

Bureau of Mines
Report of Investigations 4777



THERMAL DECOMPOSITION PRODUCTS AND BURNING
CHARACTERISTICS OF SOME SYNTHETIC
LOW-DENSITY CELLULAR MATERIALS

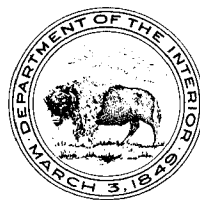
BY H. A. WATSON, H. J. STARK, R. L. BEATTY,
H. W. BUSCH, AND L. B. BERGER

United States Department of the Interior — January 1951

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**UNITED STATES DEPARTMENT OF THE INTERIOR
Oscar L. Chapman, Secretary
BUREAU OF MINES
James Boyd, Director**

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This report describes a joint investigation by the Bureau of Ships, Department of the Navy, and the Bureau of Mines, Department of the Interior.

January 1951

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LOW-DENSITY CELLULAR MATERIALS

by

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that was employed in their animal experimentation and in determining that sponge rubber foamed with PN continues to give off the vapor of TSN for extended periods.

According to information obtained by the British Intelligence Objectives Subcommittee^{8/}, the potential hazard from PN and its decomposition products was recognized by German manufacturers, who found that PN caused no skin irritation but if it or its products of decomposition were inhaled for prolonged periods serious injury to internal organs, particularly the stomach, could occur. Hence, precautions were taken to prevent formation of PN dust during the mixing operation and to remove, by ventilation, the gaseous decomposition products during the vulcanization process. Recommended manufacturing practices included the wearing of respirators by those employed in vulcanizing operations, and the storing of freshly vulcanized material in well-ventilated rooms.

Objectives of this investigation were (a) to determine whether material blown with PN contained TSN, (b) to determine whether TSN was liberated in thermal decomposition of the material and, if so, at what temperatures, (c) identification of other toxic gaseous products of thermal decomposition or combustion, and (d) to determine ignition time, burning time, and ignition temperature of the materials.

The materials tested, some of which were experimental in nature, were furnished to the Bureau of Ships by industrial suppliers. The test program was established and authorized by the Bureau of Ships, Department of the Navy, Washington, D. C., and the experimental work was conducted by the Bureau of Mines, Department of the Interior, Pittsburgh, Pa.

SUMMARY

This report covers a study of the toxic, gaseous, decomposition products and burning characteristics of the following low-density synthetic cellular materials: (1) PN-expanded polyvinylchloride, (2) UND-expanded polyvinylchloride, (3) cellular acrylonitrile hardboard, (4) soft cellular polyvinylchloride (modified). For all materials, carbon monoxide appeared as a principal gaseous product of toxicological significance, together with hydrogen chloride in the case of the polyvinylchloride materials. Other decomposition products evolved in smaller amounts were aldehydes, ammonia, cyanides, and oxides of nitrogen. The cellular acrylonitrile material produced somewhat higher concentrations of oxides of nitrogen than the other materials. Free chlorine and phosgene were not detected in the test atmospheres.

Particular attention, by special test procedures, was given material No. 1, the PN-expanded polyvinylchloride, to determine whether it contained tetramethyl-succino-nitrile (TSN), a volatile, highly toxic compound formed

^{8/} Brazier, S. A., Davey, W. C., Gurney, W. A., James, R. G., Reece, W. H., and Sutton, S. D., German General Rubber Goods Industry: Final Report No. 349, Item No. 22, circa 1946, British Intelligence Objectives Subcommittee, London, pp. 96-98.

by the action of the azo-bis-isobutyronitrile (PN) expanding agent, and whether TSN was liberated from the material under various conditions of temperature. The presence of TSN in the material was established by infra-red absorption spectroscopy and by X-ray diffraction examination. Relative rates of evolution of volatile nitrogen-containing compounds and of hydrogen chloride from this material when heated to various temperatures in a stream of air were determined by chemical analysis. The evolved nitrogen-containing compounds are reported as equivalent TSN, as no nitrogen-containing ingredients other than the foaming agent are reported to be present in the formulation of this material. Under the test conditions, evolution of TSN was not detectable at room temperature. At 75° C., a small quantity was evolved. From 75° to 300° C. increasing rates of evolution were shown. Incipient breakdown of the polyvinylchloride with the evolution of hydrogen chloride occurred at 190° C. At temperatures above 200° C., under these test conditions, the rate of evolution of hydrogen chloride relative to that of TSN became large enough so that hydrogen chloride probably would be the decomposition product of major toxicological significance.

Relative rates of evolution of hydrogen chloride from the three other materials were determined. The cellular acrylonitrile hardboard (material No. 3) did not evolve hydrogen chloride, as it apparently contained no chlorine. Materials 2 and 4 evolved hydrogen chloride when heated above 160° C.

Self-ignition temperatures, ignition and burning times, and burning characteristics of the materials are included in this report.

ACKNOWLEDGMENT

The authors acknowledge the kind assistance of Dr. R. N. Harger in furnishing a sample of pure TSN for this study and information relative to its toxicological properties, Dr. R. A. Friedel for making the infra-red spectrographic examinations, and Mrs. Gretta S. Baur for making the X-ray diffraction examinations.

MATERIALS EXAMINED

The materials examined - slabs 6 by 6 by 1 inch - were as follows:

<u>Material</u>	<u>Blowing or foaming compound</u>
1. Cellular polyvinylchloride	Azo-bis-isobutyronitrile (PN)
2. Cellular polyvinylchloride	Disnitroso-pentamethylene-tetramine (UND)
3. Cellular acrylonitrile hardboard (copolymer of butadiene, acrylonitrile and styrene)	Not known
4. Soft cellular polyvinylchloride (modified)	Not known

SCOPE OF INVESTIGATION

Because of the reported toxicity of TSN, the investigation centered mainly on the identification and determination of this compound in, or emanating from, material No. 1, which was blown or foamed with PN. Chemical analysis, infra-red spectroscopy, and X-ray diffraction examination were employed in these operations.

Since three of the materials examined were expanded polyvinylchloride, tests also were conducted to ascertain whether hydrogen chloride, free chlorine, or other chlorine-containing gases, such as phosgene, might be liberated when heat was applied to the materials. The gaseous products of burning or thermal decomposition of the materials also were examined to determine the quantities produced of carbon dioxide, carbon monoxide, aldehydes, cyanides, oxides of nitrogen, and ammonia.

Data were obtained on the self-ignition temperatures^{9/} of the materials and on the ignition time, burning time, burning characteristics, and weight loss due to burning under the test conditions.

