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DECOMPOSITION TEMPERATURES
OF POLYTETRAFLUOROETHYLENE (TEFLON)
AND POLYMONOCHLOROTRIFLUOROETHYLENE
AS INDICATED BY HALOGEN LIBERATION

BY H. A. WATSON, H. J. STARK, L. E. SIEFFERT, AND L. B. BERGER

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

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H. A. Watson, ^{2/} H. J. Stark, ^{3/} L. E. Sieffert, ^{3/}
and L. B. Berger ^{4/}

CONTENTS

	<u>Page</u>
Introduction.....	1
Summary.....	1
Tests of polytetrafluoroethylene.....	2
Test procedure.....	2
Discussion of results of tests.....	4
Tests of polymonochlorotrifluoroethylene.....	4
Test procedure.....	4
Discussion of results of tests.....	4

^{1/} The opinions or assertions contained in this report are the private ones of the authors and are not to be construed as official or reflecting the views of the Department of the Navy, the Naval service at large, or the Department of the Interior.

^{2/} Chemist, Bureau of Mines, Pittsburgh, Pa.

^{3/} Materials engineer, Bureau of Ships, Navy Department, Washington, D. C.

^{4/} Acting chief, Health Branch, Bureau of Mines, Pittsburgh, Pa.

TABLES

	<u>Page</u>
1. Fluorine and equivalent hydrogen fluoride evolved by heating a 2-gram sample of polytetrafluoroethylene to various temperatures in a stream of moist air. (Air flow-rate, 100 ml. per minute. Duration of heating at each temperature, 3 hours.).....	3
2. Acid gases produced by heating 2-gram samples of polymonochlorotrifluoroethylene, grades 240, 270, and 300 NST, to various temperatures in a stream of moist air. (Air flow-rate, 100 ml. per minute. Duration of heating at each temperature, 3 hours.)..	5

ILLUSTRATIONS

<u>Fig.</u>		<u>Follows</u>
		<u>page</u>
1. Diagrammatic representation of apparatus used to determine gaseous products of thermal decomposition of polytetrafluoroethylene and polymonochlorotrifluoroethylene.....		2
2. Weights and volumes of hydrogen fluoride produced by heating 2 grams of polytetrafluoroethylene in a stream of moist air for 3 hours at each of the temperatures shown.....		2
3. Volumes of acid gases produced by heating 2 grams of polymonochlorotrifluoroethylene in a stream of moist air for three hours at each of the temperatures shown.....		4
4. Weights of acid gases produced by heating 2 grams of polymonochlorotrifluoroethylene in a stream of moist air for three hours at each of the temperatures shown.....		4

INTRODUCTION

Fluorine-containing polymers are comparatively new materials that exhibit very desirable characteristics not usually found in many non-fluorine-containing polymers. Among these characteristics are heat and flame resistance, desirable electrical properties, and chemical inertness. Polytetrafluoroethylene and polymonochlorotrifluoroethylene are examples of such polymers commercially available.

In practical applications it is reasonable to expect thermal decomposition of these materials if they are subject to high enough temperatures. The temperatures at which thermal decomposition takes place and the nature of the gaseous products of decomposition are considered pertinent data in intelligent use of these materials.

The purpose of the tests discussed herein was to determine: (1) The temperatures at which gases were produced when small specimens of the two polymers were heated and (2) determine the identity of the major constituents of the gaseous products.

No attempt is made to draw conclusions concerning the relative merits of one material over the other. Also, no attempt is made to express the results in terms of health hazards relating to toxicity of any of the products of thermal decomposition. The matter of possible toxic hazards in connection with the use of organic polymers must be studied carefully in terms of operating requirements and conditions involved in each specific application.

Results of tests with the two types of material are presented and discussed separately. In general, the same test procedure was employed in all experiments.

