

**AN INVESTIGATION OF THE RELATIVE DETERIORATION  
TEMPERATURES AND HYDROGEN CHLORIDE EVOLUTION OF  
CHLORINATED JACKET COMPOUNDS BY MEANS OF THERMAL  
GRAVIMETRIC ANALYSIS AND DIFFERENTIAL THERMAL ANALYSIS**

**Report No. B902**

**BOSTON  
INSULATED  
WIRE & CABLE CO.**

**65 BAY STREET  
BOSTON, MASSACHUSETTS 02125**



8202090373 820204  
PDR ADOCK 05000286  
P PDR

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## I. INTRODUCTION

The destruction by fire of a reinforced concrete German plastics plant, where large quantities of polyvinyl chloride (PVC) were stored, prompted this Boston Insulated Wire & Cable Co. (BIW) research project. The aftermath of the fire, which revealed that the steel reinforcing rods were corroded, caused BIW engineers to wonder what would happen to BIW cable compounds when subjected to fire and water or steam. They engaged the services of Arthur D. Little, Inc., a prominent consulting firm, to assist in a total evaluation.

It was found that a rapid increase in the evolution of hydrogen chloride (HCl) gas occurs alike in PVC and BIW compounds of neoprene and chlorosulphonated polyethylene (CSPE) between 300°C and 350°C, with a gradual lessening at temperatures above 350°C. Above this temperature, however, the BIW neoprene compound evolves about one-half as much HCl gas as PVC, and the BIW CSPE compound evolves only about one-fifth as much HCl gas as PVC. The relative hazard of corrosion from similar quantities of BIW neoprene compound and BIW CSPE compound is less than from PVC, and BIW CSPE compound is less hazardous than neoprene. All three materials are very stable to HCl liberation at the normal-rated temperature of about 100°C and also through the maximum temperature range of 150°C, which may be encountered during an incident.

The ultimate effect of these gases and the corrosive effect of hydrochloric acid, which would be promptly formed in the case of fire extinguished by water or in the presence of steam, is open to question. Concrete is a material which would neutralize the HCl before it could reach the reinforcing rods unless a continually large volume of HCl were concentrated in a particular area of concrete.

It should be pointed out that these results are derived from representative BIW and commercial compounds, that a number of assumptions have had to be made in the calculations and that the conditions of temperature rise are arbitrary, i.e., from room temperature to 400°C in one-half hour.

This report, therefore, can be taken as an initial step in the analysis of the hazards which might be present with the adoption of flameproof cable-jacketing materials.

## II. CHOICE OF MATERIAL

Chlorinated polymers are required in jacketing materials when cables are to be exposed to oil and must be flame and radiation resistant. It is recognized that many other compositions of cable jackets are now in use, and this should be the basis for further study. However, this report concerns itself only with compounds incorporating chlorine for flame resistance in their molecules when subjected to temperatures high enough to cause thermal decomposition of these polymers.

The most generally accepted chlorinated compound cable constructions are:

- PVC . . . . . as insulation  
as jacket over insulation  
as jacket of cable
- Neoprene . . . . . as jacket over insulation  
as jacket of cable
- CSPE . . . . . as insulation  
as jacket over insulation  
as jacket of cable

Therefore, two BIW compounds and one purchased compound were taken as the basis for this study, and the following results are derived from these representative compounds.

## III. OBJECTIVE

The objective of this investigation is to determine the decomposition temperatures and relative amounts of HCl gas evolved from the decomposition of PVC, CSPE and neoprene. Typical BIW and commercial compounds were used at temperatures from 15°C to 400°C.

The compounds used were:

- PVC . . . . . purchased 90°C appliance-wire compound.
- Neoprene . . . . . BIW-SOX . . . heavy-duty neoprene jacket.
- CSPE . . . . . BIW BOSTRAD<sup>7</sup> heat and radiation-resistant.  
compound for nuclear power plants.

#### IV. PROCEDURE

Approximately 17 milligrams of each material was exposed to thermal analysis and close examination was made of the corrosive gases (HCl) evolving at particular temperatures.