TEST METHODS AND EQUIPMENT

Determinations of the composition of atmospheres produced by burning or thermal decomposition of the materials and the ignition time and burning time were conducted with equipment developed for a previous investigation^{10/} and described in detail in the covering publication. This apparatus is shown diagrammatically in figure 1. The manner of igniting or thermally decomposing the test specimen is similar to that employed by the Department of the Navy for determining flame resistance of synthetic materials^{11/12/13/}. Figure 2 shows the assembly for testing a specimen. The test specimen is centered vertically within the nichrome heater coil and supported so that 2 inches of the specimen extend above it. The sparkplug igniters are placed 1/8 inch from the specimen. The heater coil (7 turns, 1-3/16 inches diameter, No. 10 nichrome wire) is energized with a 55-ampere current. The ignition time is defined as the time elapsed between the energizing of the coil and the ignition of the specimen. Heating is continued 30 seconds after ignition. The coil then is de-energized, and the burning time is recorded as the time

-
- ^{9/} The initial air temperature at which, in the absence of an ignition source, ignition occurs of itself, as indicated by an explosion, flame, or glow.
- ^{10/} Berger, L. B., Schrenk, H. H., Gale, J. A., Stewart, R. W., and Sieffert, L. E., Toxicity of Thermosetting Plastics: Bureau of Mines Rept. of Investigations 4134, 1947, 11 pp.
- ^{11/} Gale, J. A., Stewart, R. W., and Alferts, J. B., Determining the Flammability of Thermosetting Materials: Plastics, vol. 2, June 1945, pp. 56, 58, 59, 60, 126.
- ^{12/} Gale, J. A., Stewart, R. W., and Alferts, J. B., Flame Resistance of Thermosetting Plastics: A.S.T.M. Bull. No. 131, Dec. 1944, pp. 23-27.
- ^{13/} Joint Army-Navy Specification JAN-P-14, Sept. 30, 1944.

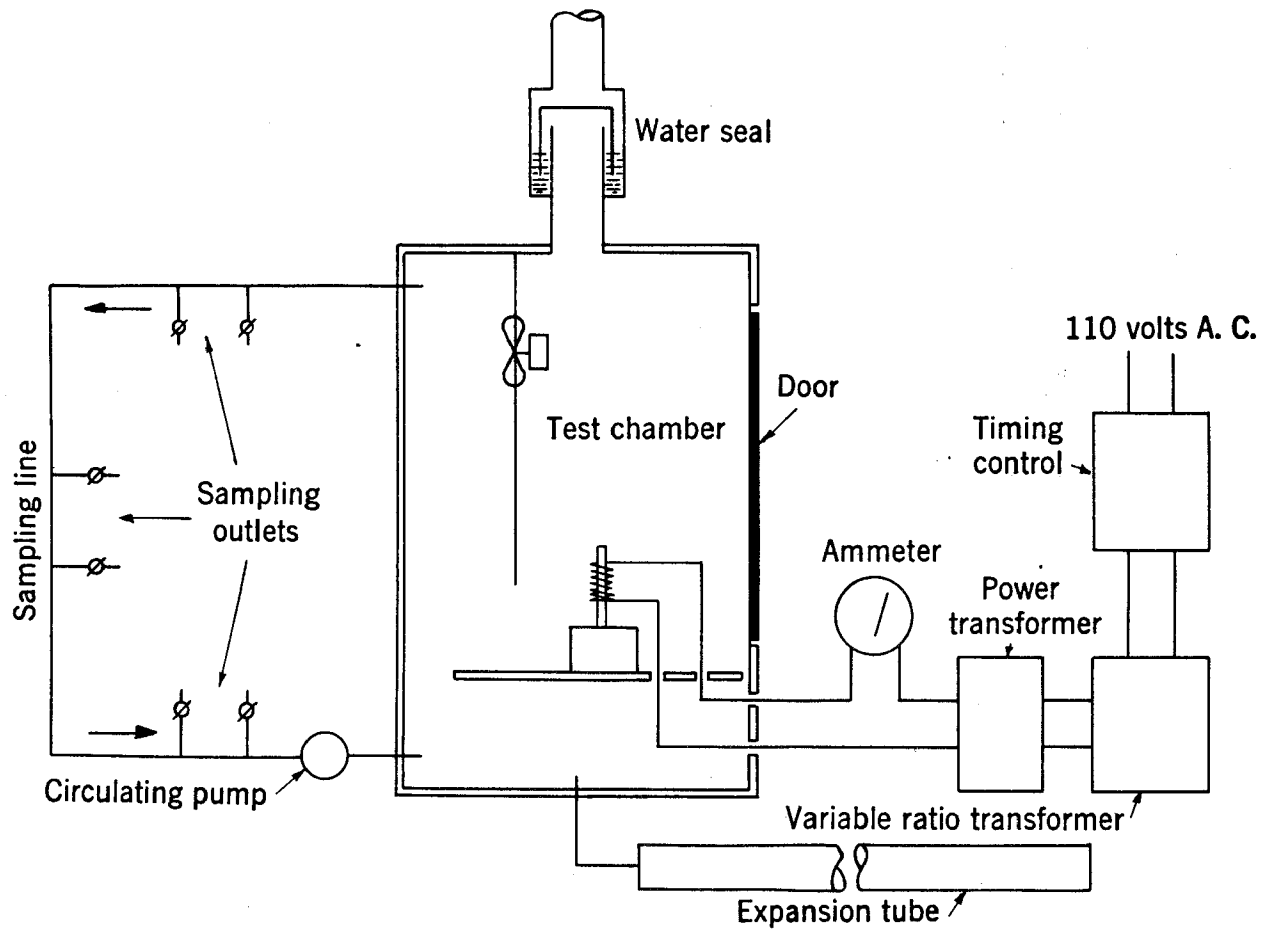


Figure 1. - Diagrammatic sketch of equipment for determining gaseous decomposition products and burning characteristics of synthetic materials, showing accessory apparatus and gas-sampling arrangement.

