COAL MINE COMBUSTION PRODUCTS IDENTIFICATION AND ANALYSIS

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ULTRASYSTEMS, INC.

USBM CONTRACT ANNUAL REPORT
CONTRACT No. H0133004

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DEPARTMENT OF THE INTERIOR
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FOREWORD

This report was prepared by Ultrasystems, Inc., Chemicals and Materials Research Department, Irvine, California, under USBM Contract No. HO133004. The investigations were performed by K. L. Paciorek, program manager, R. H. Kratzer, J. Kaufman, and J. H. Nakahara. The contract was initiated under the Coal Mine Health and Safety Research Program. It was administered under the technical direction of the Pittsburgh Mining and Safety Research Center with Dr. A. M. Hartstein acting as the technical project officer. Mr. A. L. Metheny was the contract administrator for the Bureau of Mines.

This report is a summary of the work recently completed as part of this contract during the period 8 July 1972 to 8 August 1973. This report was submitted by the authors on 31 August 1973.

In view of the analytical nature of the work performed no subject inventions were made under this program.

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1.0 ABSTRACT AND SUMMARY

The aim of the present study is to determine on a gram per gram basis the toxic products of the thermal oxidative degradations of selected compositions. Four families of materials were investigated under the subject contract namely polyvinyl chloride and neoprene compositions, rigid urethane foams, and woods.

Three methods were employed to conduct the thermal oxidative degradations: a sealed system (quiescent environment), a stagnation burner arrangement (dynamic environment), and a flow-through apparatus (dynamic, but less severe than stagnation burner conditions). The majority of tests were conducted using the first two systems; only limited experiments were carried out employing the third decomposition procedure. All decomposition was done at temperatures of 370 - 400°C, the higher temperature being used in the stagnation burner. It has to be stressed that the nature of the products and the relative product concentration are temperature dependent.

Thermogravimetric and differential thermal analyses were performed to supplement and extend the above delineated studies and to explore the feasibility of using these analyses as a method for material differentiation.

The only decomposition products identified and determined were the substances volatile at room temperature, although limited work was done on the involatile fractions, e.g., oils and tars. The analytical methods employed were vacuum line fractionations, gas chromatography, infrared spectroscopy, mass spectrometry, wet analyses, and ion specific electrode measurements. To identify and quantitate the toxic ingredients it was necessary to analyze all the species produced. In the stagnation burner degradations the materials volatile at liquid nitrogen temperature (CO, H_2, CH_4, NO) were not determined.

Four neoprene compositions were investigated, namely uncured gum, a known cured sample and two materials from actual articles used in mines. The main toxic constituent formed was hydrogen chloride; in the case of the uncured material and the known cured composition (sealed system) it amounted to 76 and 78% respectively of the total chlorine present. The first weight loss observed in the thermogravimetric analysis of these four compositions corresponded closely to the hydrogen chloride found. The other toxic ingredients identified and quantitatively determined were carbon monoxide, chloroprene, carbon disulfide, sulfur dioxide, hydrogen sulfide, acetic acid, and formic acid. Formaldehyde, acrolein, mercaptans, and benzyl chloride were tentatively identified, but not quantitated. The relative product mix found was different in the sealed tube and stagnation burner studies, in particular in the instances when glow occurred. Under this condition an increase was noted in the production of oxygenated species (CO_2, SO_2, COS), whereas the formation of materials such as, e.g., chloroprene and carbon disulfide was decreased. It should be noted that during product separation hydrogen chloride did condense with (dissolve in) water to a certain extent, whereas hydrogen sulfide, due to its lesser affinity for water, never did. This indicates that hydrogen sulfide, under certain conditions, may present a greater hazard than hydrogen chloride, even if formed in smaller quantities, in particular at locations removed from the immediate disaster area.

Five polyvinyl chloride compositions and a "virgin" PVC resin were investigated. A number of these compositions were nylon reinforced. The presence of nylon was emphasized by the detection of large quantities of both saturated and unsaturated C_6-species. The product mix obtained under the quiescent and dynamic conditions was fairly comparable due to the absence of glow. As in the case of neoprenes, except to an even higher degree, hydrogen chloride was the main toxic compound formed. The first weight loss observed during thermogravimetric analysis (TGA) corresponded

only in the case of "virgin" resin to the quantity of hydrogen chloride evolved. In all other instances the observed weight loss was much higher than the amount of hydrogen chloride measured, which indicates simultaneous decomposition and/or evaporation of the materials added to the "virgin" PVC resin in the finished articles. Yet, the TGA curves were sufficiently different from those obtained from the neoprene based materials to allow definite differentation between the two material families.

Next to hydrogen chloride benzene was the most toxic species formed in the sealed tube studies, not carbon monoxide. In the majority of samples traces of sulfur dioxide were observed, derived most likely from polymerization initiators and antioxidants. Other toxic compounds found were benzyl chloride, formic and acetic acids; formaldehyde and acrolein were only tentatively identified. It should be added that the relative concentration of the chlorinated compounds formed, believed to originate from the PVC component of the given material, is strongly dependent on the other ingredients present in the composition. From the nonvolatile fractions phthalic anhydride was isolated. It is noteworthy that it was formed predominantly in the sealed system, whereas in the stagnation burner studies the phthalate esters constituted the major portion of the room temperature involatile oils (volatile at 400^{o}C).

Three urethane foams were subjected to sealed tube degradations. Two of these appeared to be of an identical composition. Aniline, chloroethanol, ammonia, and benzene accompanied by small quantities of formic acid, acetic acid, and hydrogen cyanide were the toxic agents produced by the two apparently identical urethane foams. In addition, these formed a variety of chlorinated compounds. The third urethane foam produced carbon monoxide, acetic acid, traces of benzene and formic acid as the toxic species to be concerned with. The main products from this foam were chlorinated, brominated, and chlorobromo compounds, all of unknown toxicity. The

TGA curves of all three urethane foams showed them to be of a lower thermal stability than that usually associated with rigid foams.

Two untreated and four impregnated standard southern yellow pine samples were investigated using the quiescent and dynamic conditions. Three samples were treated with preservatives namely pentachlorophenol creosote and CCA and one sample was treated with a fire retardant, Minalith. Based on DTA and TGA data the Minalith treatment affected most drastically the thermal oxidative behavior of the pine; significantly lesser effects were observed for the other impregnations. In the stagnation burner the untreated pine, the chlorophenol and CCA impregnated materials glowed. In all the instances, with the exception of the Minalith treated material, substantial amounts of tars were afforded. The latter sample was found to form the highest quantity of carbon monoxide which was accompanied by sulfur dioxide and hydrogen cyanide. In the quiescent system sulfur dioxide presented a greater toxicity hazard than carbon monoxide. Some hydrogen chloride was found amongst the products from pentachlorophenol containing pine. Pentachlorophenol and creosote are oil based preservatives; not surprisingly, relatively high toluene concentrations were found in the volatiles produced by pines impregnated with these materials. The toxic species formic acid, formaldehyde, acetic acid, acrolein and furfural were identified and quantitated for all the woods studied. The largest quantity of formaldehyde was afforded by the CCA impregnated pine.

2.0 INTRODUCTION

The results of Contract No. HO122009, "Coal Mine Combustion Products--Identification and Analysis," show that practically all combustible materials employed in underground mining operations do produce toxic and hazardous species at elevated temperature in the presence of air. The data furthermore prove that by employing certain quantities of materials and certain heating and air flow rates the concentration of these toxic products in the gas stream can reach levels far above those dangerous to humans if breathed, e.g., for 30 minutes.

Such an accumulation of toxic species in the atmosphere of a mine must be prevented in the interest of safety. There probably exist no inherently safe materials which could fulfill the functions of, e.g., a conveyor belt and because these materials are needed from an operational standpoint, data must be developed which will make a safe trade-off possible. Such a trade-off will essentially consist of balancing the amount of material allowed in a given location with a specific rate of ventilation, the goal being that the toxic products which possibly can be formed from the material never can reach dangerous concentrations in the atmosphere at that location. To do this it is necessary to know the maximum amount of toxic products which a given quantity of a specific material can form in the most severe situation.

This program was undertaken to determine quantitatively on a gram per gram basis the amounts of individual species produced upon oxidative thermal degradation of materials used in mines both under quiescent and dynamic conditions, and to relate these data to maximum exposure limits established by the Occupational Safety and Health Act (OSHA) or to Threshold Limit Values (TLV's) recommended by the American Conference of Governmental Industrial Hygienists (ACGIH).

3.0 TECHNICAL DISCUSSION

Underground coal or ore production makes it necessary to introduce a variety of combustible material into the mine so that this operation can be carried out efficiently and safely. These materials include, for example, brattice cloth and ventilation pipe, conveyor belts, electrical insulation, wood and other cellulosic materials such as jute, synthetic resins and foams, hydraulic fluids, lubricating and cutting oils, and fire extinguishants. In addition, many of these materials have been treated with and thus contain fire retardant or decay preventing chemicals, which therefore also have to be considered.

These materials are used in a mine to make operation and production possible and safe under normal conditions. However, by virtue of their composition or the treatment they received they represent a hazard in the confines of a mine when conditions for their oxidative thermal decomposition arise. This has been proven under the Bureau of Mines Contract HO122009, "Coal Mine Combustion Products -- Identification and Analysis."[1]

Under the above referenced contract a variety of articles used in underground mining were oxidatively decomposed at elevated temperatures under controlled air flows and the nature and relative concentrations of all detectable decomposition products were established. However, the relation between decomposing material and decomposition products on a gram per gram basis was not determined. Yet, this quantity of decomposition product possibly formed per unit weight of "combustible" (or oxidatively degradable) article is a most important figure if a decision is to be made about whether the article can be tolerated in a mine, and if so, how much of this article can be safely utilized per, e.g., unit volume at predetermined ventilation air flow rates. Furthermore, investigating a number

of related compositions hopefully it can be assessed which of these form lesser quantities of toxic species thereby affording a basis for eventual material improvement.

The majority of the investigations to be reported here were performed using the stagnation burner and sealed system arrangement at roughly comparable temperatures to determine the effect of a dynamic as opposed to a quiescent environment. A third system employed only in a few instances for the determination of individual products provided also a dynamic environment , however less drastic conditions than existing in the stagnation burner insofar as the air flow rates and the temperature ranges were concerned.

Four families of materials were investigated, namely neoprene based items, polyvinyl chloride compositions, rigid urethane foams, and both untreated and variously treated wood samples. The materials studied are listed in Table I.

To make this report more comprehensible the Technical Discussion was divided into five sections. Under the heading Experimental and Analytical Procedures are grouped all the descriptions pertaining to the details of the oxidative thermal degradation insofar as the apparatus, its operation, and the general analytical methods are concerned. The next four sections deal with the discussion and presentation of the results obtained for the individual families of materials.