SUMMARY

1. Under the test conditions described, polytetrafluoroethylene liberated fluorine when heated to 350° C. or higher, the rate of evolution showing a sharp increase between 400° and 450° C. Under practical conditions of use, the gaseous product of decomposition of this material may be considered as hydrogen fluoride, because the evolved fluorine would react immediately with atmospheric moisture.
2. Under the described test conditions, three grades of polymonochlorotrifluoroethylene - 240, 270, and 300 NST - liberated fluorine and chlorine at temperatures above 250° C., the rate of evolution increasing markedly above 300° C. At the highest test temperatures - 325° - 328° C. - these gases were evolved in quantities proportional

to the molecular composition of the polymer; at lower temperatures, chlorine appeared to be detached more readily from the molecule. Under practical conditions of use, the decomposition products of this material may be considered as consisting mainly of hydrogen fluoride and hydrogen chloride, as the evolved fluorine and chlorine would react with atmospheric moisture.

TESTS OF POLYTETRAFLUOROETHYLENE

Test Procedure

According to available information^{5/6/7/} polytetrafluoroethylene may liberate the monomer, tetrafluoroethylene, when heated to high temperatures and, under some conditions, carbon tetrafluoride. Preliminary tests of the material by the Bureau of Mines indicated also that fluorine was liberated by the material when heated sufficiently. Accordingly, the liberation of fluorine was chosen as indicative of significant thermal decomposition.

The apparatus, shown diagrammatically in figure 1, was used to determine the evolution of fluorine by the material at elevated temperatures. A weighed portion of the specimen (2 grams, cut into 1/16-inch cubes) was introduced into the glass bulb A that was surrounded by an aluminum block B, which, in turn, was enclosed in an electric furnace C. Moist air was passed through flowmeter D at 100 ml. per minute, over the heated specimen in A, and thence through the bubbling type gas absorbers E. Temperature of the furnace and aluminum block was maintained at the desired level by means of a thermocouple inserted into the block, recording potentiometer, and a variable-coupling transformer in the power input line to the furnace. Experiments were conducted at 210, 300, 350, 400, and 450° C.; and the specimen was maintained at each temperature for 3 hours. The glass bulb A, figure 1, was removed and weighed at the conclusion of each heating interval to ascertain weight loss.

Acid gases given off by the material were absorbed in a 0.05 N sodium carbonate solution contained in the bubblers. At the conclusion of an experiment, this solution first was back-titrated with 0.05 N hydrochloric acid to determine total acid absorbed, and next with 0.05 N thorium nitrate solution to determine fluoride, according to the method of Matuszak and Brown.^{8/} Unless the polymer contained elements other than carbon and fluorine as impurities, this method may be considered specific for fluoride ion.

^{5/} Information supplied by manufacturer of the polymer.

^{6/} Renfrew, M. M., and Lewis, E. E., Polytetrafluoroethylene. Heat-Resistant, Chemically Inert Plastic: Ind. and Eng. Chem., vol. 38, 1946, pp. 870-877.

^{7/} Fisher Scientific Company, Recent Advances in Fluorine Chemistry: The Laboratory, vol. 16, No. 5, 1947, pp. 122-126. (Article based upon information supplied by manufacturers of fluorine chemicals.)

^{8/} Matuszak, M. P., and Brown, D. R., Thorium Nitrate Titration of Fluorides: Ind. Eng. Chem., Anal. Ed., vol. 17, 1945, pp. 100-106.