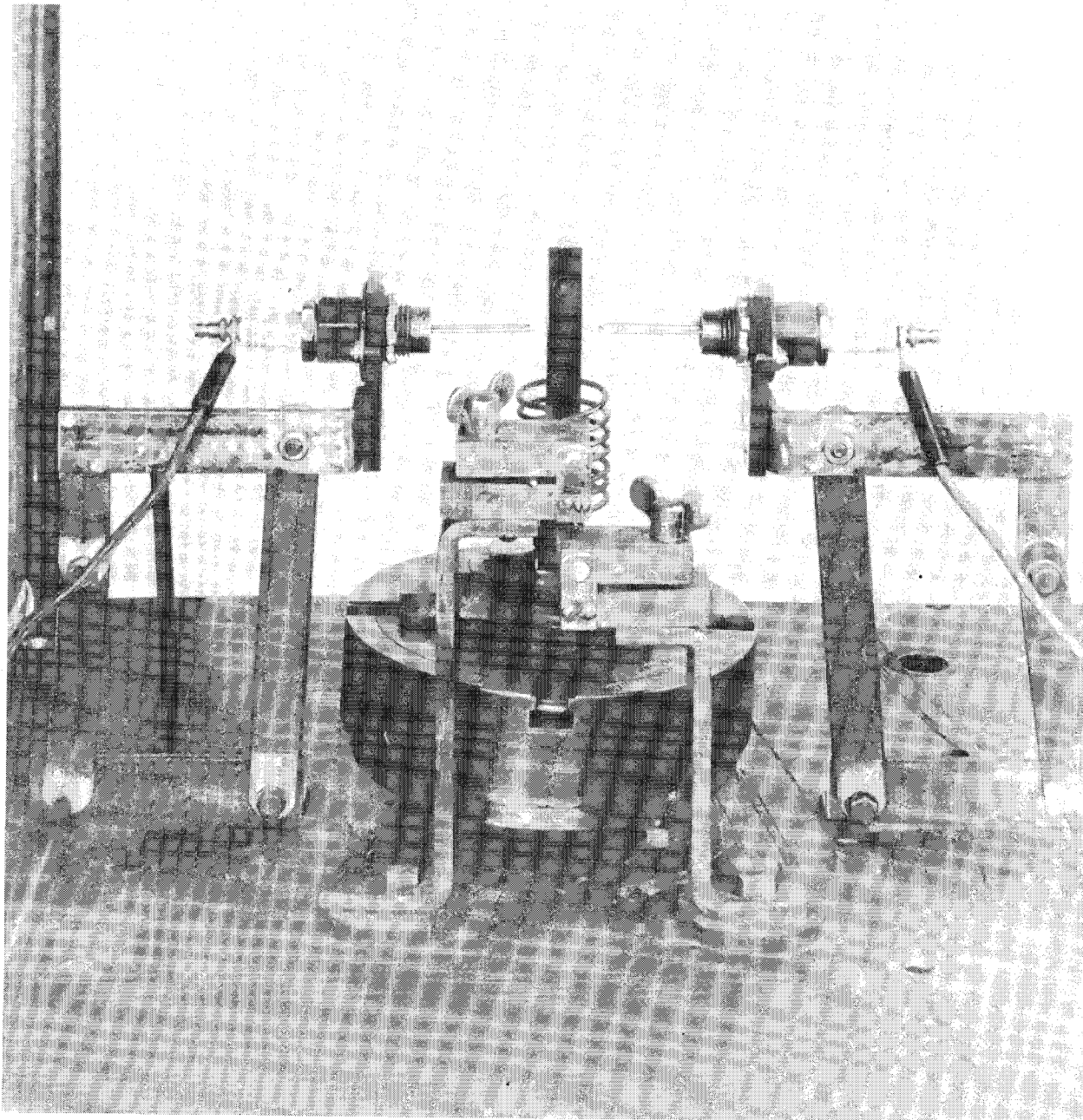


Figure 2. - Front view of assembly, showing spark plugs, heater coil, supporting legs, and specimen.

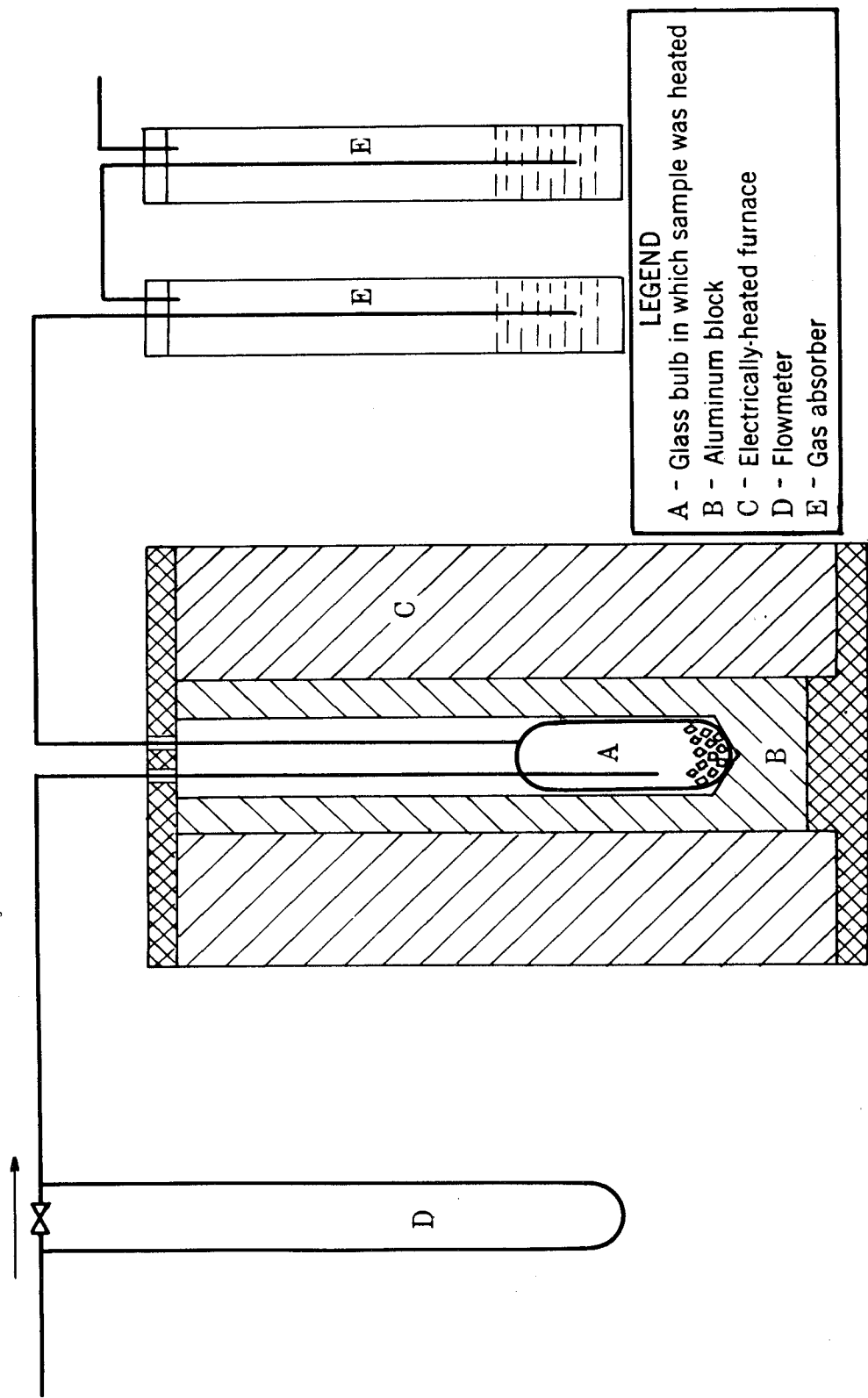


Figure 3. - Diagrammatic sketch of apparatus for determining evolution of nitrogen-containing gases and hydrogen chloride.

required for the flame to extinguish after the coil is de-energized. When burning ceases, the chamber atmosphere is stirred for 5 minutes, and samples of it are collected for chemical analysis. If the specimen does not ignite, heating is terminated after 480 seconds, and the described stirring and sampling procedure is followed.

Test pieces of conventional size (1/2 by 1/2 by 5 inches) were prepared. Only the cellular acrylonitrile hardboard material was rigid enough for mounting properly in the test equipment. The other three materials were supported by a thin steel rod thrust through the longitudinal axis of the test specimen to prevent it from bending and contacting the heater coil.

