/6 (ISG 200); based on TGA, the polymer component is PVC.
F-2	BFG/KOR/NYLOC PVC 28/6, Used (ISG 201); based on TGA, the polymer component is PVC.
F-3	H New Scan (Scan PVC) (ISG 202); based on TGA, the polymer component is PVC.
F-4	BFG ML RUB 6 (BFG Goodrich Long Life New); (ISG 203); based on TGA, the polymer component is SBR.
F-5	Rubber UNK Rayon Nylon Red Stripe (ISG 204); based on TGA, the polymer component is SBR.
F-6	Scandura PVC, Used (ISG 205); based on TGA, the polymer component is PVC.
F-7	(BFG No. 200 NF Caricoal) BFG Neocaricoal 200/NF (ISG 206); based on TGA, the polymer component is neoprene.
F-8	H/ROB PVC, Used (ISG 207); based on TGA, the polymer component is PVC.
F-9	Bridge/Nylon SBR, New, 43 (ISG 208); based on TGA, the polymer component is SBR.
F-10	Acme HNCO, Used, Cotton Nylon/7 (ISG 209); based on TGA, the polymer component is neoprene.

TABLE 2. - List of pure components studied

Material	Description
Dioctyl phtalate (plasticizer)..	Obtained from Analabs, Inc., Cat. No. GP 52006.
Carbon black (filler)..........	ISAP oil furnace black, manufactured by J. M. Huber Corp.
Chlordinated hydrocarbon (flame retardant).	Unichlor 70L-190, manufactured by Neville Chemical Co.
Nylon 6 (fiber)................	Specially prepared by Dr. J. Smith of Allied Chemical Corp.

Investigations of Conveyor Belts Under Dynamic Conditions

The 15 belts investigated were categorized according to their main polymer, or "rubber," component. The three categories were (1) neoprene, (2) polyvinyl chloride (PVC), and (3) styrene-butadiene rubber (SBR). The stagnation-burner experiments and the thermogravimetric analyses (TGA) are summarized in table 3.

The TGA scans were performed separately on the fiber and rubber portions of the belt samples. In every instance, it was possible to identify the rubber portion unambiguously, based on the characteristics of the derivative curve of the TGA scan (weight-loss change rate). Thus, at least in the case of conveyor belts, it can be safely said that the main components can be identified by TGA. As expected, the residue quantities at a given temperature for the rubber portions of belts as determined by TGA were higher in the majority of cases than those observed under stagnation-burner conditions (table 3). This is due to longer exposure time at temperatures under the stagnation-burner conditions. The exceptions found can be traced to the fact that the fibers had been removed from the belt samples for TGA but were present in the specimens subjected to degradation in the stagnation burner.

Only four of the belts tested, F-3, F-6, E-3, and E-4, did not glow at 500° C. The first two of these were PVC-derived; the other two contained SBR. It is significant that the SBR-based belts afforded higher char yields. In view of these data, SBR-based materials would appear attractive insofar as fire retardancy is concerned.