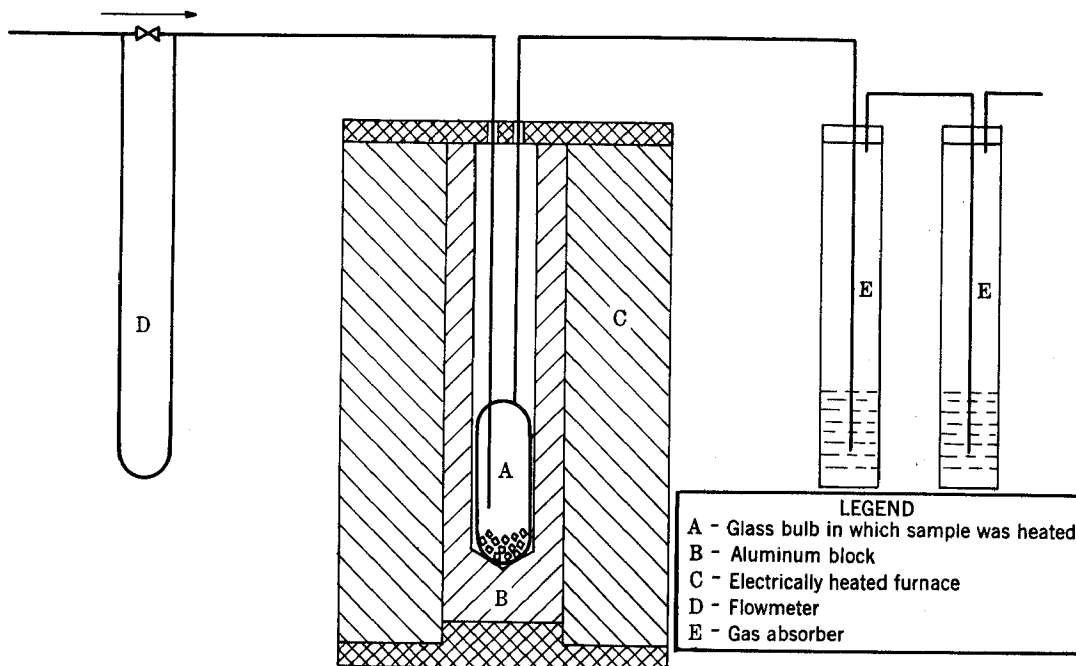


Figure 1. - Diagrammatic representation of apparatus used to determine gaseous products of thermal decomposition of polytetrafluoroethylene and polymonochlorotrifluoroethylene.

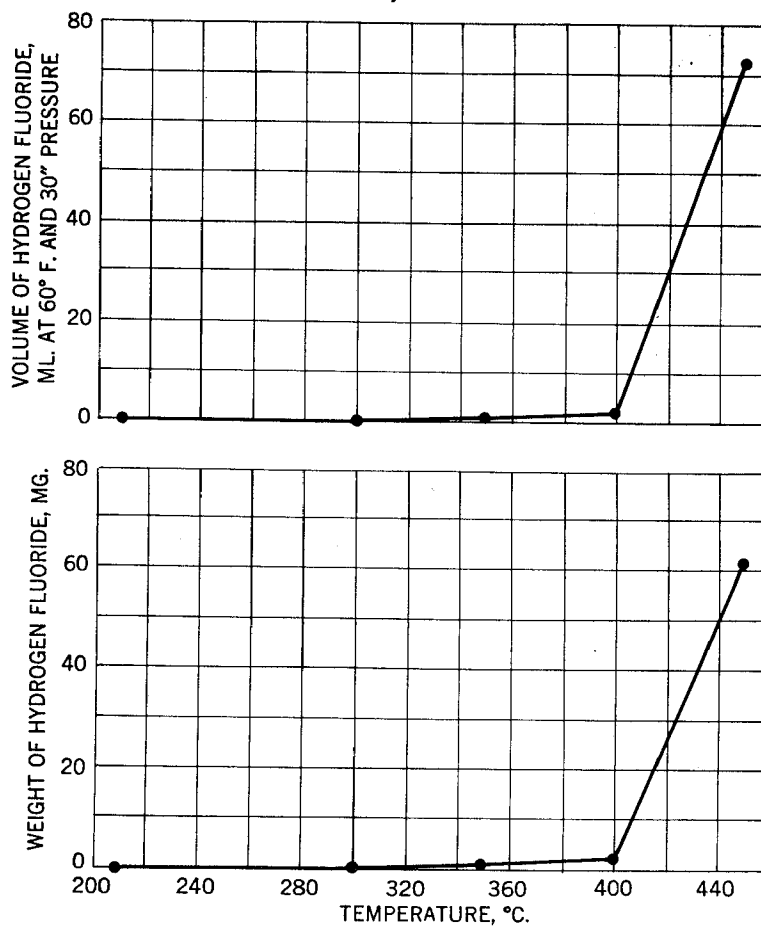


Figure 2. - Weights and volumes of hydrogen fluoride produced by heating 2 grams of polytetrafluoroethylene in a stream of moist air for 3 hours at each of the temperatures shown.