In analyzing the atmospheres produced in the test chamber, carbon dioxide, oxygen, and hydrocarbons were determined with the modified Haldane gas-analysis apparatus.^{14/} The following constituents were determined by colorimetric methods: Carbon monoxide by a palladium chloride-phosphomolybdic acid-acetone reagent,^{15/} aldehydes as formaldehyde by Schiff's reagent,^{16/} cyanides as hydrogen cyanide by a blood method,^{18/} and oxides of nitrogen by the phenol-disulfonic acid method.^{19/} Qualitative tests were made colorimetrically for phosgene with test papers impregnated with diphenylamine-p-dimethylaminobenzaldehyde reagent^{20/} and for chlorine with ortho-tolidine reagent.^{21/}

The apparatus shown diagrammatically in figure 3 was used to determine the evolution of nitrogen-containing compounds or hydrogen chloride by the materials at elevated temperatures. A weighed portion of the material cut into small pieces was introduced into the glass bulb, A, which was enclosed in an aluminum block, B, which, in turn, was enclosed in an electric furnace, C. Air was passed through a flowmeter, D, at 100 ml. per minute, over the heated sample in A, and through the bubbling-type gas absorbers, E. The

- ^{14/} Berger, L. B., and Schrenk, H. H., Bureau of Mines Haldane Gas-Analysis Apparatus: Bureau of Mines Inf. Circ. 7017, 1938, 24 pp.
- ^{15/} Polis, B. D., Berger, L. B., and Schrenk, H. H., Colorimetric Determination of Low Concentrations of Carbon Monoxide by Use of a Palladium Chloride-Phosphomolybdic Acid-Acetone Reagent: Bureau of Mines Rept. of Investigations 3785, 1944, 13 pp.
- ^{16/} Method as applied to analysis of Diesel exhaust gases described by Busch, H. W., and Berger, L. B., Sampling and Determination of Aldehydes in Diesel Engine Exhaust Gas and in Mine Air: Bureau of Mines Rept. of Investigations 4531, 1949, 9 pp.
- ^{17/} Jacobs, M. B., Analytical Chemistry of Industrial Poisons, Hazards, and Solvents: Interscience Publishers, Inc., New York, 2d ed., 1949, pp. 364-365.
- ^{18/} Lester, D., The Quantitative Determination of Cyanide in Air: Jour. Ind. Hyg. and Toxicol., vol. 26, 1944, pp. 61-63.
- ^{19/} Beatty, R. L., Berger, L. B., and Schrenk, H. H., Determination of Oxides of Nitrogen by the Phenoldisulfonic Acid Method: Bureau of Mines Rept. of Investigations 3687, 1943, 17 pp.
- ^{20/} Department of Scientific and Industrial Research, London, Methods for the Detection of Toxic Gases in Industry. Phosgene: Leaflet No. 8, 1939.
- ^{21/} Department of Scientific and Industrial Research, London, Methods for the Detection of Toxic Gases in Industry. Chlorine: Leaflet No. 10, 1939.

temperature of the furnace and aluminum block was maintained at the desired level by an electric pyrometer-controller actuated by a thermocouple inserted in the aluminum block. The solutions from the absorbers were analyzed for combined nitrogen or for chloride content.

Combined nitrogen was determined by the method of Harger and Hulpieu.^{22/} The volatile nitrogen-containing compounds were absorbed in concentrated sulfuric acid and converted to ammonium sulfate. Discoloration caused by organic material was destroyed by hot oxidation with 30 percent hydrogen peroxide. The ammonia content, from which combined nitrogen and TSN were calculated, was determined colorimetrically by Nesslerization and comparison with known ammonium sulfate standards.

Confirming evidence of the presence of TSN in material No. 1 was obtained by infra-red spectroscopic and X-ray diffraction examinations of carbon disulfide extracts of the material.

Evolved hydrogen chloride was absorbed in a 10 percent solution of sodium hydroxide and determined by a mercurimetric method.^{23/} The chloride-containing solution was acidified with nitric acid, heated, filtered, and titrated with standardized mercuric nitrate solution using sodium nitroprusside as a turbidimetric indicator.

The self-ignition temperatures of the materials were determined by a modified A.S.T.M. method,^{24/} in which a small piece of material is dropped into a glass flask surrounded by a furnace maintained at constant temperature. The furnace temperature is changed stepwise, in small increments, until the minimum temperature is reached at which ignition occurs.

RESULTS OF TESTS

Test results are given in tables 1, 2, 3, 4, 5, and 6 and in figures 4, 5, and 6.

Tables 1, 2, and 3 present the results of the flammability tests conducted on the four materials. Included are data on the weight lost from the specimens as a result of the test, ignition and burning times, composition of the test-chamber atmospheres, and the volumes of the various gases produced.

Burning characteristics of the materials are summarized as follows:

Material No. 1, PN-expanded polyvinylchloride. When subjected to heat, the material shrank considerably, thus increasing the space between test specimen and heater coil and spark igniters. This at least partly accounts

^{22/} Work cited in footnote 7.

^{23/} Kolthoff and Stenger, Volumetric Analysis, vol. II, 2d ed.: Interscience Publishers, Inc., New York, 1947.

^{24/} Scott, G. S., Jones, G. W., and Scott, F. E., Determination of Ignition Temperatures of Combustible Liquids and Gases: Anal. Chem., vol. 20, 1948, pp. 238-241.