TABLE 3. - Summary of stagnation-burner studies and TGA

Sample[1]	Stagnation-burner studies: Temp,[2] ° C	Weight used, mg	Residue, pct	Glow, min	Smoke[3]: Maximum intensity: Pct	Smoke: Maximum intensity: Duration, min	Smoke: Total, min	TGA residue,[4] pct
NEOPRENE BELTS								
E-1	395	2,901	54.1	-	100	5.0-6.0	2.0- 8.0	68
	499	2,736	24.5	9-15	100	2.8-3.7	1.0- 7.0	51
F-7	401	2,396	46.1	-	90	4.9-5.5	3.0- 8.0	72
	499	2,789	22.7	6-15	80	2.0-3.5	1.0- 9.0	59
F-10	399	2,322	49.3	-	90	6.1-6.6	3.0- 9.0	84
	497	2,098	30.6	11-15	90	3.5-3.8	1.0- 6.0	59
PVC BELTS								
E-2	406	3,218	37.5	-	85	4.0-7.0	2.0-10.0	34
	506	3,430	18.4	12-15	80	1.5-5.0	.5-12.0	23
F-1	398	3,306	45.6	-	50	4.2-6.0	1.2-11.0	35
	500	2,808	15.2	10-15	60	1.0-4.0	.3-10.0	18
F-2	404	2,344	37.3	-	80	4.5-5.3	2.0-10.0	38
	495	2,417	15.4	1-15	100	3.9-5.7	.5- 8.0	23
F-3	399	2,716	39.7	-	80	2.7-4.0	1.5-14.0	21
	498	2,077	17.2	-	75	3.0-3.7	1.0- 8.0	13
F-6	396	2,002	41.3	-	40	6.7-9.7	1.0-11.0	33
	499	1,579	21.1	-	80	4.9-5.2	1.0- 7.0	23
F-8	399	2,701	30.5	-	85	4.5-6.5	1.0-12.0	50
	498	2,306	20.3	2-15	90	3.0-4.8	.5- 7.0	40
SBR BELTS								
E-3	402	2,622	84.3	-	60	3.2-4.6	2.0- 7.0	84
	507	2,013	37.2	-	85	4.7-5.3	1.0-11.0	53
E-4	401	2,787	70.3	-	50	6.8-7.7	3.0- 9.0	78
	507	1,831	14.8	9-15	80	3.3-4.0	1.0-12.0	40
E-5	399	2,714	68.7	-	50	5.0-7.0	1.5- 6.0	80
	499	2,134	34.6	-	80	3.2-6.0	1.0- 9.0	45
F-4	401	2,379	74.9	-	60	7.5-9.6	2.0-12.0	81
	495	1,712	10.6	3- 5	90	2.6-3.5	1.0-11.0	40
F-5	398	2,519	54.9	-	50	6.7-7.2	3.0-11.0	86
	495	2,314	12.0	6-15	85	4.8-5.8	1.5- 9.0	41
F-9	399	3,266	63.8	-	80	4.0-6.0	1.5- 8.0	78
	499	2,429	28.8	5-15	90	1.8-5.2	.5- 8.0	52

[1]Sample descriptions are listed in table 1.

[2]Average temperature of heating block and air in the stagnation burner; the difference between these temperatures was always <5° C.

[3]Smoke was measured in conformance with ASTM method D-2843-70.

[4]In the case of conveyor belts, residue calculation is based on the TGA of the rubber portion.

Thermal Oxidative Degradations of Conveyor Belts

Ten belts representing the three main classes were tested using the sealed-tube method. The series F belts (table 1) were subjected to fire-gallery testing; no such investigations were conducted on the series E materials. Experimental details of thermal oxidative degradation are summarized in table 4. In table 5, the gram-per-gram data for the neoprene-based belts are compiled. As expected, hydrogen chloride (TLV, 7 mg/m^3)[6] is the major toxic species formed, accompanied by relatively low quantities of other toxic compounds, such as carbon monoxide (TLV, 55 mg/m^3), sulfur dioxide (TLV, 13 mg/m^3), carbon disulfide (TLV, 60 mg/m^3), hydrogen sulfide (TLV, 15 mg/m^3), benzene (TLV, 80 mg/m^3), chloroprene (TLV, 90 mg/m^3), cresols (TLV, 22 mg/m^3), phenols (TLV, 19 mg/m^3), chloroethanol (TLV, 16 mg/m^3), formic acid (TLV, 9 mg/m^3), and acetic acid (TLV, 25 mg/m^3).

TABLE 4. - Experimental data for sealed-tube degradations of conveyor belts

Sample[1]	Tube vol, ml	Initial pressure, mm	Final pressure, mm	Reaction temp, ° C	Sample weight, mg	Residue		Weight loss, mg	Oxygen consumed		Total volatiles	
						Mg	Pct[2]		Mg	Pct[3]	Mg	Pct[4]
NEOPRENE BELTS												
E-1	5,300	541.7	566.1	370	1,509	854	56.6	655	30.8	3.0	345.2	50.3
F-7	5,270	502.3	533.1	371	3,082	1,769	57.4	1,313	52.8	5.6	695.4	50.9
F-10	5,270	500.9	540.4	370	3,022	1,693	56.0	1,329	110.6	11.5	842.0	58.5
PVC BELTS												
E-2	5,300	504.2	541.4	369	2,507	997	39.8	1,510	52.4	5.3	772.6	49.4
F-3	5,300	491.2	539.0	368	2,561	1,503	58.7	1,058	19.3	2.1	792.5	73.6
F-6	5,300	499.5	526.0	368	2,565	1,224	47.7	1,341	25.4	2.7	1,004.0	73.5
SBR BELTS												
E-2	5,300	508.7	518.6	370	1,918	1,405	73.3	513	27.5	2.8	250.0	46.2
E-5	5,300	502.3	521.6	371	5,897	4,715	80.0	1,182	15.2	1.6	533.7	44.6
F-9	5,300	499.5	537.0	371	5,044	4,119	81.7	925	35.3	3.7	656.4	68.4
E-4	5,300	505.3	552.3	369	5,971	4,969	83.3	1,002	31.1	3.2	719.5	69.6