TABLE 1. - Fluorine and equivalent hydrogen fluoride evolved by heating a 2-gram sample of polytetrafluoroethylene to various temperatures in a stream of moist air. (Air-flow rate, 100 ml. per minute. Duration of heating at each temperature, 3 hr.)

Test No. (1)	Temperature, °C. (2)	Weight loss, mg. (3)	Total acid determined, expressed as mg. of fluorine ¹ (4)	Fluoride determined, expressed as mg. of fluorine (5)	Equivalent hydrogen fluoride produced, based upon average of col. 4 and 5. Mg. (6)	ML.2/ (7)
1	210	0.0	0.00	0.00	0.00	0.00
2	300	.8	.00	.00	.00	.00
3	350	.0	.13	.10	.13	.15
4	400	2.5	1.35	1.43	1.47	1.73
5	450	125.3	57.0	59.0	61.1	72.2

¹/ The expression of total acid in terms of fluorine is based upon the assumption that all acid determined is hydrofluoric acid.

²/ At 60° F., and 30" Hg pressure.

Discussion of Results of Tests

Results of tests conducted in the described manner are given in table 1. As shown in the table, the quantities of fluorine liberated by the material are in close agreement at any given temperature, whether determined as fluorine (column 5), or whether determined as acid assumed to be hydrofluoric acid (column 4). This is substantial evidence that fluorine is the source of all acid gas evolved by the material. In a stream of moist air the liberated fluorine is converted immediately to hydrofluoric acid and is absorbed as such by the alkaline medium in the bubblers. Evolution of fluorine became evident at 350° C., as shown in table 1 (columns 4 and 5), by the sensitive chemical methods, and evolution of gas by the material 400° C., is shown definitely by weight-loss (column 3). Because of the reactivity of fluorine with moisture and in relation to practical applications of the material in situations where it would be in contact with atmospheric moisture, hydrofluoric acid may logically be considered the decomposition product rather than fluorine. Evolution of fluorine, in terms of hydrogen fluoride, by the material at different temperatures (columns 6 and 7) is shown graphically on weight and volume bases in figure 2.

It is pointed out that the described test procedure produced results indicative only of the relative rates of evolution of fluorine by the material at different temperatures. The results probably do not represent the total quantity of fluorine that might be liberated on more prolonged heating at any temperature at which decomposition takes place.

TESTS OF POLYMONOCHLOROTRIFLUOROETHYLENE

Test Procedure

Three grades of polymonochlorotrifluoroethylene were examined: 240, 270, and 300 NST.^{9/} Test equipment and procedure were essentially the same as employed in the tests of polytetrafluoroethylene previously described. Tests were conducted at nominal temperatures of 160°, 200°, 250°, 300°, and 325° C. Evolved acid gases were absorbed in an excess of 0.05 N sodium carbonate solution. Total acid gases absorbed were determined by titrating the unreacted sodium carbonate with 0.05 N hydrochloric acid. Fluorides were determined by titration with 0.05 N thorium nitrate.^{10/}

Discussion of Results of Tests

Results of tests with the polymonochlorotrifluoroethylene materials are given in table 2 and shown graphically in figures 3 and 4. Acid gases evolved under the test conditions were calculated as equivalent hydrogen fluoride and hydrogen chloride, as shown in table 2 (columns 6, 7, 8, and 9), because, under practical conditions of use, it may be assumed that liberated fluorine and chlorine would react with atmospheric moisture to form the acids, as discussed previously in connection with the tests of polytetrafluoroethylene.

^{9/} The NST, or No-Strength Temperature, is the temperature, in degrees centigrade, at which a test strip of specified dimensions has no strength under a slight tensile load applied in a specified manner.