1. Thermogravimetric Analysis (TGA) reveals the continued change in weight during heating period.
2. Differential Thermal Analysis (DTA) measures the thermal changes of each sample with increasing temperature and determines the temperature at which these compounds become exothermic.
3. Continual monitoring of the acidity (pH) values of the evolved gases during the thermal cycle (TGA) which determines the relative amount of gases which dissolve in water, with the assumption that the pH changes are derived from HCl gas. The evolved gases were bubbled through distilled water and the pH of the water was taken as the material reached the following temperatures:

Every 50°C up to 200°C,

Every 25°C from 200°C to 300°C,

Every 5°C from 300°C to 350°C, and

At 375°C, and at 400°C.

In order to arrive at some relative values of HCl evolved, a curve of pH vs. normality of HCl was plotted, using data from page 1721 of the 1958-59 edition of the "Handbook of Chemistry and Physics," and extrapolated to a pH of 6.

In all cases, the evolved gases were bubbled through 50 milliliters of distilled water (and here we must assume 100% solution of the HCl gas). A reasonable assumption is that a conversion of pH to per cent HCl evolved from the gas can be made.

## V. RESULTS

1. GRAPH A . . . the results of the TGA up to temperatures of 475°C indicate that there is only slight weight loss up to 300°C. Above 350°C, CSPE has slightly less weight loss than neoprene, and both have considerably less than PVC. At 475°C, the per cent weight losses were as follows:

CSPE (BOSTRAD <sup>7</sup> )	= 35%
Neoprene (BIW-SOX)	= 39%
PVC	= 62%

It is possible that the weight loss of neoprene may be overshadowed by its rapid oxygen absorption at these temperatures.

2. GRAPH B . . . The results of the DTA indicate that all three materials become exothermic at approximately 250°C, which is indicative of decomposition. The sharp rise in the curve with neoprene and the dip in the curve with CSPE, in the temperature range from 300°C to 350°C, is not easily explained. One possible explanation is that, in neoprene, oxidation first exhibits itself by a lowering of elongation and an increase, or a very slight change, in tensile strength. (This is quite similar to what happens in the vulcanization process, which is an exothermic process.) This cross-linking process, due to oxidation, is probably more exothermic than chain scission and results in a decrease in the length of the polymer chain which follows this high rise. CSPE is more stable to oxidation in this temperature range and may become endothermic due to evaporation of volatile materials in the compound.

From this data, the conclusion may be drawn that jackets of CSPE compound are better than neoprene and possess about the same degree of stability as PVC jackets from the aspect of thermal degradation due to overheating up to 400°C.

3. The results of the analysis of the decomposition gases by measuring the pH of the solution, through which the HCl gas passes during the heating periods, are shown in the following graphs:

GRAPH C . . . plots the pH of the solutions as observed for the three materials over the temperature range to 400°C.

GRAPH D . . . plots the pH vs. normality of hydrochloric acid for use in computation of the amount of HCl gas evolved. The extrapolation to an original pH of 6 was necessary as the initial values of pH were noted as 5.8 - 5.9.

An example of the calculation of the per cent HCl gas by weight from a specimen follows:

Material . . . PVC  
 Temperature . . . 350°C  
 pH of Solution at 350°C = 2.85 (Graph C)  
 Normality of HCl corresponding to a pH of 2.85 = .00135 (Graph D)  
 Molecular weight of HCl = 36.47  
 Concentration of HCl per liter of water at pH of 2.85 = .00135 x 36.47 = .0482 grams per liter

Since 50 milliliters of water were used in the test:

$$\text{HCl evolved} = .0482 \times \frac{50}{1000} = .00241 \text{ grams} \\ \text{2.41 milligrams}$$

Original weight of PVC = 16.82 milligrams

$$\text{Per cent HCl evolved is } \frac{2.41}{16.82} = 14.3\%$$

GRAPH E . . . portrays the percentages of the three materials calculated in this manner over the temperature range to 400°C. The actual calculated values and the relationship of one material to another are as follows:

#### PERCENTAGE OF EVOLVED HCl

°C	CSPE	Neoprene	PVC
150	0	0	0
300	.15%	.10%	3.6%
350	2.7%	7.6%	14.3%
400	3.2%	8.7%	16.3%