[1]Sample descriptions are listed in table 1.
[2]Percentage of the weight of the starting material; this is only the solid removable portion of the residue and does not include the tars and oils deposited on the side of the tube.
[3]Percentage of oxygen available.
[4]Percentage of total products expected, based on sample weight loss and oxygen consumed.

[6]The threshold limit value (TLV) is the maximum amount of a substance that can be safely tolerated in a work atmosphere for an 8-hour, 5-day, 52-week work year, according to the American Conference of Governmental Industrial Hygienists.

TABLE 5. - Volatile products obtained on thermal oxidative degradation of neoprene-containing conveyor belts,[1] milligrams per gram

Products	Sample E-1	Sample F-7	Sample F-10
H_2	0.50	0.30	0.63
CO	9.12	6.68	5.06
CH_4	.60	1.12	.68
H_2O	31.4	58.0	110.8
HCl	116.8	80.7	68.0
CO_2	14.4	29.3	64.5
SO_2	.20	.61	.28
COS	.23	.34	.29
CS_2	1.02	.45	.34
H_2S	1.21	6.04	.56
C_2- and C_3-species	4.45	2.11	5.35
C_4-species	2.46	1.96	.81
C_5-species	.32	1.53	.66
Isoprene	-	1.19	-
C_6-species	-	2.12	2.32
C_7-species	.13	.78	.57
C_8-species	5.87	.31	.11
Benzene	2.98	.35	.30
Toluene	.70	.11	.11
Xylenes	.50	.15	.10
Ethylbenzene	.23	.02	.10
C_3-benzene	.54	.22	.13
C_4-benzenes	.05	.15	.13
Phenylcyclohexane	-	([2])	-
1-Phenylcyclohexene	-	-	([2])
Styrene	([2])	([2])	.04
Methylstyrenes	-	-	.02
Dimethylstyrenes	-	-	.17
Methylnapthalenes	-	-	.03
Methyltetrahydronapthalenes	-	-	.01
Indene	-	-	.41
Indan (2,3-dihydroindene)	.17	.17	.54
Methylindans	-	.18	.23
Dimethylindans	-	.03	.09
γ-Terpinene	-	-	.07
Santene	-	.04	-
Azulene	-	.02	.13
Methyl chloride	.50	.62	.49
Vinyl chloride	-	-	([2])
Ethyl chloride	1.05	.53	.34
2-Chloropropene	([2])	([2])	.04
3-Chloropropene	1.24	-	-
Chloroprene	1.80	.70	.93
2-Chloro-2-methylpropane	-	.06	-
2-Chloro-2-butene	.11	-	-

See footnotes at end of table.

TABLE 5. - Volatile products obtained on thermal oxidative degradation of neoprene-containing conveyor belts,[1] milligrams per gram--Continued

Products	Sample E-1	Sample F-7	Sample F-10
Chloroprene dimer	[3]0.18	[3]0.09	1.22
Chlorobenzene	.22	.02	.06
Chlorotolunes	.52	.13	.26
Benzyk chloride	[3].43	-	-
Chloro-C_2-benzenes	.09	.20	.13
3-Methylbenzul chloride	-	-	([2])
Methanol	.05	-	-
Ethanol	.02	([2])	([2])
Butanols	.04	.29	.04
3-Methyl-1-Pentynol	2.16	-	-
Purfuryl alcohol	-	-	.04
Phenol	([2])	.01	-
Cresols	[3].43	([2])	.01
2,5-Dimethyl benzyl alcohol	.15	-	-
2-Chloroethanol	.13	2.15	.04
Acetaldehyde	-	([2])	.01
Butyraldehydes	-	([2])	([2])
2,4-Hexadienal	-	-	.03
1-Methyl-3-cyclohexene-1-carboxaldehyde	-	.08	-
Acetone	.23	.51	.63
Methyl ethyl ketone	-	.23	.68
Methyl n-propyl ketone	-	.02	.11
Methyl isopropyl ketone	-	.12	-
Cyclopentanone	.72	.82	1.12
Cyclohexanone	([2])	.02	.06
p-Dioxane	-	-	([2])
Methyl-2-furyl ketone	-	.04	.05
Methyl-p-tolyl ketone	-	.02	-
1-Indanone	-	-	.08
4,7-Dimethyl-1-indanone	-	.04	-
3,4,7-Trimethyl-1-indanone	-	.01	-
Chloroacetone	-	.21	.06
Formic acid	([2])	.30	.60
Acetic acid	.38	2.10	3.51
Propionic acid	-	12.0	.38
Methyl acetate	([2])	.03	.00
Phenol ethers	-	([2])	-
Dimethylfurans	-	-	.01
Benzofuran	-	-	([2])
1,2-Dimethylaminopyridine	-	-	.10
Methyl mercaptan	-	([2])	-
Dimethylsulfide	-	([2])	-