TABLE I

LIST OF MATERIALS INVESTIGATED[a]

Material	Origin	Material Description
Uncured neoprene	Air Force Materials Laboratory	Neoprene gum, WRT (duPont product)
Cured neoprene	Air Force Materials Laboratory	Neoprene gum, WRT (duPont product) cured as denoted in Table V
Neoprene composition 4A	Bureau of Mines	Manufactured by U. S. Steel Corporation (labeled D0500W)
Neoprene composition 3A	Bureau of Mines	Hose conduit #1949; composed of neoprene polymer reinforced with polyester; manufactured by H. K. Porter, Thermoid Division
Polyvinyl chloride "pure" resin	Air Force Materials Laboratory	Polyvinyl chloride resin; manufactured by U.S. Rubber Company; pressed into pellets
Polyvinyl chloride - nylon composition 6A	Bureau of Mines	Brattice cloth #1800y composed of nylon scrim laminated with thin PVC layer; manufactured by C. R. Daniels
Polyvinyl chloride composition 7A	Bureau of Mines	O'Koseal 200 type THW or MTW; composed of PVC; manufactured by O'Konite Cable (subsidiary of LTV)
Polyvinyl chloride - nylon composition 13A	Bureau of Mines	Reinforced plastic fabric rip-proof #75 clear III, nylon reinforced PVC; manufactured by Griffolyn Company, Inc.

TABLE I CONT'D.

Polyvinyl chloride - nylon composition 9B	Manufacturer	#3 Nylon (Glasstex) (composition : PVC-Antimony Trioxide ?); manufactured by Johnston-Morehouse-Dickey Company
Polyvinyl chloride - composition 10B	Manufacturer	#4 Plastic 15Y (appearance : solid yellow plastic; composition: PVC-Antimony Trioxide ?) manufactured by Johnston-Morehouse-Dickey Company
Polyurethane rigid foam system composition 1B	Manufacturer	Resin component - CCl_3F 22%; polyols, amines, catalyst 78%. Activator component - CCl_3F 5%, isocyanate polymeric, MDI type 94%; manufactured by Callery Chemical Company
Polyurethane rigid foam system composition 2B	Manufacturer	Same as preceding
Polyurethane rigid foam system composition 16A	Bureau of Mines	Urethane-Isocyanurate #4 foam; manufactured by Callery Chemical Company
Untreated pine sample 1D	Bureau of Mines	Standard southern yellow pine
Untreated pine sample 6D	Bureau of Mines	Standard southern yellow pine
Treated pine sample 2D	Bureau of Mines	Standard southern yellow pine treated with oil-borne preservative (pentachloro-phenol); 0.37 lbs/ft^3; impregnation by Koppers Company

TABLE I CONT'D.

Treated pine sample 3D	Bureau of Mines	Standard southern yellow pine treated with creosote (coal tar distillate); 10.6 lbs/ft^3; impregnation by Koppers Company
Treated pine sample 4D	Bureau of Mines	Standard southern yellow pine treated with fire retardant type-C, Minalith ($(NH_4)_2HPO_4$, 10%; $(NH_4)_2SO_4$, 60%; $Na_2B_4O_7$, 10%; H_3BO_3, 20%); 0.4 lbs/ft^3; impregnation by Koppers Company
Treated pine sample 5D	Bureau of Mines	Standard southern yellow pine treated with water-borne preservative-CCA (CrO_3, CuO, As_2O_5); 0.40 lbs/ft^3; impregnation by Koppers Company

a Some of the materials listed, namely those denoted by letters A and B, have been subjected to some testing previously.[1] The letter identification has been continued in this report to facilitate cross referencing.

3.1 EXPERIMENTAL AND ANALYTICAL PROCEDURES

This section will deal with the methods and apparatus used for the decomposition studies, the procedures employed for product separation and analyses, and other experimental tests performed. The results of actual experiments will be given in the sections discussing specific materials and their thermal oxidative degradations.

3.1.1 Apparatus and Its Operation

Three different methods were employed for the thermal oxidative degradations: the stagnation burner arrangement, sealed tubes, and a flow-through system. All three procedures allowed the quantitative collection of all products condensible at liquid nitrogen temperature. The sealed system permitted also the analysis of all the liquid nitrogen noncondensibles such as nitrogen, oxygen, methane, carbon monoxide and hydrogen. The stagnation burner arrangement and the flow-through system afforded a dynamic environment; the stagnation burner providing high temperature and high air flow rates and the flow-through system somewhat lower temperatures and medium air flow rates. The majority of investigations were conducted using the stagnation burner and the sealed system. Only a limited number of tests were carried out using the flow-through apparatus.

The stagnation burner was employed under the previous contract [1] as an open system for intermittent sampling. Under the present program the total amount of all products formed per given weight of material was of major interest. In order to accomplish quantitative sampling of all decomposition products except those not condensible at liquid nitrogen temperature (e.g., CO, CH_4, H_2, O_2, N_2) the stagnation burner as described in the final report under Contract No. HO122009 [1] was modified as follows: (a) the provision for operation at reduced pressure was removed, (b) the two exit side ports were connected via 2" diameter metal flanges welded into the side ports

by a 1" diameter stainless steel flexible metal hose, (c) the right exit port flange was enlarged to accept the glass connector leading to the sampling system, (d) two more 2" diameter ports were welded into the burner body in the same plane as the two exit ports (and the top of the heating block) at a $\sim 40^{\circ}$ angle (to these ports) to make illumination and/or observation of the reaction zone possible. Details of the stagnation burner as modified are shown in Figures 1,2, whereas in Figure 3 the detailed drawing of the stagnation zone is given. To assure effective trapping a three trap arrangement was used with trap "A" being attached at the exit of the burner, followed by two traps "B". The schematics of the traps are given in Figures 4 and 5.

The experimental procedures employed were as follows: After temperature equilibrium was reached in the burner (block and gas temperatures) trap "A", cooled in a Dry Ice slush bath, was attached to the burner outlet (see Figure 2) followed by connecting two traps of the "B" type (see Figure 5) to it. Subsequently the gas flow was measured, (6.2 SCFH) the window "W" opposite the burner exit (see Figure 2) removed and the two "B" type traps cooled with liquid nitrogen. After the boil off of liquid nitrogen ceased (the trap reached -196°C) the test sample was placed on the heating block and the window "W" put back into place. All tests were run for 15 minutes. Trapping was so efficient that practically all the air which passed over the sample was condensed in the two "B" type traps together with all liquid nitrogen condensible products. After completion of the test, the three traps were closed, removed from the burner, and attached to a high vacuum system while still cooled to -78 and -196°C, respectively. Subsequently all noncondensibles (e.g., air, carbon monoxide, methane, argon) were pumped away through three more liquid nitrogen cooled traps. After removal of all noncondensibles, the condensible products were separated by fractional condensation by allowing trap "A" and both traps "B" to reach room temperature and collecting the thus evaporated products in traps kept at -23°, -78°, and -196°C, respectively.

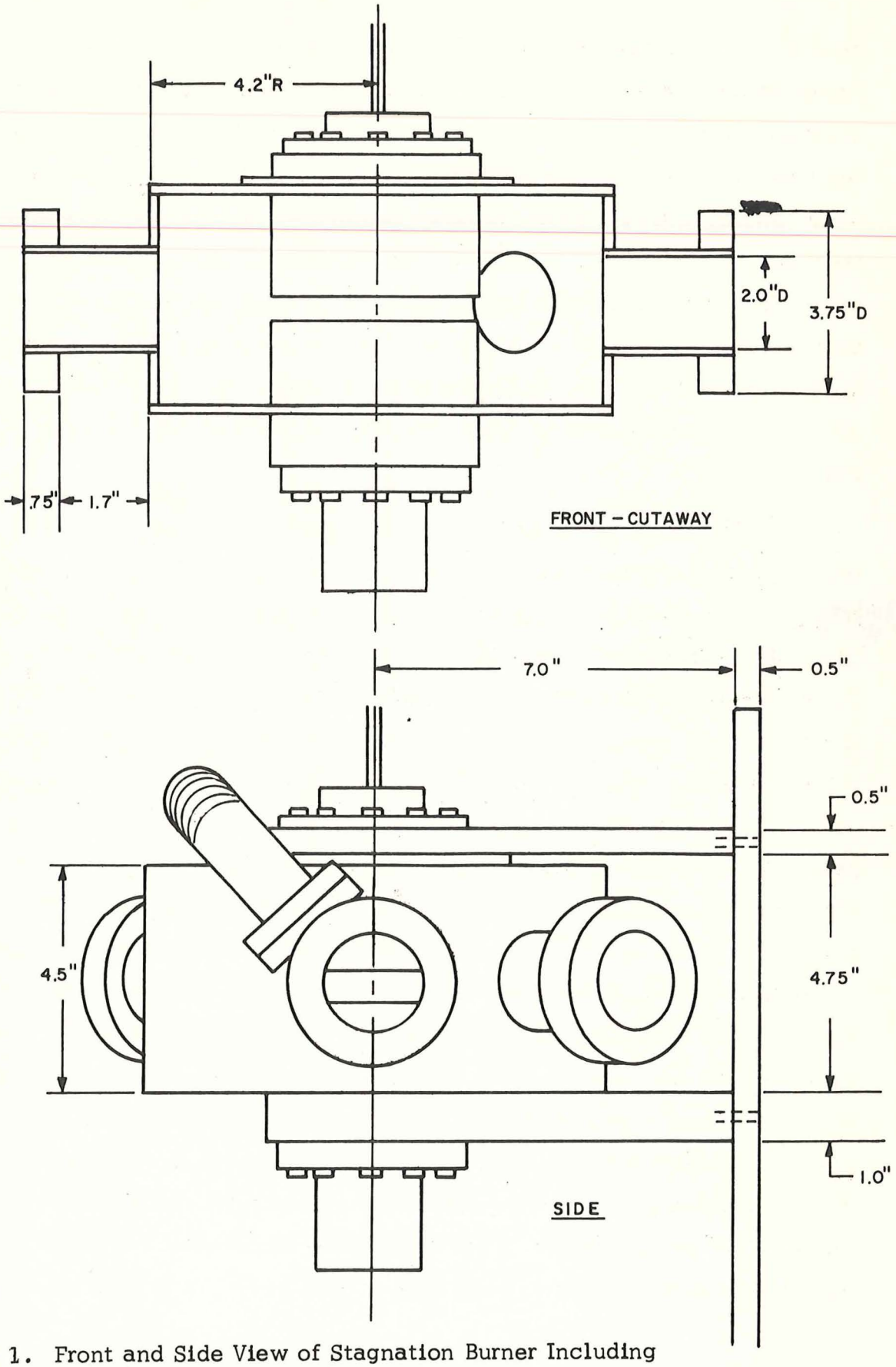


Figure 1. Front and Side View of Stagnation Burner Including Mounting System.