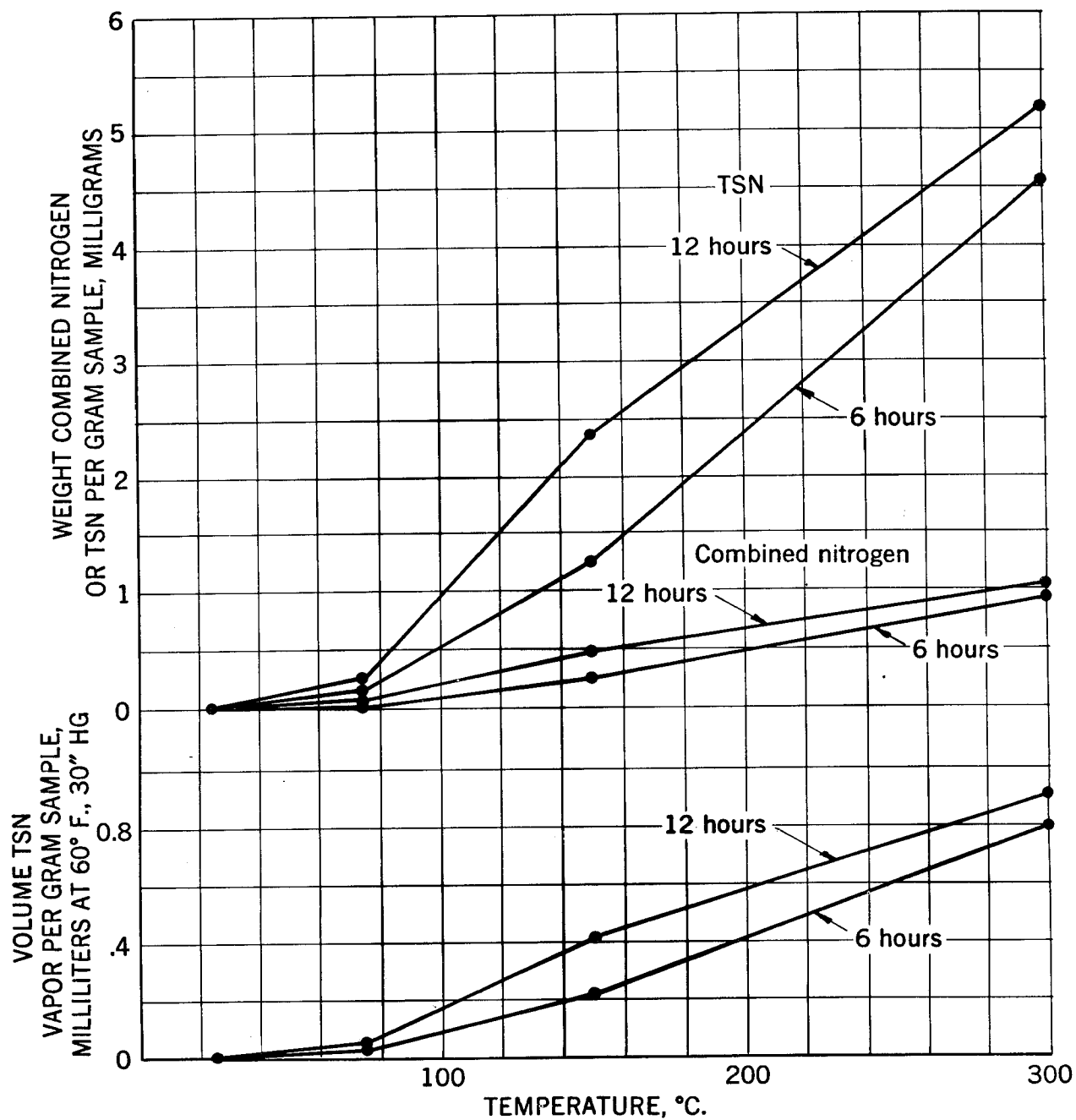


Figure 4. - Combined nitrogen expressed as weight of nitrogen and TSN (tetra-methyl-succino-nitrile), and as volume of TSN, evolved when 1.5-gram samples of PN-expanded polyvinylchloride were heated to the indicated temperatures in a stream of air; each sample was heated for two 6-hour periods.

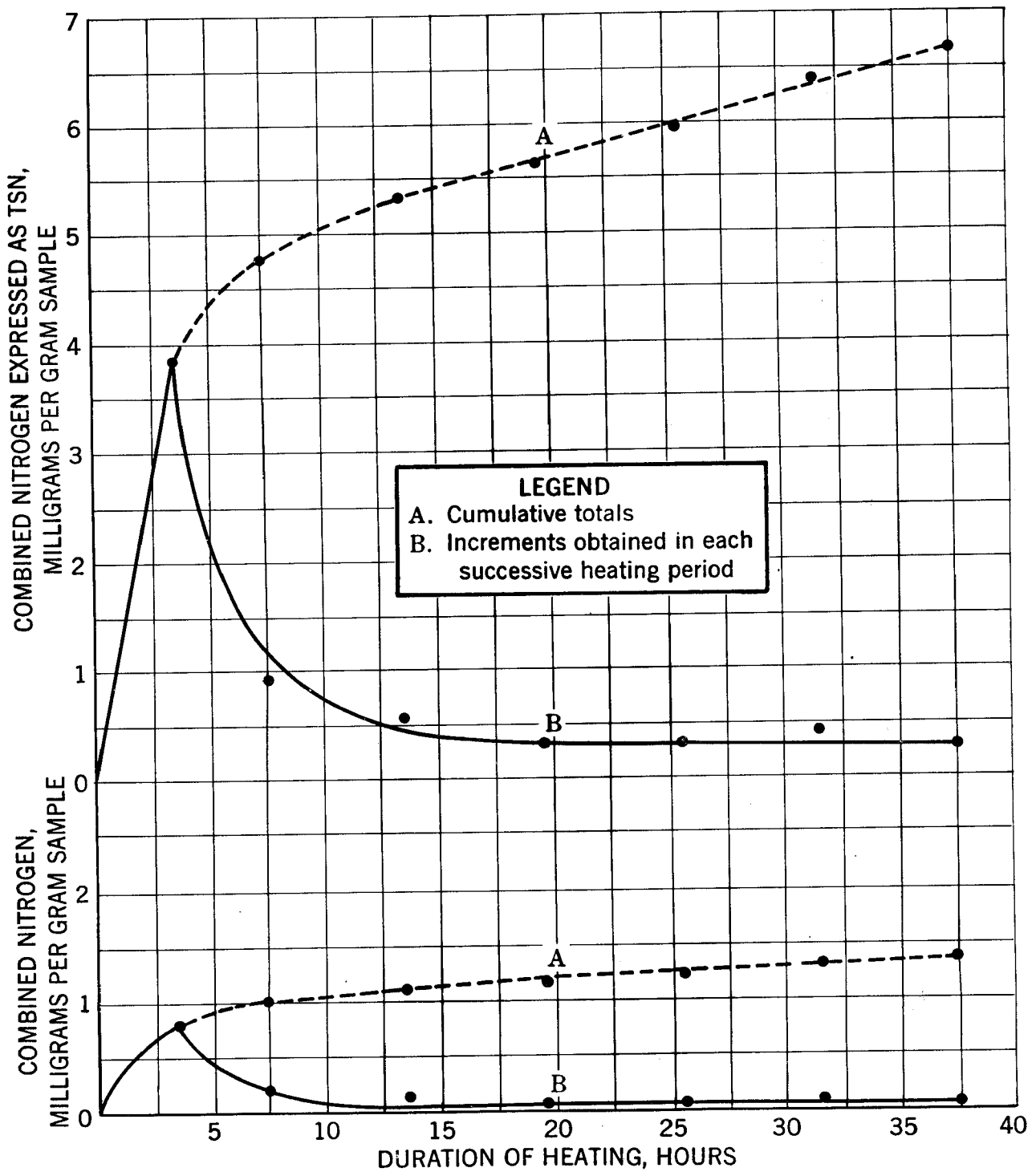


Figure 5. - Combined nitrogen expressed as nitrogen and as TSN (tetramethyl-succino-nitrile) evolved by a 1.5-gram sample of PN-expanded polyvinylchloride heated to 300°C. for an extended period.