^{10/} Matuszak, M. P., and Brown, D. R., Work cited in footnote 8.

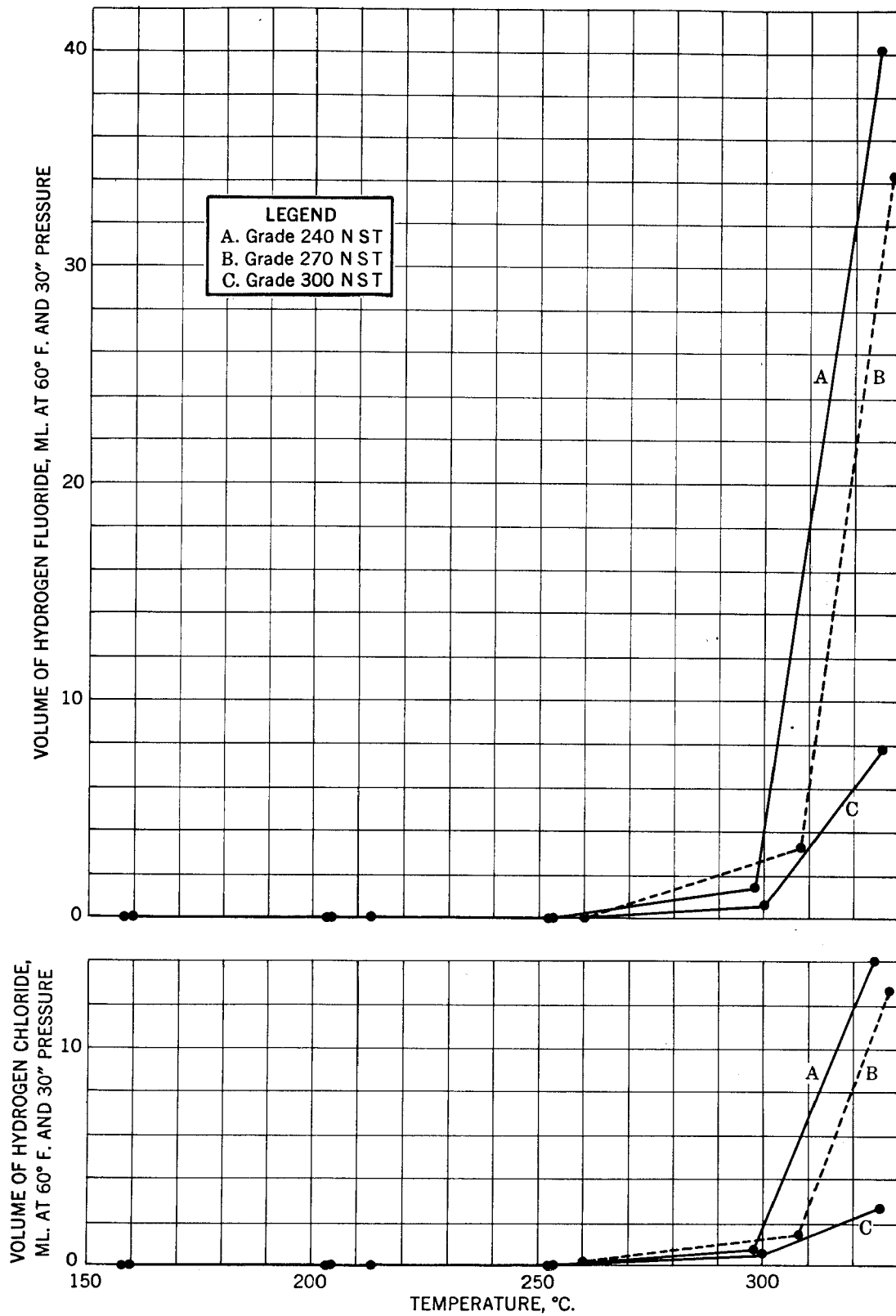


Figure 3. - Volumes of acid gases produced by heating 2 grams of polymonochlorotrifluoroethylene in a stream of moist air for 3 hours at each of the temperatures shown.