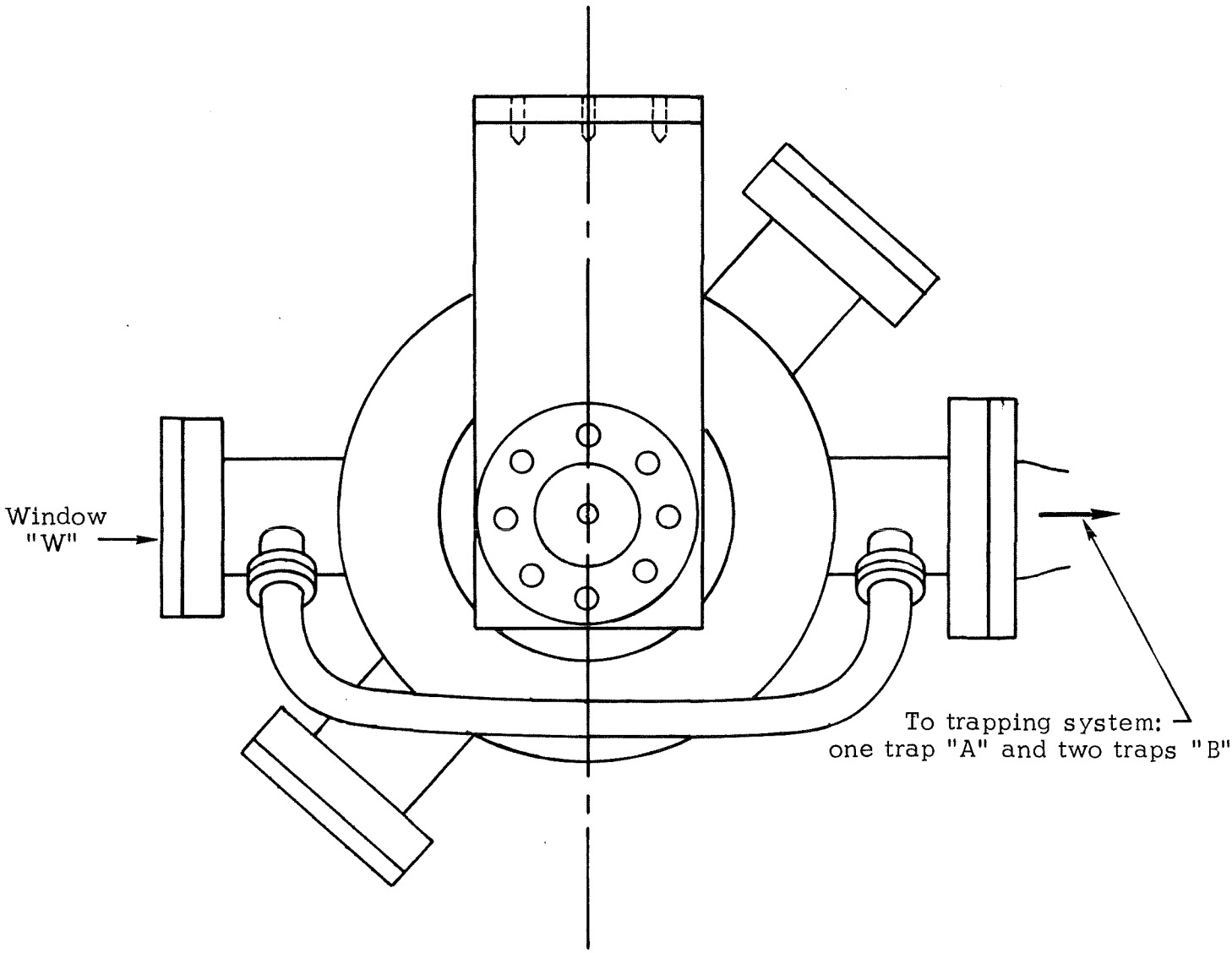


Figure 2. Top View of Stagnation Burner with Mounting System.

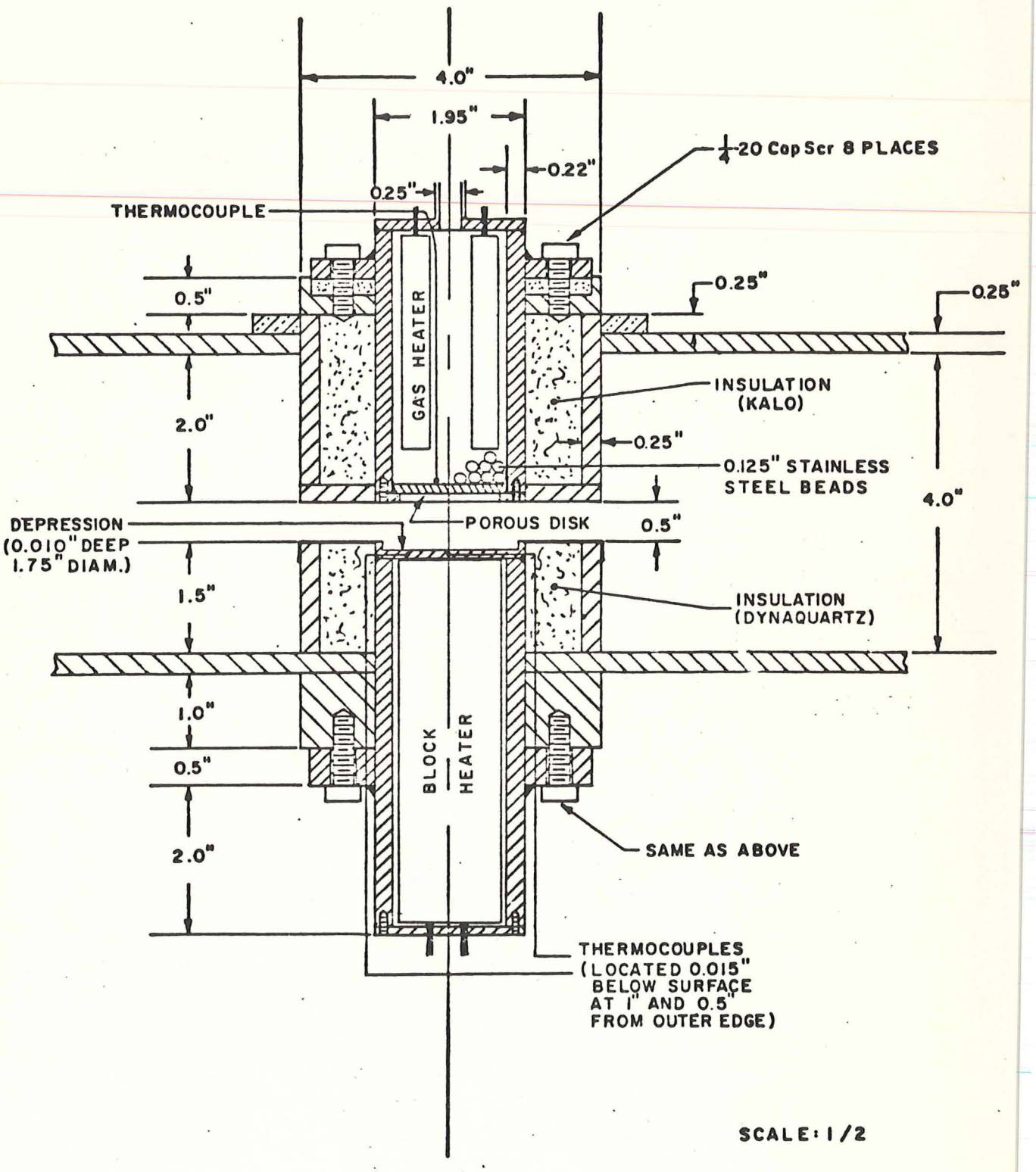


Figure 3. Detailed Drawing of Stagnation Zone with Gas, Block, and Auxiliary Heaters and Sample Pan.