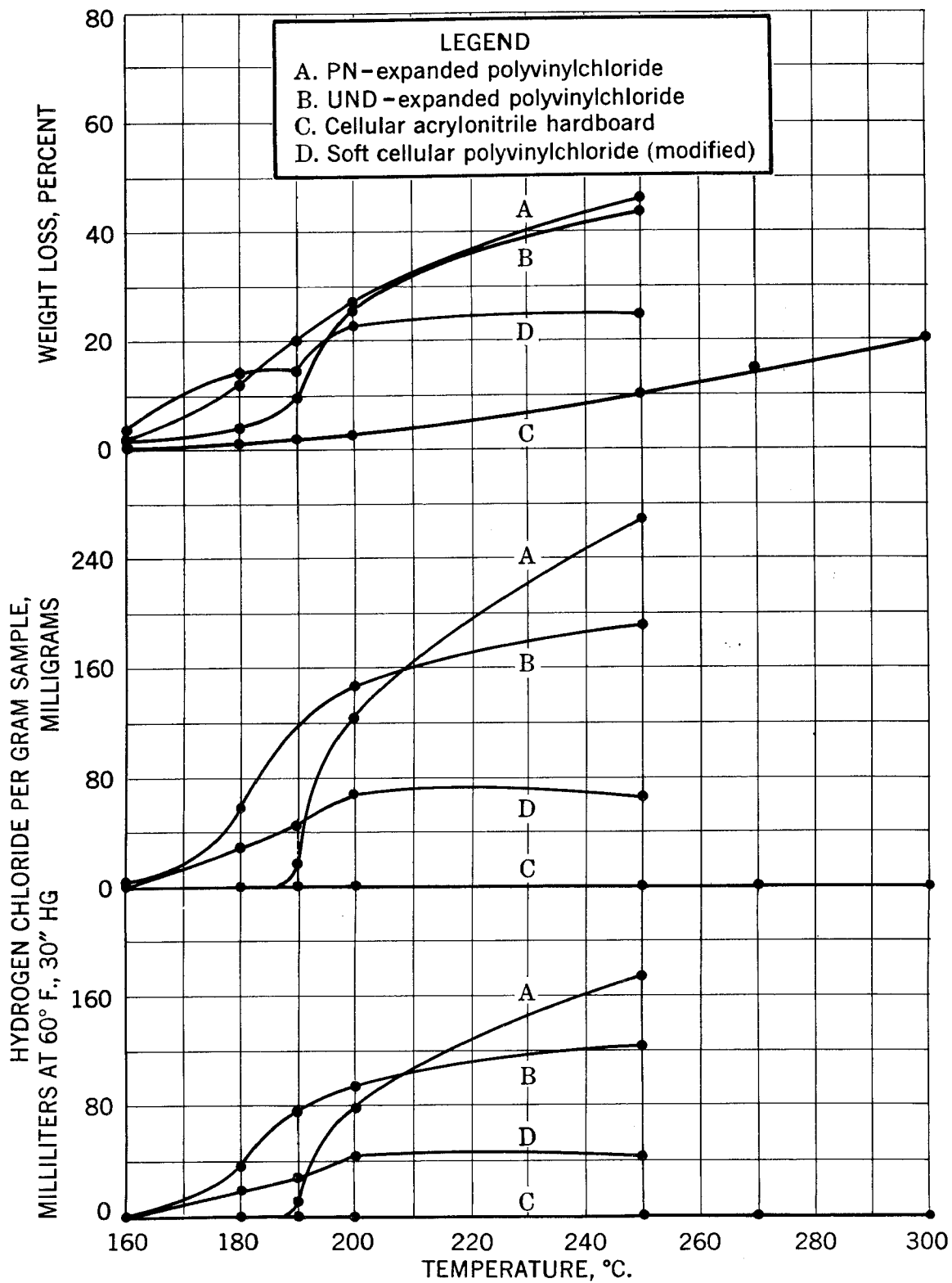


Figure 6. - Weight and volume of hydrogen chloride and weight loss produced by heating low-density cellular materials in a stream of air for 3 hours at each of the temperatures shown.

for the instances in which ignition did not occur. Test piece burned over the entire length with a luminous flame, which formed a light deposit of soot in the chamber. Some afterglowing occurred. Atmosphere produced contained a light-colored smoke and was irritating to the nose and throat. Residue was a black, light-weight, crisp, friable ash.

Material No. 2, UND-expanded polyvinylchloride. Fewer ignitions of this material were obtained than with the PN-expanded material. Material shrank when heated and exhibited burning characteristics similar to those of material No. 1.

Material No. 3, cellular acrylonitrile. When subjected to heat, the material expanded considerably, burst into flame, and burned vigorously with a large, luminous, sooty flame. A small residue of a black, fused, brittle material remained. The atmosphere produced contained an extremely black smoke and had a sweetish, irritating odor. The smoke particles rapidly coalesced, forming a heavy deposit of black, fluffy soot.

Material No. 4, soft cellular polyvinylchloride (modified). Material expanded when heated and burned with a medium-sized, luminous flame. Some afterglowing occurred. The atmosphere produced contained a light-colored smoke and had a sweetish, irritating odor. Upper and middle portions of the specimen were decomposed. Residue was a black, crisp, friable ash.

Table 4 and figures 4 and 5 present data on the evolution of volatile nitrogen-containing compounds, expressed also as TSN, from the PN-expanded material during heating tests under controlled conditions.

Table 5 and figure 6 present data on the evolution of hydrogen chloride by the four materials during 3-hour heating tests.

Table 6 presents ignition-temperature data for the four materials.

TABLE 1. - Low-density cellular materials; description
and burning characteristics

Material	Plastic type	Foaming agent	Weight loss, gm.	Weight loss, percent	Ignition time, seconds	Burning time, seconds
1	Cellular polyvinylchloride ^{3/}	PN	1.16	55.1	<u>1/</u>	<u>1/</u>
			1.12	54.2	31.1	14.6
			1.64	53.7	46.7	2/0
			1.56	51.8	63.1	6.6
2	Cellular	UND	.87	49.3	63.5	<u>2/0</u>
			1.04	54.3	<u>1/</u>	<u>1/</u>
			.99	56.7	<u>1/</u>	<u>1/</u>
			.98	56.2	<u>1/</u>	<u>1/</u>
3	Cellular acrylonitrile hardboard ^{4/ 5/}	Not known	2.76	75.4	34.3	71.8
			2.63	70.5	34.7	62.8
4	Soft cellular polyvinylchloride (modified) ^{4/}	Not known	.94	41.1	21.4	4.8
			.95	43.5	18.8	3.6

^{1/} Test terminated after 480 seconds when material did not ignite.

^{2/} Flame persisted less than 30 seconds after ignition occurred.

^{3/} Quadruplicate tests. ^{4/} Duplicate tests.

^{5/} A copolymer of butadiene, acrylonitrile, and styrene.

TABLE 4. - Combined nitrogen, expressed as nitrogen and as tetramethyl-succino-nitrile (TSN), evolved by heating 1.5-gram samples of FN-expanded polyvinylchloride to various temperatures in a stream of air.
(Air-flow rate, .100 ml. per minute)

Sample no.	Temperature, °C.	Duration of heating, hr.	Combined nitrogen, milligrams of nitrogen per gram of sample	Combined nitrogen expressed as TSN, per gram of sample	
				Milligrams	Milliliter ¹
1	25	8	0.000	0.00	0.00
2	75	6	.030	.15	.03
		6	.020	.10	.02
		Total 12	.050	.25	.05
3	150	6	.259	1.26	.22
		6	.227	1.10	.19
		Total 12	.486	2.36	.41
4	300	3.5	.791	3.84	.67
		4	.189	.92	.16
		6	.117	.57	.10
		6	.063	.31	.05
		6	.065	.32	.06
		6	.090	.44	.08
		6	.058	.28	.05
Total 37.5	1.373	6.68	1.17		

¹/ At 60° F. and 30 inches mercury pressure.