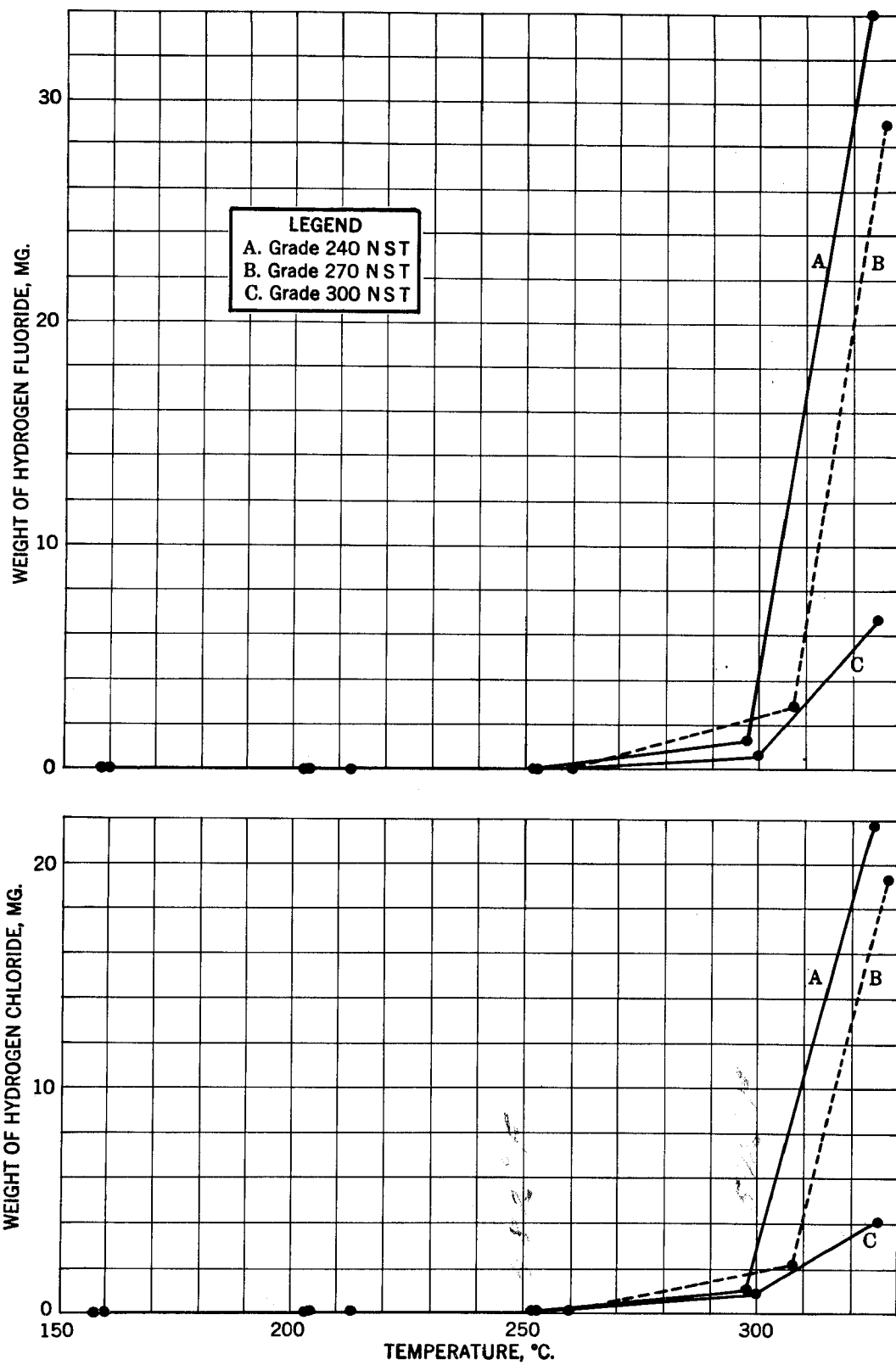


Figure 4. - Weights of acid gases produced by heating 2 grams of polymonochlorotrifluoroethylene in a stream of moist air for 3 hours at each of the temperatures shown.