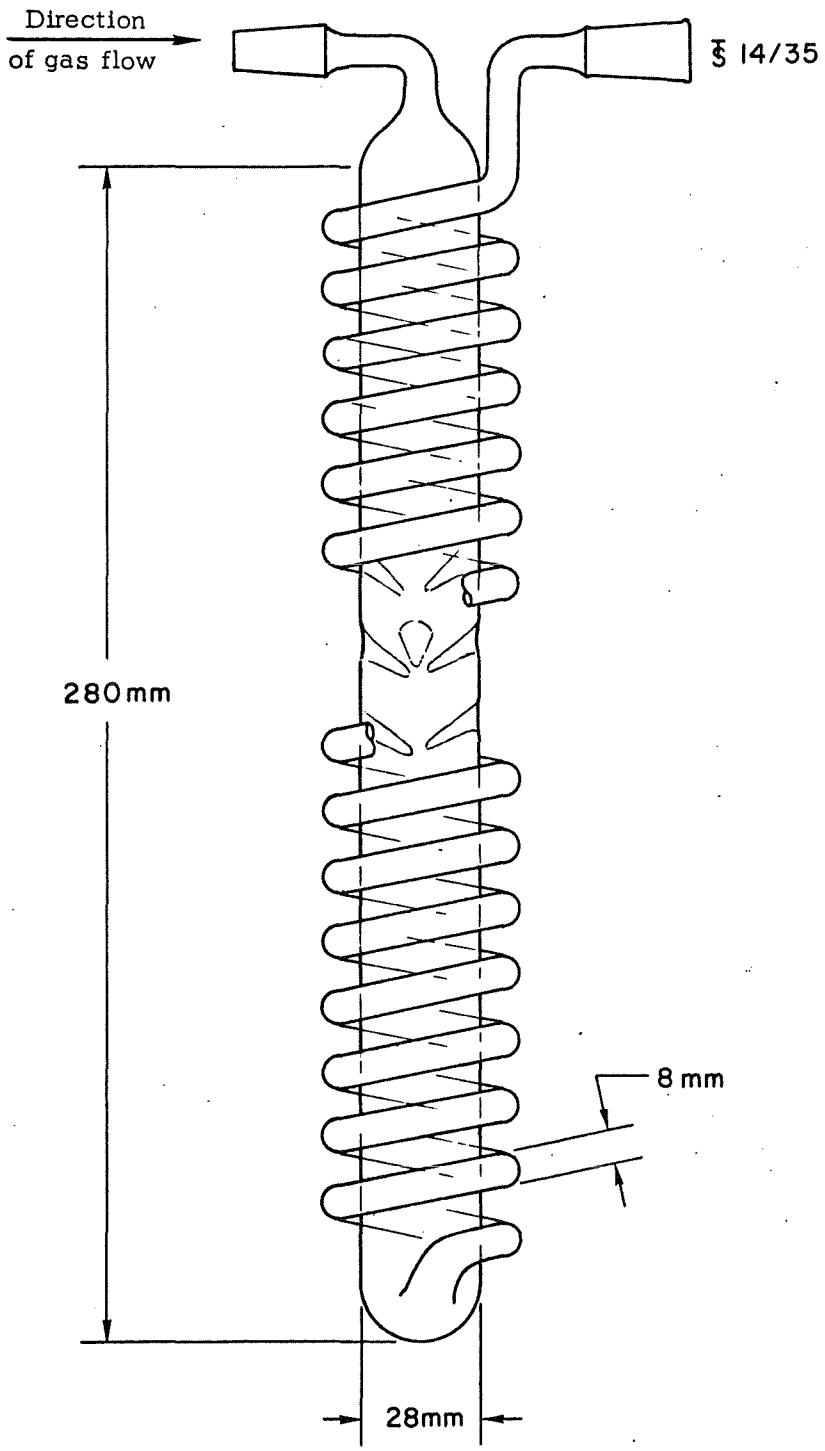


Figure 4: "A" Type Trap Cooled to -78°C

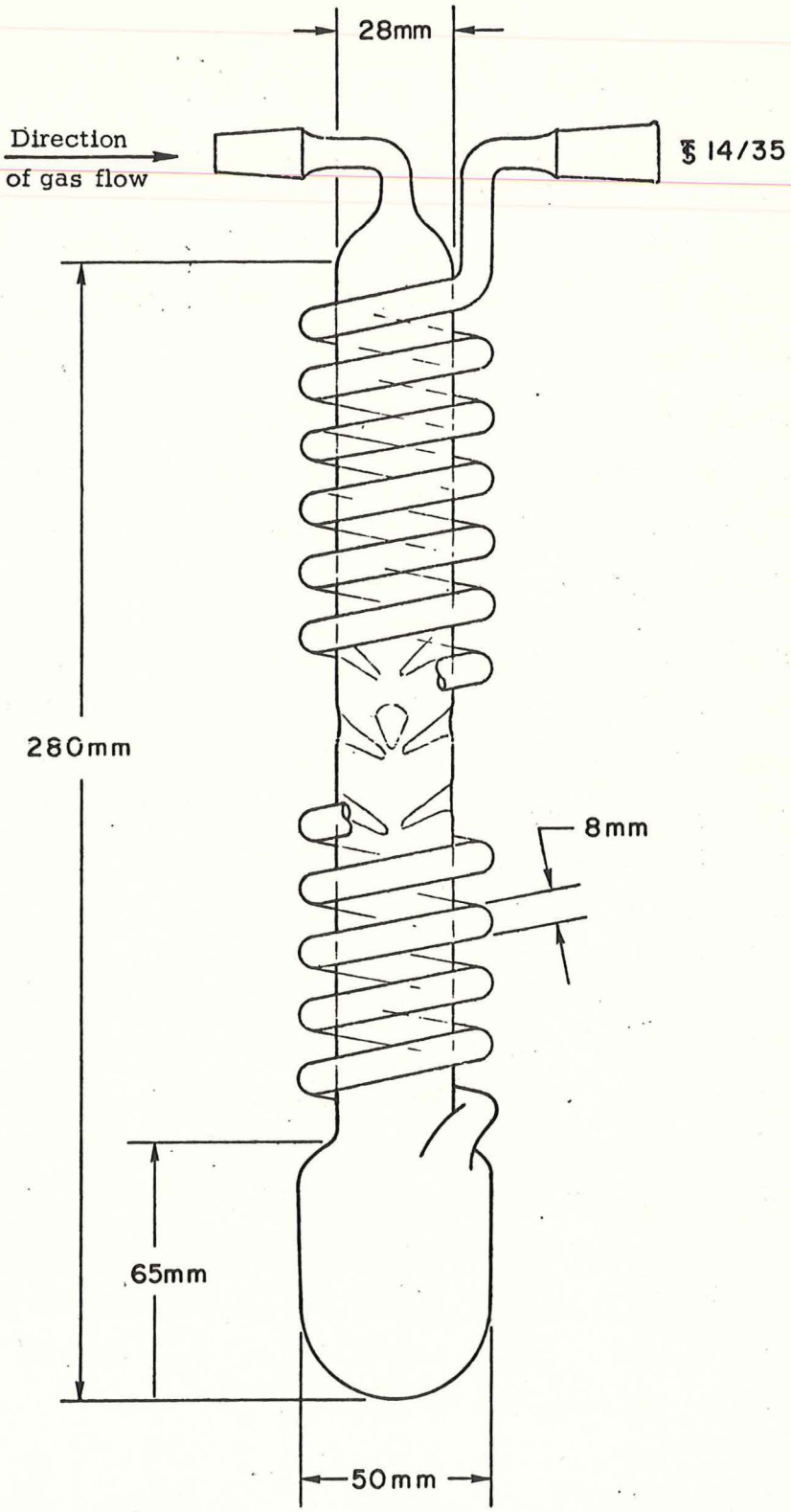


Figure 5: "B" Type Trap Cooled to -196°C

The nonvolatile materials remaining in the three burner traps were washed out with acetone and the washings made up to volume in a volumetric flask. An aliquot of this solution was analyzed for chloride ion; from another portion the solvent was removed by evaporation to determine on the residue the nature and quantity of the involatile decomposition products. Both the weight and volume of the liquid nitrogen fractions were measured, whereas on the -23 and -78°C fractions only the weight and vapor pressure were determined prior to analysis by infrared and mass spectrometry, gas chromatography, and other appropriate methods.

The details of all stagnation burner experiments, e.g., actual temperatures, weights of samples, residues, and product fractions, as well as the results of all analyses will be given in tabular form in the sections dealing with the particular material classes investigated under this program.

The sealed tube system is depicted in Figure 6. It essentially consists of a 2 liter round bottom flask to which a quartz finger had been blown wherein the sample could be placed for decomposition. The flask was connected via a pair of standard taper joints to a stopcock through which air could be admitted or samples withdrawn. The volume sealed by stopcock "A" (see Figure 6) was determined by measuring the amount of water contained in it.

The general experimental procedure was to place a weighed sample of the material to be tested into the quartz heating finger, to seal the pair of ground joints with high temperature wax, and to evacuate the system on a high vacuum line to less than 1 mm Hg. Then the system was filled with pure, dry breathing air to a known pressure and stopcock "A" (Figure 6) was closed. By knowing the volume of the flask and by measuring the temperature and pressure of the air in it the total amount of gas and the number of mmoles of oxygen present could accordingly be calculated. The finger of the flask was then inserted into a Woods Metal Bath which was preheated to the desired constant temperature. The heating period in all the instances was 30 minutes.

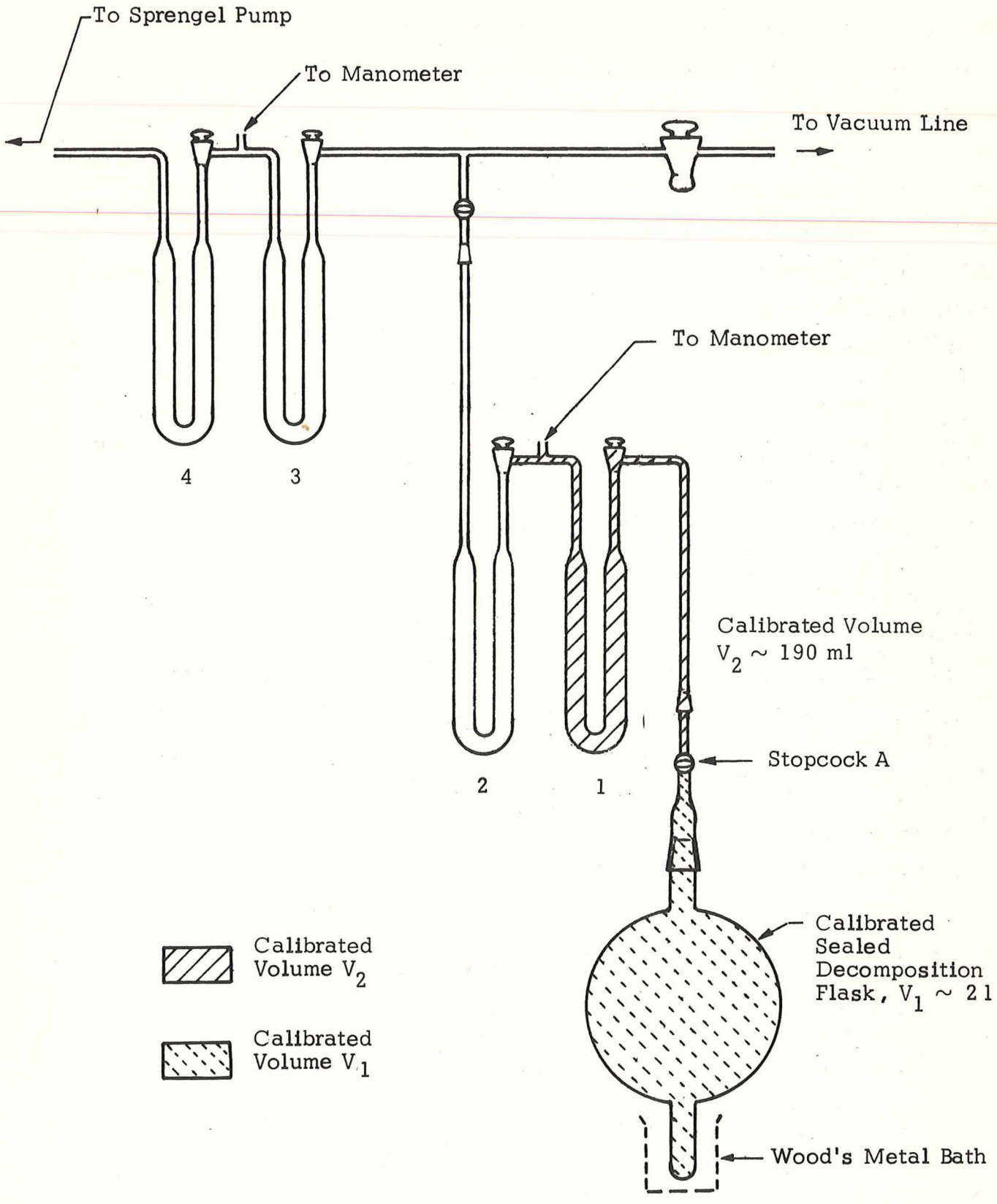


Figure 6: Sealed System for Thermal Oxidative Degradations

Subsequently, the flask was cooled by removing the bath of molten metal, the gases were expanded into the calibrated volume V_2 and pressure and temperature were measured. The amount of expanded gaseous sample contained in volume V_2 was then isolated from the bulk left in volume V_1 by closing stopcock "A"; traps 1,2,3, and 4 were cooled with liquid nitrogen and the noncondensibles were transferred quantitatively into the Sprengel pump where they were measured and then subjected to infrared and mass spectral analyses. The condensibles left in the four liquid nitrogen cooled traps (mainly in trap 2) were condensed back into volume V_2 (trap 1), measured and then condensed either onto frozen (-196°C) aqueous sodium hydroxide or water and analyzed for specific ions by titration and ion specific electrodes.

The bulk of the products left in volume V_1 was then freed from noncondensibles (air, CO, CH_4) by passing the volatiles through four liquid nitrogen cooled traps and discarding the noncondensibles. The materials condensed in these four traps were then separated by fractional condensation in traps kept at -23, -78, and -196°C in a manner analogous to that employed for the products formed in the stagnation burner. The solid residue left in the finger of the reaction flask was removed and weighed whereas the involatile oils and tars deposited on the walls of the finger were investigated by infrared spectroscopy. Then the flask was rinsed with distilled water and these washings used for extraction of chloride out of the weighed residue, followed by chloride ion determination.