TABLE 5. - Hydrogen chloride evolved by heating samples of low-density cellular materials in a stream of air.
 (Duration of heating at each temperature - 3 hours;
 air flow rate - 100 ml. per minute)

Sample no.	Temperature, °C.	Weight loss, percent	Hydrogen chloride, per gram of sample	
			Milligrams	Milliliters ^{1/}
PN-expanded cellular polyvinylchloride				
1.....	160	1.7	0	0
2.....	180	4.0	0	0
3.....	190	9.8	16	10.4
4.....	200	25.6	122	79.1
5.....	250	45.8	269	174.3
UND-expanded cellular polyvinylchloride				
1.....	160	2.1	2	1.3
2.....	180	11.5	57	36.9
3.....	190	19.5	117	75.8
4.....	200	26.8	147	95.3
5.....	250	43.4	191	123.8
Cellular acrylonitrile hardboard				
1.....	160	0.3	0	0
2.....	180	1.0	0	0
3.....	190	1.4	0	0
4.....	200	2.8	0	0
5.....	250	10.1	0	0
6.....	270	14.6	Trace	Trace
7.....	300	20.1	Trace	Trace
Soft cellular polyvinylchloride (modified)				
1.....	160	3.3	0	0
2.....	180	13.4	30	19.4
3.....	190	14.1	42	27.2
4.....	200	22.5	68	44.1
5.....	250	24.5	65	42.1

^{1/} At 60° F. and 30 inches mercury pressure.

TABLE 6. - Ignition temperatures of low-density cellular materials

Material	Blowing compound	Ignition temperature, °C.
1. Cellular polyvinylchloride.....	PN	375
2. Cellular polyvinylchloride.....	UND	417
3. Cellular acrylonitrile hardboard.....	-	435
4. Soft cellular polyvinylchloride (modified)...	-	417

*Polyvinyl chloride
Foam Samples*

TABLE 2. - Composition of test chamber atmospheres, parts per million by volume.

Material	Carbon dioxide	Oxygen	Carbon monoxide	Hydrocarbons	Nitrogen	Aldehydes as H.CHO	Ammonia	Cyanides as HCN	Oxides of nitrogen as NO ₂	Hydrogen chloride	Chlorine and phosgene
12/	1,600	207,300	230	500	790,400	15	24	10	10	51	1/
	3,600	204,800	250	300	791,000	1	19	21	18	77	-
	3,500	204,100	400	400	791,600	1	32	27	15	229	1/
	3,200	203,900	340	400	792,200	5	31	27	9	204	-
22/	2,100	206,800	200	200	790,700	5	30	11	15	25	1/
	1,600	206,100	270	300	791,700	7	40	19	14	99	-
	1,500	207,700	270	0	790,500	8	43	13	10	70	1/
	1,700	208,000	270	0	790,000	6	42	16	9	78	-
33/	12,600	193,200	410	0	793,800	3	37	19	83	25	1/
	13,100	192,800	460	0	793,600	5	37	24	77	25	-
43/	3,900	203,300	330	200	792,300	0	18	16	16	25	1/
	3,700	203,500	320	400	792,100	0	19	17	16	25	-

1/ Absent by qualitative colorimetric test.

2/ Quadruplicate tests.

3/ Duplicate tests.

*Bureau of Mines
R14797 Jan 1951*

TABLE 3. - Volume of gases produced, milliliters at 60° F. and 30 inches mercury pressure. 1/

Material	Carbon dioxide		Carbon monoxide		Aldehydes		Ammonia		Cyanides		Oxides of nitrogen		Hydrogen chloride	
	Total	Per gm. weight loss	Total	Per gm. weight loss	Total	Per gm. weight loss	Total	Per gm. weight loss	Total	Per gm. weight loss	Total	Per gm. weight loss	Total	Per gm. weight loss
12/	400	345	57	49	3.7	3.2	6.0	5.2	2.5	2.2	2.5	2.2	13	11
	900	804	63	56	0.3	0.3	4.8	4.3	5.3	4.7	4.5	4.0	19	17
	900	549	100	61	0.3	0.2	8.2	5.0	6.9	4.2	3.8	2.3	59	36
	820	526	87	56	1.3	0.8	7.9	5.1	6.9	4.4	2.3	1.5	52	33
22/	530	609	51	59	1.3	1.5	7.6	8.7	2.8	3.2	3.8	4.4	6.3	7.2
	400	385	67	64	1.7	1.6	9.9	9.5	4.7	4.5	3.5	3.4	24	23
	370	374	67	68	2.0	2.0	11	11	3.2	3.2	2.5	2.5	17	17
	420	429	66	67	1.5	1.5	10	10	3.9	4.0	2.2	2.2	19	19
33/	3,170	1,149	100	36	0.8	0.3	9.3	3.4	4.8	1.7	21	7.6	6.3	2.3
	3,280	1,247	120	46	1.4	0.5	9.3	3.5	6.0	2.3	19	7.2	6.3	.4
43/	970	1,032	82	87	0	0	4.5	4.8	4.0	4.3	4.0	4.3	6.2	6.6
	920	968	80	84	0	0	4.7	4.9	4.2	4.4	4.0	4.2	6.2	6.5

1/ Calculated from volume of test chamber and concentration of constituent.

2/ Quadruplicate tests.

3/ Duplicate tests.

DISCUSSION OF RESULTS

Table 1, which gives results of flammability tests, indicates that materials 1 and 2 did not ignite in all instances, whereas materials 3 and 4 ignited in all tests. Partly responsible for this is the behavior of the materials when subjected to heat. Materials 1 and 2 quickly shrank, thus increasing the distance separating the specimen from the heater coil and the spark igniters. Materials 3 and 4 expanded considerably, allowing the specimen actually to contact the coil and igniters in some instances.

As shown in table 2, the concentrations of decomposition products in the atmospheres produced are rather low, particularly for the polyvinylchloride materials. Because of the low density of these materials only a small weight of sample was available for combustion. The heavier cellular acrylonitrile burned more vigorously, suffered more extensive decomposition, and produced higher concentrations of decomposition products.

The atmospheres produced by the PN-expanded polyvinylchloride materials were tested for nitrogen-containing gases other than hydrogen cyanide and ammonia. No significant quantity was detectable, hence TSN is not reported. It is possible that TSN is decomposed at the temperatures produced by the heater coil or in the flame during combustion and thus does not persist as such in the resultant atmosphere. Some incidental tests conducted to determine the decomposition temperature of pure TSN, although not entirely conclusive, indicated that when heated in vacuo to approximately 320° C., decomposition of the material became evident - evolution of gas and discoloration of the originally white crystals - but the extent of the decomposition was not determinable. The rate of decomposition appeared to be slow under the particular experimental conditions. At the still higher temperatures obtained in the flammability-test apparatus, the rate of decomposition would be enhanced.