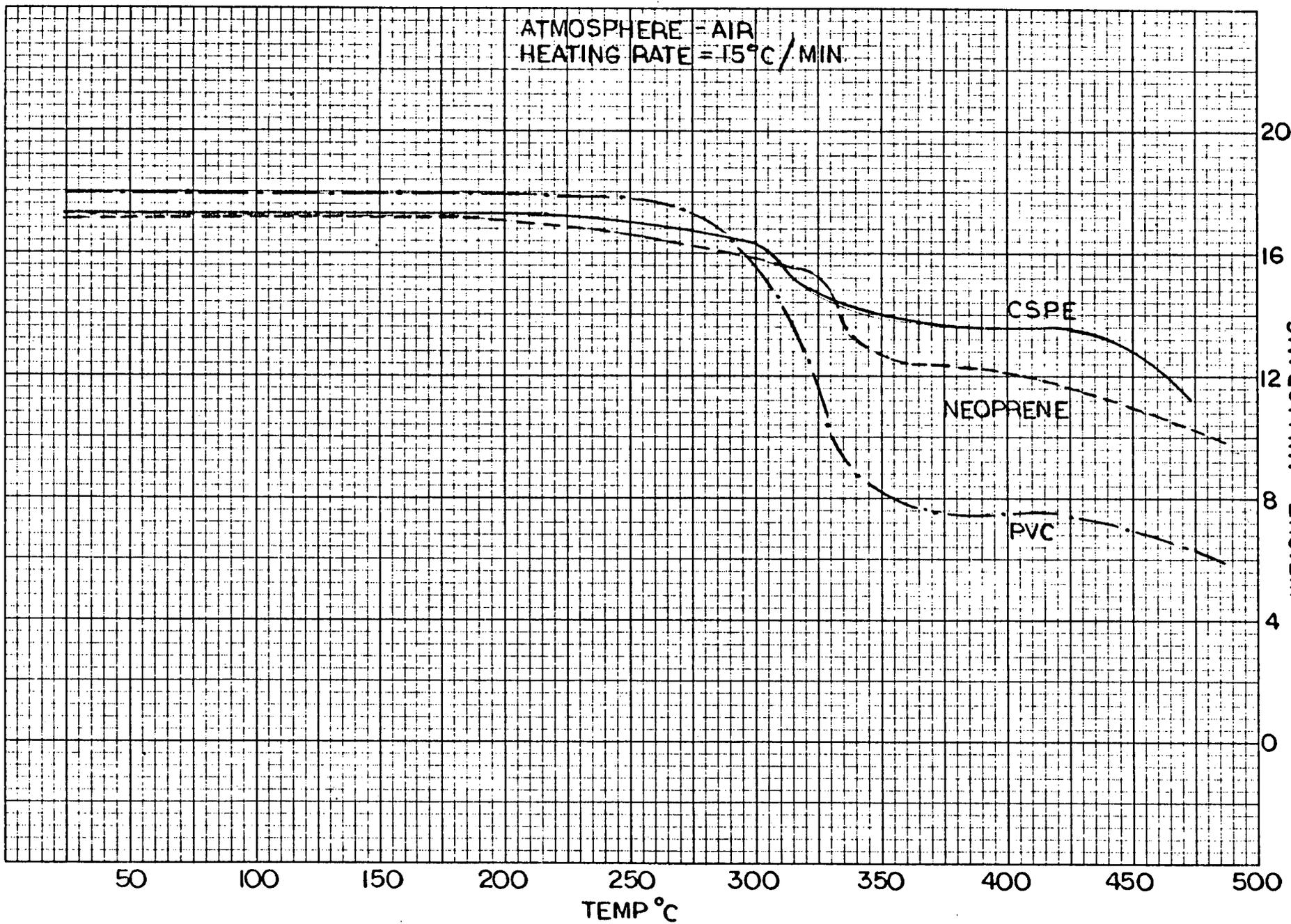
  

°C	CSPE Relative to Neoprene	CSPE Relative to PVC	Neoprene Relative to PVC
150	0	0	0
300	0	4%	3%
350	35%	19%	53%
400	37%	20%	53%