[1]Sample descriptions are listed in table 1.
[2]Trace (<0.005 mg/g).
[3]Tentatively identified.

The PVC-based belts afforded similar results (table 6); however, in this case, the sulfur-containing compounds were present in much lower quantities than in the neoprenes. On the other hand, vinyl chloride (TLV, pending), benzyl chloride (TLV, 5 mg/m^3), and phenol (TLV, 19 mg/m^3) were produced in significant quantities from some of the compositions. It is noteworthy that wide variations (factor of two) existed in the quantities of hydrogen chloride evolved between the different belts. This is most likely due to different PVC contents. It should be stressed that each of the PVC-containing materials produced room-temperature-involatile phthalic annhydride (TLV, 12 mg/m^3), which was identified by infrared spectral analysis. Its production can be correlated to a degree with the C_8-ene present among the volatile products, assuming that dioctyl phthalate is the plasticizer used.

TABLE 6. - Volatile products obtained on thermal oxidative degradation of PVC-containing conveyor belts,[1] milligrams per gram

Products	Sample E-2	Sample F-3	Sample F-6
H_2	0.02	([2])	0.01
CO	3.01	-	-
CH_4	.01	0.07	-
H_2O	60.6	7.14	140.1
HCl	89.6	155.5	95.0
CO	33.9	4.54	40.0
COS	-	-	.05
CS_2	.01	-	-
H_2S	-	.15	.34
C_4- and C_3-species	19.5	.87	.24
C_4-species	([2])	.04	.32
C_5-species	-	-	.64
Isoprene	-	-	1.03
C_6-species	([2])	-	1.21
C_7-species	.10	1.05	.07
C_8-ene species	19.6	81.5	24.8
C_9-ene species	-	7.00	-
1-Undecene	-	3.38	-
Benzene	2.62	13.9	4.56
Toluene	3.73	2.90	.21
Xylenes	.23	([2])	.11
Ethylbenzene	([2])	([2])	.06
Methylstyrenes	([2])	([2])	.06
Divinylbenzene	-	.18	-
Methyl chloride	.16	.29	.45
Vinyl chloride	.34	2.36	([2])
Ethyl chloride	3.46	.76	([2])
1,2-Dichloroethane	5.87	2.33	.01
2-Chloropropene	-	-	.03
1-Chlorohexane	-	-	.43
1-Chloroheptane	-	1.72	-
1-Chloro-2-ethylhexane	-	-	12.8
1-Chlorodecane	-	1.00	-

See footnotes at end of table.

TABLE 6. - Volatile products obtained on thermal oxidative degradation of PVC-containing conveyor belts,[1] milligrams per gram--Continued