The flow-through system was operated under this contract only for determination of hydrogen chloride amongst the decomposition products. To collect HCl an aqueous scrubbing tube was employed and no attempt was made to collect the other decomposition products quantitatively, although this could be readily accomplished if desired. A detailed drawing of the system as it was operated is given in Figure 7. As can be seen it consisted of an air supply, regulating valve, flow meter, quartz decomposition tube with furnace, and water scrubbing tube. Temperatures were measured at

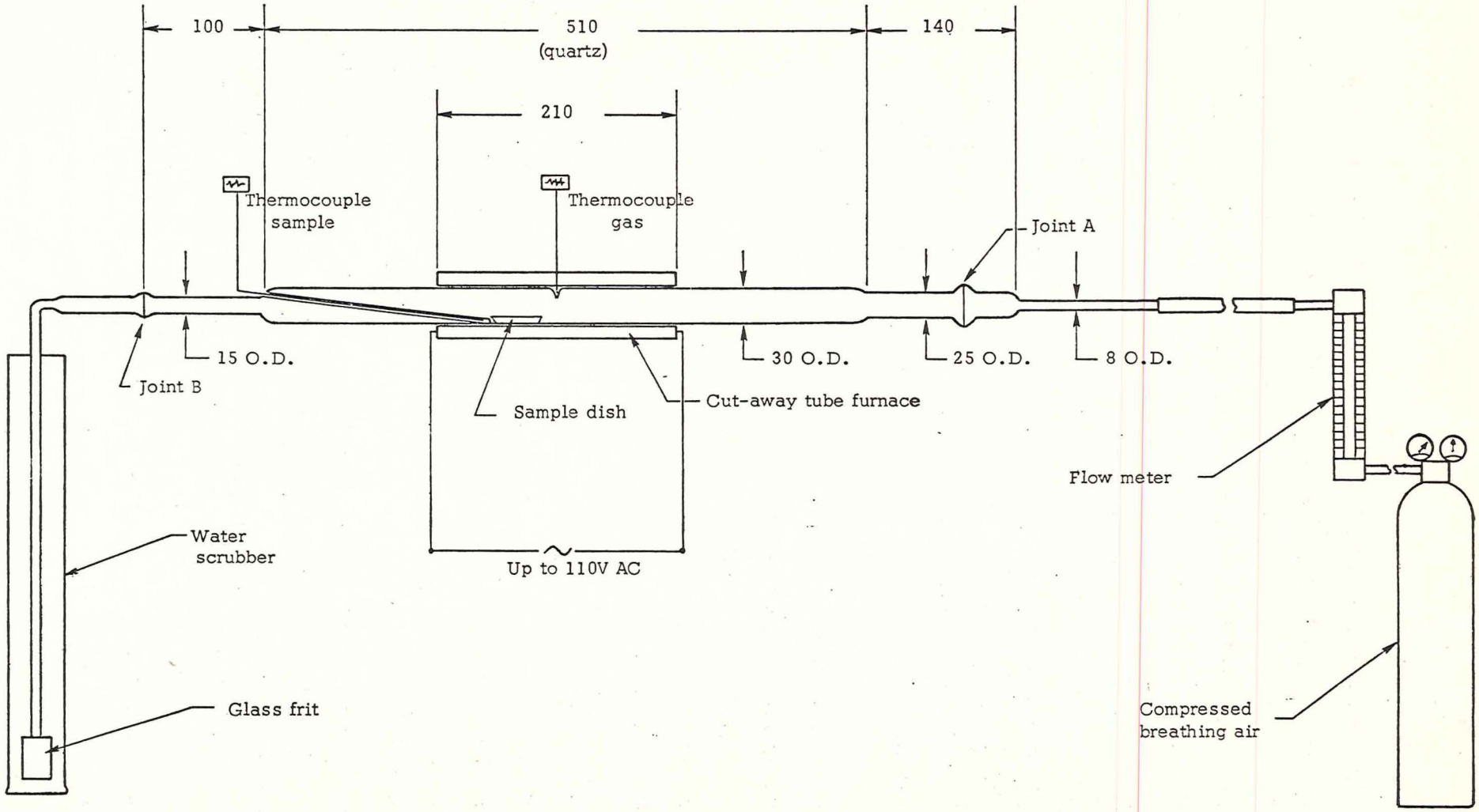


Figure 7

Diagram of Flow-Through System

two points. The gas temperature was monitored at a point just before the air passed over the sample; the sample temperature was taken by making contact between the platinum sample dish and the quartz sheath protecting the thermocouple. At both ends of the decomposition tube joints were provided to facilitate disassembly and sample introduction at joint "A".

At the start of an experiment an air flow of 2 SCFH was established and the tube furnace brought to the desired temperature. Meanwhile a weighed sample was placed in the platinum dish and the water scrubbing system containing a fritted glass plug was connected to the decomposition tube via the ball joint "B". After achieving temperature equilibrium the test sample was pushed into the decomposition tube through joint "A" so that the platinum dish would make contact with the thermocouple measuring "sample temperature", whereupon joint "A" was resealed. All decompositions were carried out for 30 minutes, after which the sample dish was retrieved, the residue weighed, and the scrubbing solution made up to volume, of which aliquots were analyzed for chloride ion using both titration and ion specific electrodes. The results of these tests are described in Section 3.2.

3.1.2 Analytical Procedures

As already delineated in Section 3.1.1 the decomposition products condensible at liquid nitrogen temperature and volatile at room temperature were separated using vacuum line techniques into fractions condensing at -23, -78, and -196^{o}C. All fractions condensing at -196^{o}C vaporized completely when allowed to warm to room temperature, thus both volumes and weights were determined. Measured aliquots of these completely vaporized fractions were condensed at liquid nitrogen temperature onto water or aqueous sodium hydroxide for the determination of Cl^- and CN^- by titration or with the aid of ion specific electrodes. The remainders of the -196^{o}C fractions were subjected to qualitative and quantitative analysis by infrared spectroscopy, gas chromatography, and mass spectroscopy.

The -23 and -78°C fractions consisted of both gas and liquid phases after being warmed to room temperature. Thus vapor pressures and total weights were determined. The gas phases of the -23 and -78°C fractions were analyzed by infrared spectroscopy, mass spectrometry, and gas chromatography, whereas the liquid phases were analyzed only by gas chromatography and infrared spectroscopy. To obtain weight factors for the liquid and gas phase portions of the -23 and -78°C fractions the weights of the liquid portions were determined after the ampoules were cut apart and the weights of the gas phase portions were taken as the differences between total and liquid weights. Samples from the liquid phases were withdrawn with micro syringes for gas chromatographic analyses and the remaining liquid was reweighed and analyzed for Cl^- and CN^- by titration.

Gas chromatographic separations were conducted using a Loenco Model 70 dual column gas chromatograph equipped with calibrated gas inlet system. The column employed was stainless steel, 1/8" x 8' packed with Porapak Q, 80/100 mesh; the helium flow was 36 ml/min, column temperatures were programmed either from 50-180° or 50-220°C, at 8° C/min; the thermal conductivity detector was operated at 100 ma. To the outlet of the sample column a 7/20 ground joint was attached to which liquid nitrogen cooled U-tubes for trapping of individual peaks could be connected. After trapping the helium was removed on the high vacuum line and the trapped sample subjected to mass spectrometric analysis.

Retention times and area factors for all definitely identified products were obtained by calibrating with substances of known purity. Only those decomposition products were considered definitely identified for which retention time, infrared, and the mass spectral breakdown patterns were found to be in agreement. In Table II are given the retention times and area factors obtained for the standards; these data has been compiled employing programming at 8°C/min from 50-220°C. The individual gas chromatographic results, including un-

TABLE II

STANDARDS

RETENTION TIMES AND FACTORS[a]

Compound	Vapor r.t. min.	Area $Inch^2/mm$	Liquid r.t. min.	Area $Inch^2/\mu l$	G.C. No.
Carbon Dioxide	1.83	1.31			1198
Ethylene	2.74	1.42			1190
Acetylene	2.81	1.54			1164
Ethane	3.55	1.81			1164
Ammonia	4.21	1.39			1209
Hydrogen Sulfide	4.80	1.41			1201
Water	5.83	2.21	5.84	512	1160, 1161
Carbonyl Sulfide	6.35	2.21			1282
Propylene	7.78	2.23			1191
Propane	8.25	2.76			1164
Sulfur Dioxide	8.31	2.20			1199
Methyl Chloride	8.66	2.26			1166, 2100
Formaldehyde			9.53	408	1183
Methanol	9.72	2.25	9.42	680	1162, 1163
Vinyl Chloride	11.14	3.05			1165
Acetaldehyde	11.40	2.60			1203
Methyl Formate	13.12	3.46	12.80	1106	1463, 1508
1,3-Butadiene	13.44	3.42			1204
2-Butene	13.59	4.34			1196
Ethanol			13.60	773	1169
Ethyl Chloride	13.96	3.70			1182
Acetonitrile			15.19	1183	1454
Formic Acid			15.30	955	1207
Acrolein	16.21	3.61	16.18	820	1208, 1250
Furan	16.40	4.76	16.21	1306	1439, 1434
Propionaldehyde			16.55	607	1206
Acetone	16.82	5.77	16.75	563	1173, 1212
Methylene Chloride			16.93	944	1219
Trichlorofluoromethane	17.00	6.15			1365
Ethyl Formate	17.43	5.28	17.30	1039	1382, 1512
Ethyl Bromide	17.70	5.03	17.41	998	1386, 1391
2-Propanol			17.52	840	1356B
1-Pentene			17.64	829	1379
Pentane			17.77	717	1333
Carbon Disulfide	17.85	4.88			1362B
Methyl Acetate	17.94	5.78	17.39	1247	1440, 1437

TABLE II CONT'D.

STANDARDS

RETENTION TIMES AND FACTORS[a]

Compound	Vapor r.t. min	Area $Inch^2/mm$	Liquid r.t. min	Area $Inch^2/\mu l$	G.C. No.
3-Chloropropene			18.05	1121	1376
Allyl Alcohol			18.12	1160	1380
1-Propanol			18.26	1126	1356
Acetic Acid			18.30	983	1355B
1,1-Dichloroethane			19.96	1149	1377
Vinyl Acetate	20.47	8.02	20.16	1331	1432, 1520
2-Methylfuran	20.94	8.05	20.50	1175	1496, 1510
Methyl Ethyl Ketone	20.92	11.39	20.67	1180	1378, 1509
Butyraldehyde	20.70	7.90			1354B
Chloroform	20.81	6.64	20.90	1482	1223, 1355
Chloroprene	21.22	4.93			1357B
Ethyl Acetate	21.31	13.32	21.31	1147	1367, 1445
1-Hexene			21.93	684	1336
Hexane			22.20	806	1334
1,2-Dichloroethane			22.33	1341	1362
2-Chloroethanol			22.38	1556	1412
Benzene	22.69	9.06	23.29	1293	1205, 1354
Cyclohexane			23.67	1050	1368
1,4-Dioxane			24.30	1340	1407
Trichloroethylene	24.83	7.43	24.14	1364	1247, 1357
1-Chloro-2-propanol			25.02	1571	1410
2-Chloro-1-propanol			26.59	1571	1410
Heptane			27.27	822	1383
Toluene	30.48	12.38	29.56	993	1358, 1511
1,2-Dibromoethane			31.12	1352	1413
Furfural			31.71	1413	1464
Furfuryl Alcohol			33.28	1300	1524

a All of these materials were examined under the following conditions:
Column - stainless steel 1/8" x 8' Porapak Q
Detector - T.C.: 100 ma
He Flow - 36 ml/min
Column Temperature - 50-220°C programmed at 8°C/min.

identified peaks are presented in the sections dealing with the specific compositions tested.