TABLE 2. - Acid gases produced by heating 2-gram samples of polymonochlorotrifluoroethylene, grades 240, 270, and 300 NST, to various temperatures in a stream of moist air. (Air-flow rate, 100 ml. per minute. Duration of heating at each temperature, 3 hr.)

Test No. (1)	Temperature, °C. (2)	Weight loss, mg. (3)	Fluoride determined, expressed as mg. of fluorine (4)	Acid gases other than hydrogen fluoride, expressed as mg. of chlorine (5)	Fluoride determined, expressed as hydrogen fluoride ^{1/}		Acid gases other than hydrogen fluoride, expressed as hydrogen chloride ^{2/}	
					Mg. (6)	Ml. (7)	Mg. (8)	Ml. (9)
1	158	0.0	0.00	Grade 240 NST	0.00	0.00	0.07	0.05
2	203	.0	.01	.04	.01	.01	.04	.03
3	252	.6	.03	.12	.03	.04	.12	.08
4	298	6.2	1.22	1.01	1.29	1.52	1.04	.67
5	325	167.8	32.3	21.1	34.0	40.2	21.7	14.0
6	160	0.0	0.00	Grade 270 NST	0.00	0.00	0.00	0.00
7	213	.1	.01	.06	.01	.01	.06	.04
8	260	.6	.04	.14	.04	.05	.14	.09
9	308	12.2	2.69	2.11	2.84	3.35	2.16	1.40
10	328	138.4	27.6	18.7	29.0	34.3	19.2	12.5
11	158	0.0	0.00	Grade 300 NST	0.00	0.00	0.05	0.04
12	204	.0	.00	.09	.00	.00	.09	.06
13	253	1.1	.04	.13	.04	.05	.13	.09
14	300	3.7	.54	.84	.57	.66	.86	.56
15	301	3.5	.59	.79	.63	.74	.81	.53
16	326	156.7	6.33	3.89	6.66	7.87	4.00	2.59

^{1/} Fluoride determined directly by thorium nitrate titration expressed as hydrogen fluoride.

^{2/} Acid gases other than hydrogen fluoride were determined by difference and expressed as hydrogen chloride. This may not be strictly accurate, as other chlorine-containing acids may have been present.

^{3/} At 60° F. and 30" Hg pressure.

As polymonochlorotrifluoroethylene contains 3 atoms of fluorine per atom of chlorine, it might be anticipated that these gases would be liberated in such proportions upon thermal decomposition of the polymer. From table 2 it may be noted (columns 7 and 9), in respect to tests 5, 10, and 16, in which experimental variations were at the minimum due to quantity of substance determined, that the volume ratio of hydrogen fluoride to other gases calculated as hydrogen chloride is approximately of this order. However, in test 10 a direct gravimetric determination of chlorides by precipitation of silver chloride indicated somewhat less than the calculated equivalent of hydrogen chloride, which may indicate that some amount of chlorine-containing acids that do not form precipitates with silver nitrate was produced. The apparent predominance of acid gases other than hydrogen fluoride at the lower test temperatures may indicate that chlorine is detached from the molecule more readily than fluorine at such temperatures.

As shown in table 2, significant decomposition of the three grades of polymonochlorotrifluoroethylene, as evidenced by weight loss and evolution of acid gas, did not occur until the test temperatures exceeded 250° C., from which temperature the decomposition rate increased slowly until, when over 300° C., it increased markedly. Data obtained at the highest test temperature, 325-328° C., indicate that the decomposition rate for grade 270 NST and the decomposition rate for grade 300 NST is appreciably less than that for the other two materials.

It is pointed out that the test procedure described produced results indicative only of the relative rates of evolution of fluorine and chlorine (and the products of their immediate reactions with moisture) by the materials at different temperatures. The results probably do not represent the total quantities of fluorine and chlorine that might be liberated on more prolonged heating at any temperatures at which decomposition takes place.