Products	Sample E-2	Sample F-3	Sample F-6
Myristyl (C_{14}) chloride	-	0.02	-
Benzyl chloride	16.0	-	-
Chlorotoluenes	1.51	.50	-
Methanol	.02	-	-
Ethanol	.50	([2])	([2])
C_3-alcohols	.04	-	-
C_4-alcohols	5.09	-	([2])
C_5-alcohols	.93	-	0.03
Cyclic C_6-alcohol	-	4.43	-
C_8-alcohols	.11	.52	.05
C_9-alcohols	-	.29	-
Dodecanols	-	.53	-
Phenol	-	-	17.5
2-chloroethanol	6.66	.35	.04
Acetaldehyde	.98	1.10	([2])
C_4-aldehyde	-	.13	-
C_5-aldehyde	-	5.54	-
Acetone	.10	.02	.31
Methyl ethyl ketone	([2])	.02	.82
Methyl n-propyl ketone	-	-	.01
Methyl 2-furyl ketone	-	-	.01
Cyclopentanone	6.51	.07	4.00
Chloroacetone	([2])	-	.27
p-Dioxane	-	.27	.01
Bis (2-Chloroethoxy) methane	-	2.77	-
Acetic acid	.13	.01	1.19
Methyl acetate	.02	.23	.03
Ethyl formate	.01	.01	.01
Ethyl acetate	.03	-	.01
n-Butyl formate	.33	.03	.06
n-Butyl acetate	.10	-	.08
Chloroethyl acetate	.40	([2])	.01
Methyl mercaptan	-	-	([2])
Dimethyl dissulfide	-	-	([2])
1-Hexanethiol	-	-	.48
2-Methylpyridine	-	-	.14
Benzonitrile	.15	-	-

[1]Sample descriptions are listed in table 1.
[2]Trace (<0.005 mg/g).

Comparing the results obtained with the SBR-based beltings (table 7) with the data given for the other belt classes (tables 5-6), a formulation represented by composition E-3 would seem to offer an optimum system with respect to toxic-product evolution. It is gratifying that this particular material performed best in the stagnation-burner investigation. It is unfortunate that no full fire-gallery test data are available for this belting. This data is mandatory for valid material correlation and selection.

TABLE 7. - Volatile products obtained on thermal oxidative degradation of SBR-containing conveyor belts,[1] milligrams per gram

Products	Sample E-3	Sample E-4	Sample E-5	Sample F-9
H_2	0.11	0.12	0.15	0.17
CO	12.0	2.53	3.67	-
CH_4	.27	1.23	.21	.39
H_2O	71.4	42.8	33.9	20.2
CHl	2.8	15.9	14.1	39.4
CO_2	18.7	25.5	12.5	10.8
SO_2	.17	([2])	.09	-
COS	.56	.45	1.34	.36
CS_2	.03	-	.33	1.72
H_2S	.02	.25	.74	7.63
HCN	-	-	.50	([2])
C_2- and C_3-species	.84	6.01	1.80	6.03
C_4-species	.56	.95	.62	2.91
C_5-species	.23	.88	.60	5.32
C_6-species	1.06	.71	1.59	2.81
C_7-species	.34	.56	.12	.99
C_8-species	6.87	.05	.90	2.49
C_9-species	-	-	-	.03
1-Methyl-4-isopropenyl-1-cyclohexene	-	8.21	-	-
C_{11}-species	-	-	-	.01
C_{12}-species	-	-	-	.07
C_{13}-species	-	-	-	.02
Benzene	.50	.35	.32	1.98
Toluene	1.03	.79	.17	.16
Xylenes	.33	.96	.60	.18
Ethylbenzene	.28	.83	.50	.16
C_3-benzenes	.27	.05	.50	.15
C_4-benzenes	.02	.05	.02	.04
O-Allyltoluene	-	-	-	.02
C_5-benzenes	-	-	-	.02
Styrene	.95	1.12	.27	.56
Methylstyrenes	.08	.11	.03	.12
C_2-Styrenes	.06	([2])	[3].02	.19
Tetrahydronapthalenes	[3].01	[3].02	[3].02	.02
Methylnapthalenes	[3].01	-	[3].03	([2])
Methyltertrahydro-napthalenes	[3].01	[3].01	[3].02	.01
Indene	[3].02	.06	[3].02	.10
Indan (2,3,-dihydro-indene)	[3].02	[3].06	[3].03	.10
Methylindans	[3].01	[3].01	[3].02	.01
Dimethylindans	([2])	[3].01	[3].03	.01
Azulene	-	-	-	.10
Methyl chloride	([2])	.01	.39	10.39
Vinyl chloride	-	([2])	-	.34
Ethyl chloride	-	.13	.12	2.77
2-Chloroproprene	-	-	-	.26
Chloroprene	-	-	-	.27

See footnotes at end of table.