It should be noted that the Porapak Q column does not lend itself to determination of high boiling materials and is not particularly suitable for hydrocarbon separations. Consequently it was not possible to identify phenols and highly substituted aromatic materials as well as alcohols higher than C_3. On the other hand Porapak Q does offer definite advantages over other columns, especially when a wide variety of oxidative thermal degradation products is to be separated. Porapak Q is particularly well suited for the separation of oxygenated and chlorinated species, water, and inorganic materials such as HCl, H_2S, SO_2, or COS. Since from past experience the presence of these compounds was expected, this column was chosen for all gas chromatographic separations.

There were, however, instances where materials were found to be present amongst the decomposition products, where standards of known purity for identification and calibration purposes were not available. In these cases identification was based on infrared spectroscopy by comparing the sample spectra obtained with those published in several infrared spectra collections.[2-4] This identification was corroborated by trapping these materials from the gas chromatograph effluent, subjecting the samples to mass spectral analysis, and comparing the spectra with those published in reference works.[5,6] The mass spectrometry results then were quantitated by relating the mass spectrometer output for the test samples to the output obtained with either n-butane or toluene, both of which are used in the cited reference spectra[5,6] as the basis for relative sensitivities.

Mass spectral analyses were performed on all gas samples using a modified CEC Model 21-620 mass spectrometer. Calibrations were carried out with samples of known purity. Infrared spectral analyses were obtained

both on gas (10 cm gas cells) and liquid samples (sample squeezed between two sodium chloride windows either with or without silver spacer) with the aid of a Perkin-Elmer Model 21 double beam infrared spectrophotometer.

Chloride ion was determined by Volhard titration because the results obtained using specific ion electrodes were erratic and unreliable in these solutions. As can be seen in Table III in some cases acceptable agreement between the chloride concentrations measured by the two methods was obtained, whereas otherwise the chloride values determined with the ion specific electrode interestingly were lower. It should be mentioned that to all these aqueous samples there was added hydrogen peroxide to oxidize sulfide ion and that in all cases the pH was adjusted to approximately 7. It is believed that these procedures are not responsible for the erratic performance of the ion specific electrode, since accurate reproducible results were obtained when hydrogen peroxide was added to a neutral sodium chloride solution. It therefore must be concluded that the chloride ion electrode is affected by unknown combustion products present in the aqueous solutions tested.

In the cases where free ammonia was present in the -196°C fractions it was determined, in addition to infrared spectroscopy and mass spectrometry, by acid titration on an aliquot of the -196°C fraction which had been condensed onto water at liquid nitrogen temperature. Cyanide ion was determined using Liebig's method of titration in the presence of potassium iodide. However this method was found to be of low sensitivity. In conjunction with the generally low cyanide concentrations and the small sample sizes available the results for CN^- obtained by titration normally were of the same order as the experimental error of the method.

TABLE III

CHLORIDE ION ANALYSIS

COMPARISON OF VOLHARD TITRATION AND ION SPECIFIC ELECTRODE MEASUREMENTS[a]

Sealed Tube Samples	Sample Weight mg	Titration Cl^- meq	Ion Specific Electrode Cl^- meq
Uncured neoprene -196°C fraction	55.9	1.43	1.33
Known cured neoprene portion of -196°C condensibles	9.5	0.094	0.068
Known cured neoprene -196°C fraction	21.7	0.348	0.280
Neoprene composition 4A portion of -196°C condensibles	8.0	0.062	0.048
Neoprene composition 4A -196°C fraction	28.8	0.184	0.028
Neoprene composition 3A -196°C fraction	10.2	0.136	0.071

a In all instances the total volume of the aqueous solution was 50 ml and for each determination a 25 ml aliquot was used.

3.1.3 Thermal Analyses

All the materials or compositions studied under this contract were subjected to thermogravimetric analysis, TGA, using a DuPont 990-951 system programmed from 20 - 600°C at a heating rate of 10°C per minute. In addition the wood samples were investigated by differential thermal analysis, DTA, employing the above instrumentation programmed from 20 - 450°C at the same heating rate as above. The curves thus recorded are presented in the sections dealing with the particular materials.

3.2 NEOPRENE COMPOSITIONS

Neoprene compositions are used extensively in mine operations in conveyor belts, hose conduits, cable insulations, and related applications. Being a chlorined elastomer neoprene is less flammable than for instance natural rubber; furthermore it is relatively solvent redistant.

Four neoprene compositions were studied under the current contract and these are listed in Table IV. The known cured neoprene composition was prepared by the Air Force Materials Laboratory, courtesy of Mr. W. R. Griffin; its composition is given in Table V.

Thermogravimetric analyses were performed to attain an understanding of the thermal oxidative behavior of these materials insofar as weight loss is concerned and to determine whether thermal analysis can be employed as a tool in material classification for practical application. The TGA curves are given in Figures 8-11. Examining these it is apparent that they are very similar. In particular, Figures 9 and 10, tend to indicate that these are very closely related compositions. The sealed tube and stagnation burner data support this as will be discussed later. If one looks at the derivative curves one can see that the uncured neoprene decomposes at the fastest rate at ca 375°C, whereas this temperature is lowered by ca 50°C for the cured compositions. Also, the decomposition onset is lower for the cured materials. This finding is in agreement with the work performed

TABLE IV

LIST OF NEOPRENE COMPOSITIONS STUDIED

Material	Origin	Material Description
Uncured neoprene	Air Force Materials Laboratory	Neoprene gum, WRT (DuPont product)
Cured neoprene	Air Force Materials Laboratory	Neoprene gum, WRT (DuPont products) cured as denoted in Table V.
Neoprene composition 4A	Bureau of Mines	Manufactured by U.S. Steel Corporation (labeled D0500W)
Neoprene composition 3A	Bureau of Mines	Hose conduit #1949; composed of neoprene polymer reinforced with polyester; manufactured by H. K. Porter, Thermoid Division

TABLE V

COMPOSITION OF CURED NEOPRENE

Ingredient Name	Ingredient Description	Ingredient %
Neoprene WRT	poly 2-chlorobutadiene 1,3 (DuPont)	62.50
Neozone A	N-phenyl-alpha-naphthylamine (DuPont)	1.25
Wecoline 300	distilled stearic acid (Drew Chemical Corporation)	0.31
Maglite Y	magnesium oxide (Merck and Company)	1.25
NA-22	2-mercaptomidazoline (DuPont)	0.31
Protox-166	zinc oxide surface treated with propionic acid (The New Jersey Zinc Company)	3.13
ISAF	intermediate superabrasion oil furnace black (J. M. Huber Corporation)	31.25