# THERMAL GRAVIMETRIC ANALYSIS

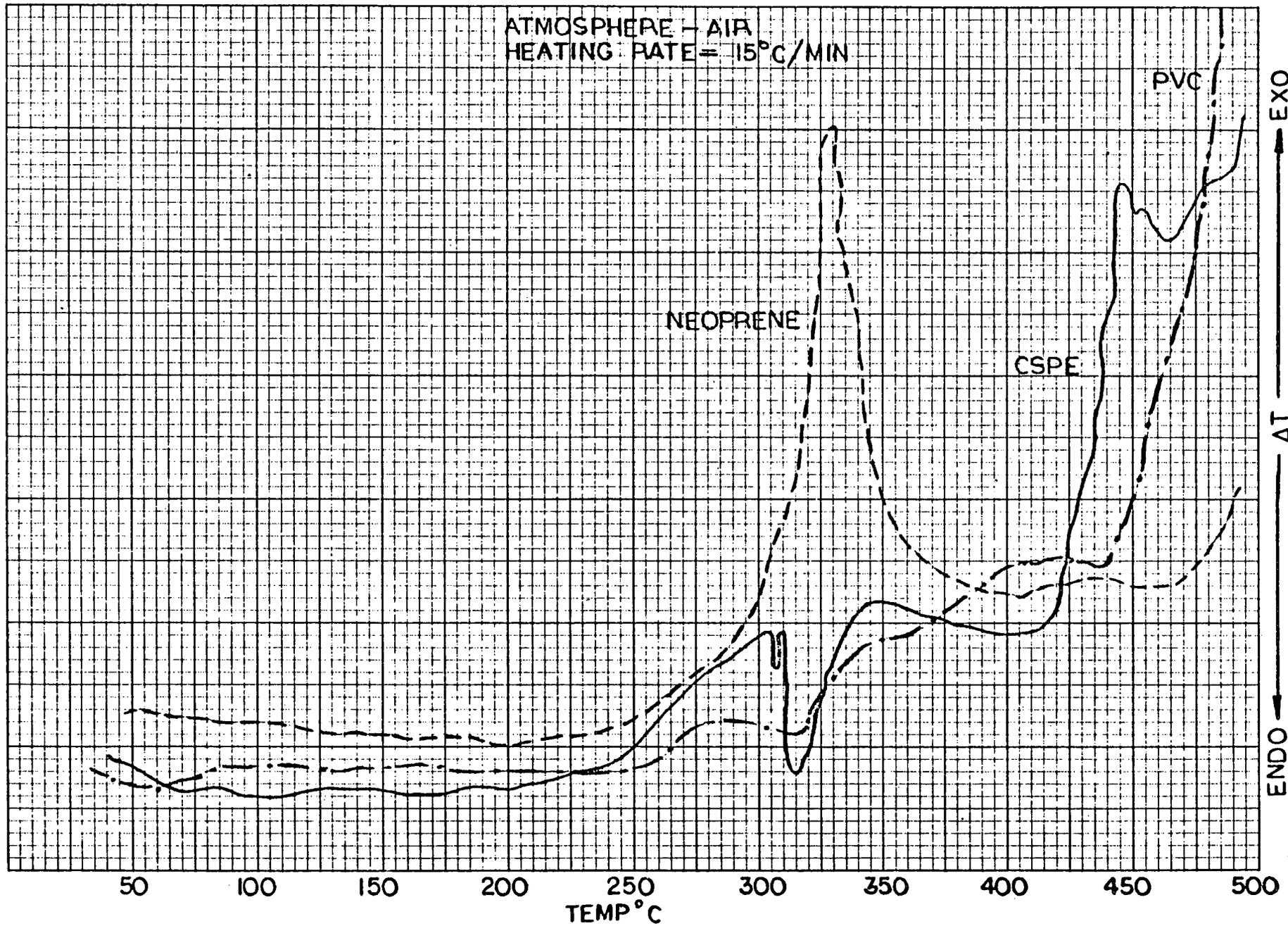
ATMOSPHERE = AIR  
HEATING RATE = 15°C/MIN