TABLE 7. - Volatile products obtained on thermal oxidative degradation of SBR-containing conveyor belts,[1] milligrams per gram--Continued

Products	Sample E-3	Sample E-4	Sample E-5	Sample F-9
2-Chloro-2-butene	-	-	-	0.63
3-Chloro-2-methylpropane	-	-	-	.06
Chlorobenzene	0.01	([2])	0.01	.09
Chlorotoluenes	.02	-	-	.12
Chloro-C_2-benzenes	-	-	-	.01
Dichlorobenzene	-	-	.01	.03
Methanol	.23	0.04	([2])	2.74
Ethanol	.04	.11	([2])	([2])
Allyl alcohol	-	.02	-	-
C_3-alcohols	-	([2])	-	-
C_4-alcohols	.08	([2])	.05	.01
C_5-alcohols	-	-	-	([2])
Phenol	.02	.06	.67	.03
Cresols	-	-	-	1.77
4-Methyl-2-ethylphenol	-	-	-	.02
2-Chloroethanol	.01	.04	([2])	.03
Acetaldehyde	-	.71	-	.46
Acetone	.02	.21	.09	.06
Methyl ethyl ketone	.03	.10	.02	.06
Methyl n-propyl ketone	-	-	-	([2])
4-Methyl-2-pentanone	-	.07	-	-
Methyl-2-furyl ketone	-	-	-	([2])
p-Dioxane	-	-	.04	.01
Cyclopentanone	2.46	.02	1.78	.02
Methylcyclopentanone	-	-	-	.06
Cyclohexanone	-	.02	.10	.02
Dimethylindanones	-	-	-	.01
Trimethylindanones	-	-	-	.03
Formic acid	-	-	-	2.91
Acetic acid	([2])	.23	.14	.71
Methoxyacetic acid	-	-	1.73	-
Methyl acetate	.12	([2])	-	.02
Vinyl acetate	-	.07	-	-
Ethyl formate	.01	-	-	([2])
Ethyl acetate	.08	-	-	-
2-Methylfuran	-	.28	.01	-
Dimethylfurans	-	-	.12	-
Ethylmethylfurans	-	-	-	.02
Methyl mercaptan	-	-	-	.01
Dimethyl sulfide	([2])	-	([2])	.02
Dimethyl disulfide	-	-	-	.21
Methylthiophenes	-	-	-	.08
Thiacyclopentane	-	-	-	.01
Acetonitrile	-	-	.22	-
5-Cyanohexene	-	-	-	.25

[1]Sample descriptions are listed in table 1.
[2]Trace (<0.005 mg/g).
[3]Tentatively identified.

Thermal Oxidative Degradation of Selected Pure Components

Each of the pure ingredients studied (table 2), namely dioctyle phthalate plasticizer, carbon black filler, the chlorinated hydrocarbon flame retardant, and nylon-6 fiber, represent constituents used in substantial quantities in conveyor-belt formulation. Consequently, the products formed by these ingredients on thermal oxidative degradation have a significant impact on the total product mix from a given conveyor-belt composition.

The experimental details of the degradation studies are summarized in table 8; the gram-per-gram data are compiled in table 9. Based on these results, it is apparent that carbon black and nylon-6, under the conditions employed here, do not contribute greatly to the production of volatile decomposition products. On the other hand, the chlorinated hydrocarbon exhibits a behavior closely comparable to that of the PVC resin, whereas dioctyl phthalate formed relatively volatile C_8-olefin and the room-temperature-involatile, yet toxic, phthalic anhydride (TLV, 12 mg/m^3). It is noteworthy that the latter was deposited on the sides of the 5-liter bulb, indicating that the decomposition occurred in the vapor phase.

TABLE 8. - Experimental data on degradation of pure components

Component[1]	Tube vol, ml	Initial pressure, mm	Final pressure, mm	Reaction temp, ° C	Sample weight, mg	Residue		Weight loss, mg	Oxygen consumed		Total volatiles	
						Mg	Pct[2]		Mg	Pct[3]	Mg	Pct[4]
Dioctyl phthalate	5,270	506.4	518.2	370	4,841	4,169	86.1	672	19.5	2.0	571.5	13.9
Carbon black....	5,270	482.7	500.6	369	5,164	4,970	96.2	194	58.3	6.3	189.1	75.0
Chlorindated hydrocarbon...	5,300	452.7	597.6	373	2,518	729	28.9	1,789	11.8	1.4	1,388.5	77.1
Nylon 6...	5,300	472.4	489.3	368	2,900	2,595	89.5	305	9.8	1.1	69.7	22.1

[1]Description of components is given in table 2.