The reported values for hydrogen chloride in the flammability tests probably are low, because some of it may have reacted with the walls and metal surfaces in the test chamber during heating and sampling periods.

Qualitative tests for chlorine and phosgene in the atmospheres produced by all materials were negative.

As indicated by the flammability tests, carbon monoxide was a major product of toxicologic importance for all materials, and for the polyvinylchloride materials carbon monoxide and hydrogen chloride predominated in this respect. The cellular acrylonitrile material produced somewhat greater quantities of oxides of nitrogen than the other materials. As pointed out previously, TSN was not detectable in the atmospheres produced in flammability tests of the PN-expanded material. TSN is liberated from this material at elevated temperatures, however, as shown in the following discussion.

Table 4 and figures 4 and 5 present data on the evolution of nitrogen-containing compounds expressed as combined nitrogen and as equivalent TSN. Figure 4 represents data from table 4 on the evolution of volatile nitrogen-containing compounds at various temperatures during tests under comparable

conditions. At room temperature, no evolved nitrogen-containing compounds were detectable under the described test conditions. At 75° C., small amounts of nitrogen-containing compounds were evolved. From 75° to 300° C., the amounts evolved increased almost uniformly with temperature.

It is pointed out that these tests indicate only the relative rates of evolution at various temperatures and do not represent total quantities that might be produced by more prolonged heating. Table 4 (sample 4) presents data, shown graphically in figure 5, on a sample heated to 300° C. for a total of 37-1/2 hours. Throughout the test, evolved nitrogen-containing compounds were collected over periods ranging from 3-1/2 to 6 hours. The amounts evolved during each period and the cumulative totals are shown in figure 5. Of the total obtained at this temperature during 37-1/2 hours, approximately 68 percent was evolved during the first 6 hours and 78 percent in the first 12 hours. The evolution then decreased to a low rather constant rate for the remainder of the test. Even after 37-1/2 hours, nitrogen-containing compounds still were detectable in the effluent gases. Such evolution curves probably are dependent on the test temperature and vary as the physical condition of the sample changes. At low temperatures, where the physical character of the material is changing very slowly, the rate of evolution is low. As the temperature is increased - particularly to the point where the polyvinylchloride itself begins to decompose - the physical character due to loss of plasticizer and decomposition changes much more rapidly, thus enhancing the rate of evolution of entrapped TSN.

The evolution of volatile, nitrogen-containing compounds by the PN-expanded material was not taken as conclusive evidence of the presence of TSN, even though information supplied by the manufacturer indicated that no nitrogen-containing ingredients other than PN had entered into formulation of the materials. X-ray diffraction examination of the material as received did not indicate the presence of TSN, but this result may have been due to the extremely small weight of the low-density material that could be utilized for X-ray diffraction examination and the state of fine subdivision of the TSN particles, if present as such in the material. However, a carbon disulfide extract of the foamed material and a solution of pure TSN in the same solvent exhibited light absorption at the same wave length in the infra-red region of the spectrum. Also, all lines of an X-ray diffraction pattern of crystalline material obtained by evaporation of a carbon disulfide extract of material No. 1 agreed with those of pure TSN.

Table 5 and curve A of figure 6 show data relative to the decomposition of the PN-expanded polyvinylchloride with evolution of hydrogen chloride. Incipient breakdown occurred near 190° C. Above 200° C., the rate of decomposition increased rapidly. It is pointed out that these tests indicate only relative evolution rates at various temperatures and do not represent total quantities that might be produced by more prolonged heating.

At temperatures above 190° C., hydrogen chloride from the PN-expanded polyvinylchloride material may become the decomposition product of major toxicological significance, because the quantities of hydrogen chloride evolved are much greater than those of nitrogen-containing compounds. Direct comparison of the two series of tests is difficult, inasmuch as the heating

periods for the hydrogen chloride tests were shorter than those for volatile combined nitrogen. However, by interpolation in figure 4 and from table 5, the following comparison may be drawn:

Temperature, °C.	Volume, milliliters at 60° F., 30 inches Hg.	
	TSN	Hydrogen chloride
200	0.41 (6 hr.)	79.1 (3 hr.)
	0.57 (12 hr.)	
250	0.60 (6 hr.)	147.3 (3 hr.)
	0.74 (12 hr.)	

Thus, at these temperatures the volume of hydrogen chloride evolved under the described test conditions was 200 to 300 times that of TSN vapor.

Although results of animal experiments to determine acutely toxic reactions of different materials may not be compared with mathematical accuracy, such experimentation yields information on the general order of the toxicity of the materials in question. Following are summarized data on the acute toxicity of TSN and of hydrogen chloride:

Material	Concentration, p.p.m. by volume	Exposure, hr.	Effect	Reference
TSN.....	60	2-3	Death	<u>25/</u>
Do.	31	3-7	do.	do.
Do.	15	8-23	do.	do.
Do.	8	20-24	do.	do.
Do.	5.5	31-46	do.	do.
Hydrogen chloride	4,350	1/2	do.	<u>26/</u>
Do.	675	6	do.	do.

The foregoing data indicate that the concentration of hydrogen chloride required to produce death after exposure of 6 hours is approximately 20 times the lethal concentration of TSN for exposures of about the same duration (3 to 7 hours). However, as the volume production of hydrogen chloride under certain test conditions was 200 to 300 times that of the assumed TSN, it appears that the greater hazard would be created by hydrogen chloride at elevated temperatures. In the range of temperatures at which both TSN and hydrogen chloride are liberated, the highly irritating properties of the latter gas would give warning of decomposition of the material and would cause persons to retreat, if possible, from the contaminated atmosphere. The foregoing discussion does not, of course, take into account the possibility of synergistic action with a combination of gases such as that produced by decomposition of the test material.

25/ Harger, R. N., and Hulpieu, H. R., Work cited in footnote 5.

26/ Machle, W., Kitzmiller, K. V., Scott, E. W., and Treon, F. J., The Effect of Inhalation of Hydrogen Chloride: Jour. Ind. Hyg. and Toxicol., vol. 24, 1942, pp. 222-224.

Table 5 and figure 6 present data obtained in 3-hour heating tests in which were determined weight loss and evolution of hydrogen chloride from the four subject materials. From the curves showing evolution of hydrogen chloride versus temperature, the approximate temperature of incipient breakdown of the materials may be determined. The cellular acrylonitrile material is not a polyvinylchloride type, and no appreciable quantity of hydrogen chloride was evolved.

Table 4 gives results of tests to determine ignition temperatures. The previously used method for determining ignition temperatures of thermosetting materials - by wrapping a thermocouple around the test specimen and heating it within the coil of the flammability test apparatus - was not suitable for these low-density cellular materials, because physical changes in the test pieces (shrinking and swelling) before ignition occurred caused the thermocouple to lose contact with the specimen, thus precluding true temperature readings.