GRAPH A

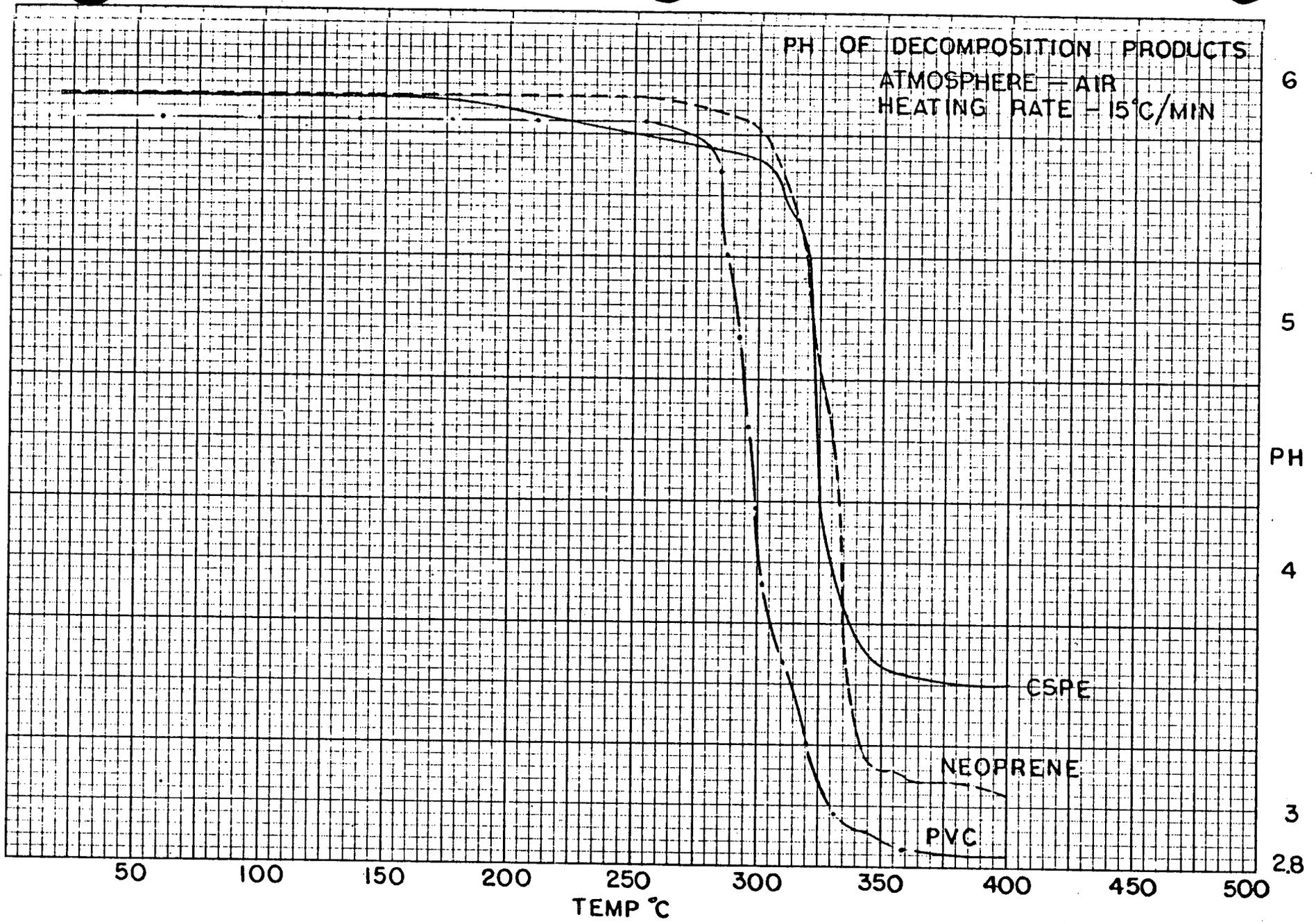


# DIFFERENTIAL THERMAL ANALYSIS

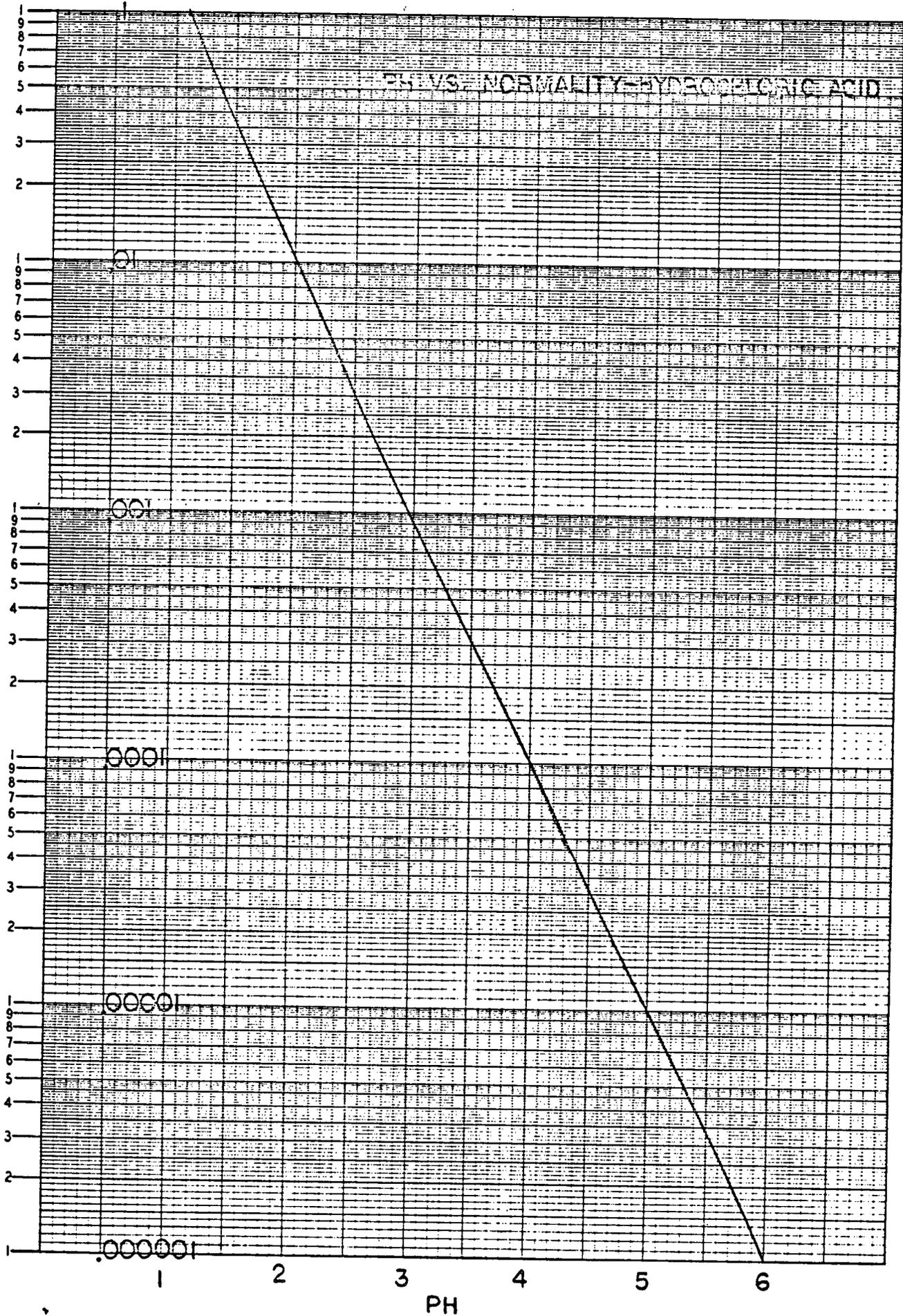
GRAPH B



GRAPH C



# GRAPH D



# GRAPH E

PERCENT BASED ON ORIGINAL  
WT. OF POLYMER OF HCL FORMED  
FROM EVOLVED GASES.