[2]Percentage of the weight of the starting material; with the exception of the dioctyl phthalate sample, this is only the solid removable portion of the residue and does not include the tars and oils deposited on the sides of the tube.

[3]Percentage of oxygen available.

[4]Percentage of total products expected, based on sample weight loss and oxygen consumed. These are the materials involatile at room temperature that remained in the bulb; they were composed of dioctyl phthalate and phthalic anhydride, and some of the C_8-olefin.

TABLE 9. - Volatile products obtained on thermal oxidative degradation of pure components,[1] milligrams per gram

Products	Dioctyl phthalate	Carbon black	Chlorinated hydrocarbon	Nylon 6
H_2	0.02	-	-	-
CO	4.11	3.80	7.38	-
CH_4	.14	.08	.47	-
H_2O	1.37	19.4	9.21	18.4
HCl	-	-	499.7	-
CO_2	5.03	12.5	2.51	4.86
SO_2	-	.59	-	-
COS	-	.07	-	-
NH_3	-	-	-	.17
C_2- and C_3-species	.51	([2])	1.67	.01
C_4-species	1.20	-	-	-
C_5-species	1.01	-	-	([2])
C_6-species	.08	([2])	.30	-
C_7-species	.72	-	-	-
C_8-ene species (2[8]-methyl-1-heptene)	119.4	-	-	-
Benzene	.32	.03	7.73	.01
Toluene	.04	.08	1.01	([2])
Xylenes	-	-	.06	-
Styrene	-	-	.01	-
Methyl chloride	-	-	.87	-
Vinyl chloride	-	-	.76	-
Ethyl chloride	-	-	.55	-
1,1-Dichloroethane	-	-	.01	-
1,2-Dichloroethane	-	-	.02	-
3-Chloropropane	-	-	.51	-
Dichloropropenes	-	-	.40	-
Chlorobutanes	-	-	.14	-
Chlorobutenes	-	-	.32	-
Dichlorobutenes	-	-	.09	-
Chlorobenzene	-	-	9.69	-
Dichlorobenzenes	-	-	1.91	-
Chlorotoluenes	-	-	.80	-
2-Propanol	-	-	-	.22
Phenol	-	-	.05	-
2-Chloroethanol	-	-	.37	-
1-Chloro-2-propapanol	-	-	.27	-
Acetaldehyde	.06	.01	.75	([2])
Acetone	4.78	.01	.61	-
Cyclopentanone	-	-	-	.01
Phthalic anhydride	194	-	-	-

[1]Description of components is given in table 2.
[2]Trace (<0.005 mg).

SUMMARY

Conveyor belts are an integral part of mining operations. Consequently, it is of great importance to develop sound principles for the selection of belts that pose the least possible and practical hazard insofar as toxic-product formation is concerned, yet retain the required flame resistance.

Accordingly, the Bureau of Mines sponsored this investigation at Ultrasystems, Inc.,[7] to provide mine operators and mine inspectors with guidelines, to be later translated into regulations, regarding the toxicity aspects of thermal oxidative decomposition products formed by conveyor belts and other articles used underground. The program was concerned with (1) thermal oxidative degradation of actual belts, including the determination of all volatile products formed on a gram-per-gram basis, and (2) the products of the decomposition of pure ingredients used in the standard belt formulations. Belts containing styrene-butadiene rubber appeared to perform the best of all the materials tested with regard to (1) the relative quantities and nature of the toxic species produced at elevated temperatures and (2) the thermal oxidative behavior, as indicated by glow characteristics, char yields, and smoke formation. Thus, it appears that acceptable flame resistance can be achieved without paying the penalty of increased toxic-product evolution.

To provide more general guidelines regarding material selection for underground use, as well as to develop regulations governing such materials, thermal oxidative degradations were also conducted on pure belt ingredients. Four compounds were studied: dioctyl phthalate plasticizer, carbon black filler, chlorinated hydrocarbon flame retardant, and nylon-6 fiber.

Future efforts will be concerned with additional evaluation of pure components, which will include the testing of "synthetic," that is, quantitatively known, formulations. The end result of the overall program will be the development of meaningful regulations for material employment in underground operations to assure that miners are exposed to the least potential danger arising from decomposing and/or burning organic materials.

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[7] Third work cited in footnote 3.