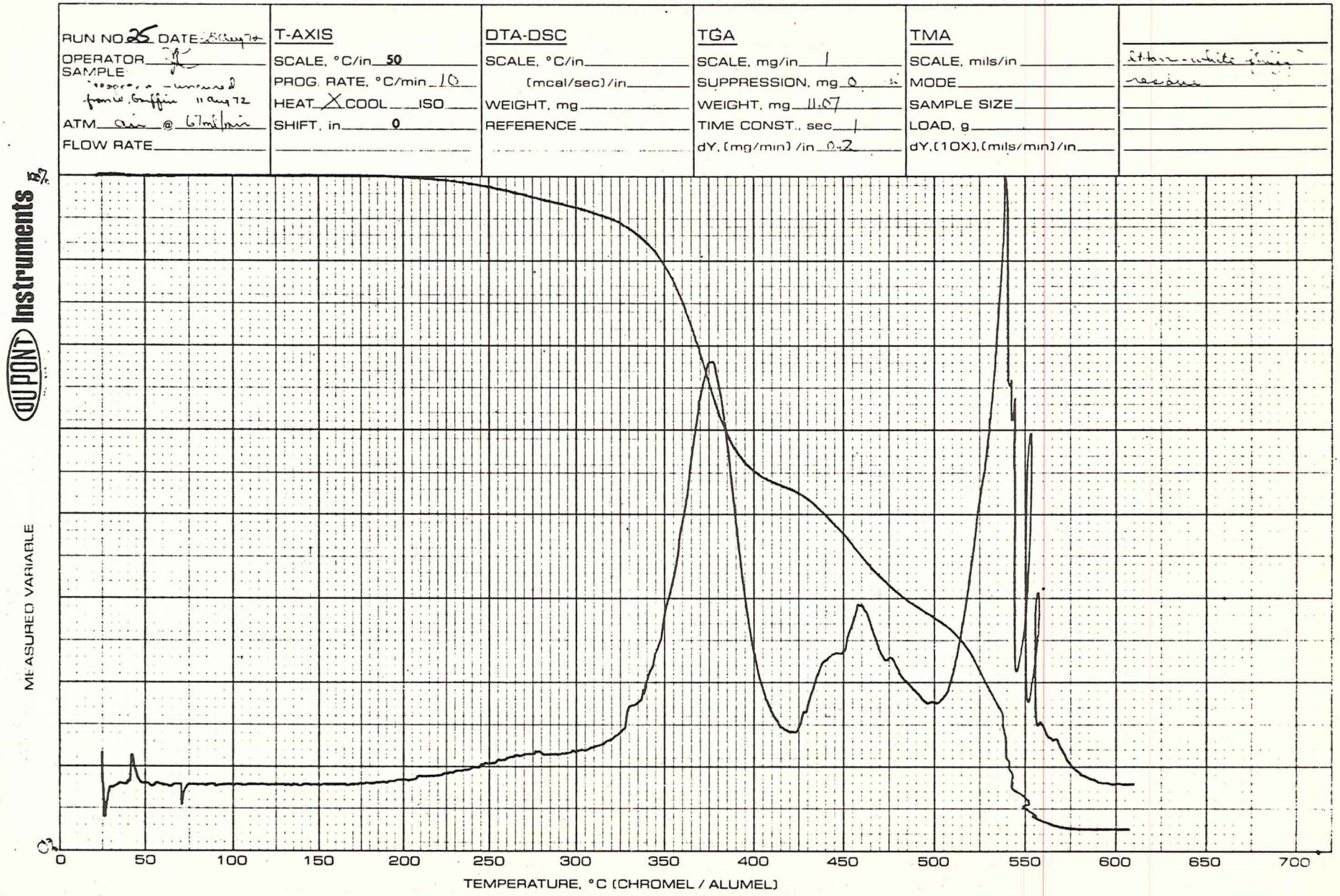


Figure 8

TGA of Uncured Neoprene

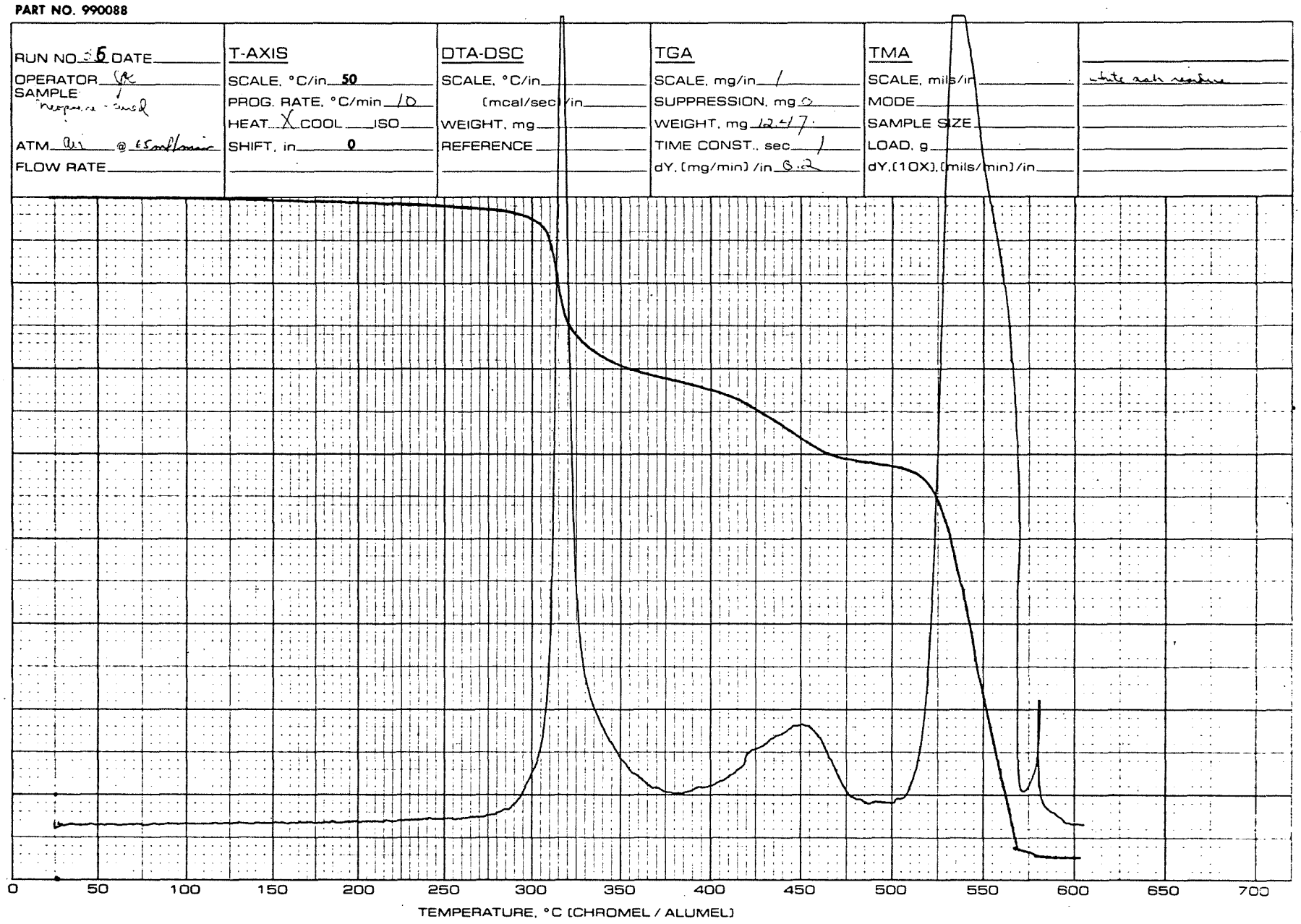


Figure 9

TGA of Known Composition Cured Neoprene

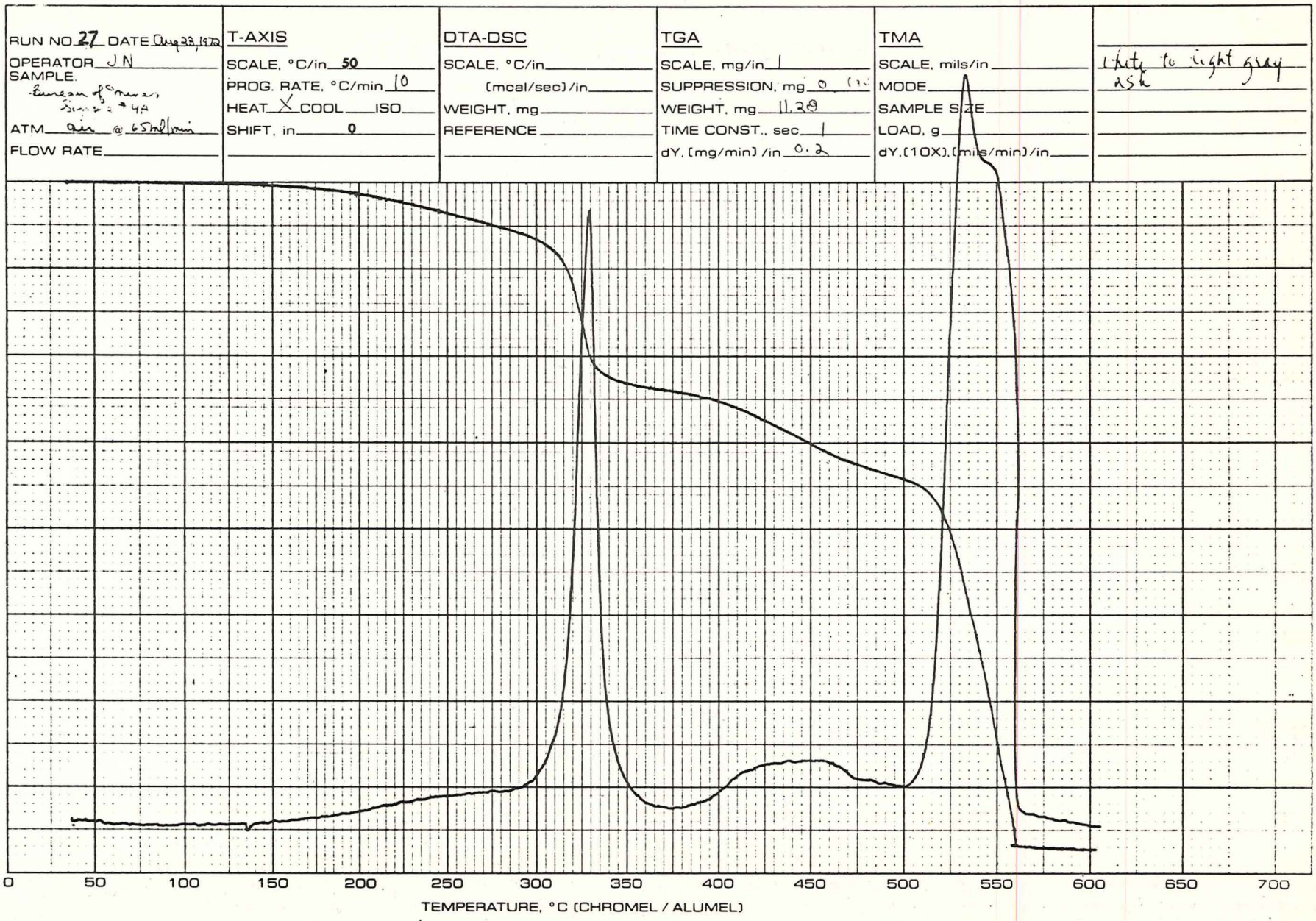


Figure 10

TGA of Neoprene Composition 4A

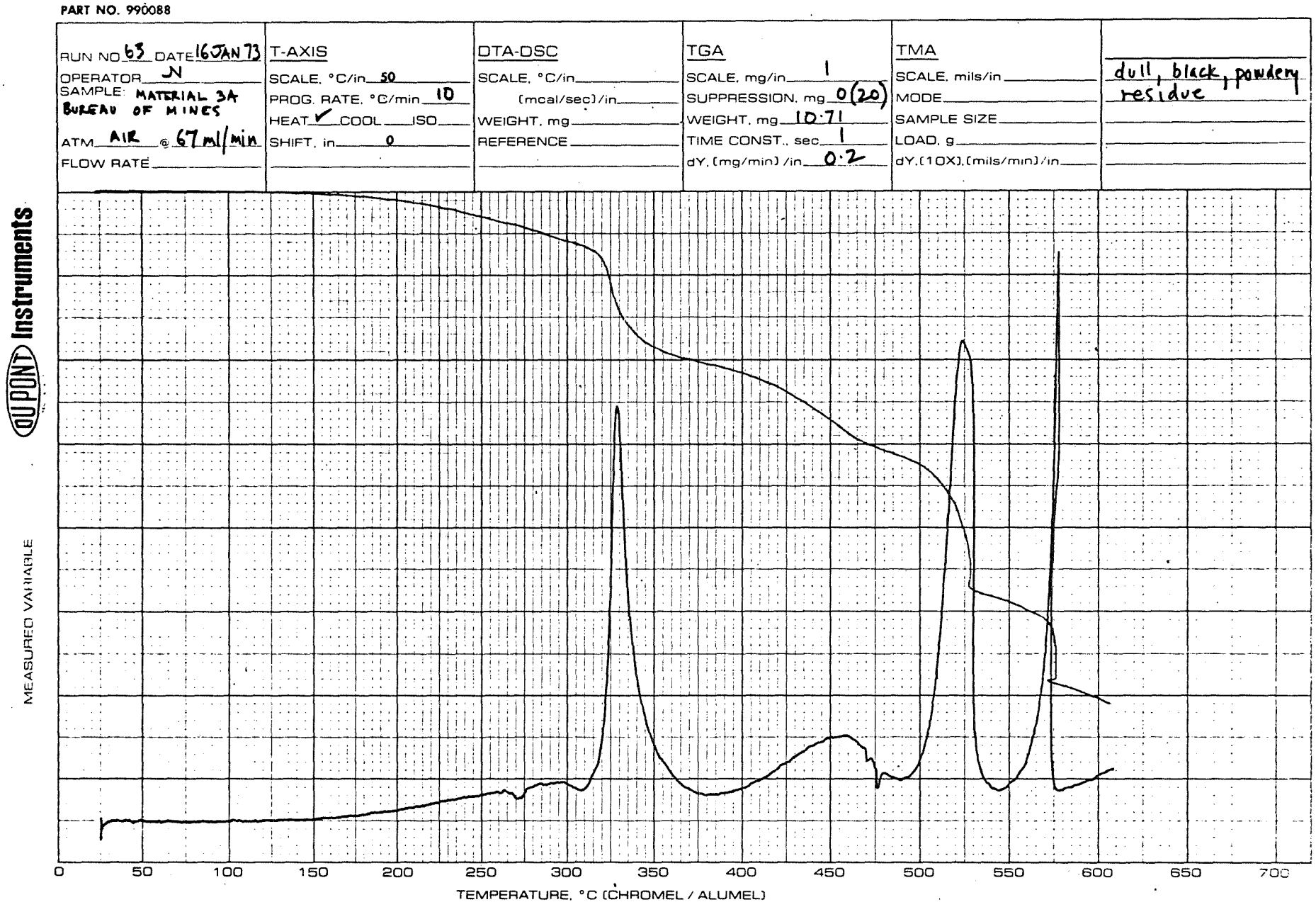


Figure 11

TGA of Neoprene Composition 3A

on other elastomers [7,8] where it was found that curing usually degrades the thermal stability of a given elastomer.

The TGA curves of chlorinated materials are also informative regarding the chlorine content of a particular material providing that a major portion of it is liberated by dehydrohalogenation, since the first material loss, as emphasized by the derivative curve, is usually associated with dehydrohalogenation. This was found to be true for vinyl chloride-acrylonitrile copolymer [9] and our studies, as can be seen from the results given in Table VI, show this to apply to neoprenes as well, even insofar as certain cured compositions are concerned. However, when one deals with composites such as material 3A, which is polyester reinforced, the method can no longer be applied.

TABLE VI

COMPARISON OF CHLORINE CONTENT VALUES AS OBTAINED BY DIFFERENT MEANS FOR NEOPRENE COMPOSITIONS

Sample	HCl Found %		Weight Loss % TGA	Theory %
	Sealed System	Stagnation Burner		
Uncured neoprene	31.2	30.0	32.0	41.24
Known cured neoprene	20.0	18.1	19.0	25.78
Composition 4A	11.0	9.9	10.0 or 12.3	-
Composition 3A	6.5	4.5	11.3 or 16.3	-

The neoprene compositions were subjected to thermal oxidative degradations using three procedures, namely the sealed tube, stagnation burner and the flow-through arrangement. The experimental data and product distribution for the sealed system studies are presented in Tables VII and VIII, whereas the gas chromatographic separations are given in Tables IX - XII. The stagnation burner experimental results are summarized in Table XIII and the gas chromatographic separations are shown in Tables XIV - XVII. In the case

TABLE VII

EXPERIMENTAL DATA FOR SEALED TUBE DEGRADATION OF NEOPRENE COMPOSITIONS

Sample Ident[a]	Tube V ml	Initial P mm	Final P mm	React. Temp °C	Sample Wt mg	Residue		Weight Loss mg	Oxygen Consumed		Total Products	
						mg	%[b]		mg	%[c]	mg[d]	%[e]
"Uncured"	2047	505.6	542.1	368	582	244	42.0	338	30.6	8.4	281.2	76.3
"Cured"	2045	559.1	570.0	371	278	168	60.3	110	53.5	13.1	122.3	74.6
4A	2047	580.0	592.9	366	278	176	63.4	102	61.1	14.3	104.8	64.3
3A	2045	495.3	500.2	372	506	361	71.4	145	42.4	11.5	73.5	39.3

a Material identification is given in Table IV.

b Percent 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 sides of the tube.

c Percent of oxygen available.

d Includes the HCl found in the residue and in the bottom of the reaction flask.

e Percent of total products expected based on sample weight loss and oxygen consumed.

TABLE VIII

PRODUCT DISTRIBUTION FOR SEALED TUBE DEGRADATION OF NEOPRENE COMPOSITIONS

Sample Ident [a]	Noncondensibles					Condensibles								
	Total mmoles [b]	CO		CH_4		Total mg	-196°C Frac		-78°C Frac		-23°C Frac		R.T. [d] Frac	
		mg	%[c]	mg	%[c]		mg	%[c]	mg	%[c]	mg	%[c]	mg	%[c]
"Uncured"	54.36	8.52	1.46	1.39	0.24	269.5	216.4	37.2	23.0	3.9	2.1	0.4	28.0	4.8
"Cured"	61.31	1.72	0.62	0.29	0.10	108.8	71.2	25.6	16.0	5.7	16.5	5.9	5.1	1.8
4A	63.36	5.32	1.91	0.20	0.07	91.8	50.1	18.0	14.5	5.2	4.6	1.7	22.6	8.1
3A	53.12	3.72	0.74	0.59	0.12	67.0	35.7	7.1	16.7	3.3	3.1	0.6	11.5	2.3

a Material identification is given in Table IV.

b This is mainly air.

c Percent of the weight of the starting material.

d Room temperature.

TABLE IX

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON UNCURED NEOPRENE [a]

R.T.[b] Frac r.t.[c]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
		3.0	C_2H_4
		3.7	C_2H_6
5.8	5.9	5.9	H_2O, HCl
		8.1	C_3H_6
		8.6	C_3H_8
		11.6	C_2H_3Cl
		13.6	C_4-ene
		14.1	C_2H_5Cl
	16.0		HCOOH ?
	17.4		$(CH_3)_2CO$, CH_2=CHCHO ?
19.6	19.6	19.7	n-C_3H_7OH, CH_3COOH
	23.3	23.0	C_4H_5Cl
	23.8		C_4-species (oxygenated) ?
		25.2	CH_3CCl=$CHCH_3$
	25.4		$(CH_2Cl)_2$
	27.7		C_6-species ?
	28.9		C_6H_6
	34.8		C_7-species ?
	37		$C_6H_5CH_3$?
	39		?

a Material identification is given in Table IV.

b Room temperature.

c Retention time in minutes.

TABLE X

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON KNOWN CURED NEOPRENE [a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	Peak Identification
1.9	1.8	1.8	CO_2
5.6	5.7	5.7	H_2O
11.2			CH_3CHO
12.5	12.4	12.5	RSH ?
	14.4		C_2H_5Cl
16.6	16.6	16.6	$(CH_3)_2CO$, CH_2=CHCHO ?
		17.0	C_5-species ?
18.3	18.2	18.1	i-C_3H_7OH ?, CS_2
20.5			n-C_3H_7OH, CH_3COOH
20.9			CH_3COOH
	23		C_4H_5Cl

a Material identification is given in Table IV.

b Room temperature.

c Retention time in minutes.

TABLE XI

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON NEOPRENE COMPOSITION 4A[a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	Peak Identification
1.8	1.9	1.9	CO_2
5.8	5.8	5.8	H_2O
8.9		8.9	CH_3Cl
9.6	9.8		CH_3OH, HCHO ?
	11.3		CH_3CHO
12.2			R'SH ?
12.5	12.5	12.5	R"SH ?
13.1	13.2	13.1	C_4-ene ?, $HCOOCH_3$?
	14.2		C_2H_5Cl
	15.7		HCOOH
		16.1	?
	16.7	16.2	CH_2=CHCHO ? $(CH_3)_2CO$
17.0		17.1	C_5-species ?
18.4	18.3	18.3	i-C_3H_7OH ?, CS_2
23.0		23.6	C_4H_5Cl

a Material identification is given in Table IV.

b Room temperature.

c Retention time in minutes.

TABLE XII

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE

DEGRADATIONS PERFORMED ON NEOPRENE COMPOSITION 3A[a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
1.8	1.8		1.7	CO_2
			2.7	C_2H_4
			3.5	C_2H_6
			4.7	H_2S
		5.1	5.2	HCHO ?
	5.7	5.6	5.6	H_2O, HCl
			6.5	COS
			7.8	C_3H_6
		8.3	8.3	SO_2, C_3H_8
		8.8	8.7	CH_3Cl
11.1	11.0	11.1	11.3	CH_2=CHCl
12.4	12.4	12.6		R'SH ?
13.0	12.9	12.9	12.9	R"SH ?
			13.3	C_2H_5OH
14.2	14.1		14.0	C_2H_5Cl, C_4-species ?
15.0				HCOOH
	16.5			CH_2=CHCHO ?
		16.8	16.8	$(CH_3)_2CO$
18.2	18.0	18.1	18.0	i-C_3H_7OH, ?, CS_2
			19.0	n-C_3H_7OH ?
			19.6	C_5-species ?
			22.2	?
		22.7	22.8	C_4H_5Cl
	25.6	25.5	25.5	$(CH_2Cl)_2$
		29.6	28.5	C_6H_6

a Material identification given in Table IV.

b Room temperature.

c Retention time in minutes.

TABLE XIII

SUMMARY OF EXPERIMENTAL DATA

FOR STAGNATION BURNER EXPERIMENTS PERFORMED ON NEOPRENE COMPOSITIONS

Sample Ident[a]	Gas Temp °C	Block Temp °C	Glow min	Sample Wt mg	Residue		-196°C Frac		-78°C Frac		-23°C Frac		R.T.[c] Frac	
					mg	%[b]	mg	%[b]	mg	%[b]	mg	%[b]	mg	%[b]
"Uncured"	401	395	No glow	963	357	37.1	307.2	31.9	32.8	3.4	164.9	17.1	174.3	18.1
"Cured"	403	404	2-15	930	76	8.2	1208	130	42.0	4.5	208.4	22.4	189.2	20.3
4A	406	396	4-15	931	141	15.2	1068	115	131.1	14.1	20.0	2.1	206.6	22.2
3A	402	393	No glow	1009	618	61.3	53.7	5.3	40.1	4.0	149.2	14.8	93.6	9.3

a Material identification is given in Table IV.

b Percent of the weight of the starting material.

c Room temperature.

TABLE XIV

GAS CHROMATOGRAPHY RESULTS FOR

STAGNATION BURNER TEST PERFORMED ON UNCURED NEOPRENE[a]

-23°C Frac r.t.[b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
	1.8	1.9	CO_2
		3.0	C_2H_4
		3.7	C_2H_6
5.5	5.8		H_2O
		6.4	?
		8.1	C_3H_6
		8.6	CH_3Cl, C_3H_8
		11.6	CH_2=CHCl
12.3	12.6		RSH ?
		13.7	C_4-ene
		14.3	C_2H_5Cl
	17.1		CH_2=CHCHO ?, $(CH_3)_2CO$
	18.8		?
	19.5	19.3	n-C_3H_7OH ?, C_5-species ?
	20.0	20.0	CH_3COOH
	23.3	23.0	C_4H_5Cl
	25.1	25.1	CH_3CCl=$CHCH_3$, $(CH_2Cl)_2$
	28.4		C_6H_6

a Material identification is given in Table IV.

b Retention time in minutes.

TABLE XV

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON A KNOWN CURED NEOPRENE COMPOSITION [a]

-23°C Frac r.t. [b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
	1.8	1.7	CO_2
		2.8	C_2H_4
		3.6	C_2H_6
5.8	5.9	5.9	H_2O
		6.6	COS
		8.1	C_3H_6
		8.6	SO_2, C_3H_8
		9.0	CH_3Cl
	9.7		CH_3OH
	12.6		RSH ?
		13.7	C_4-ene
		14.3	C_2H_5Cl
	17.3		$(CH_3)_2CO$, CH_2=CHCHO ?
	18.9		CS_2
	19.5		n-C_3H_7OH, CH_3COOH
	23.0		C_4H_5Cl
	27.3		C_6H_6

a Material identification is given in Table IV.

b Retention time in minutes.

TABLE XVI

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON NEOPRENE COMPOSITION 4A[a]

-78°C Frac r.t.[b]	-196°C Frac r.t.	Peak Identification
	1.8	CO_2
	3.0	C_2H_4
	3.8	C_2H_6
6.1	6.3	H_2O
	8.2	C_3H_6
	8.7	C_3H_8, SO_2
	9.2	CH_3Cl
11.5		CH_2=CHCl, CH_3CHO
12.7		RSH ?
13.4	13.7	C_2H_5OH, C_4-ene ?
	14.4	C_2H_5Cl
15.8		HCOOH
17.3		$(CH_3)_2CO$, CH_2=CHCHO ?
18.5		CS_2
19.5		CH_3COOH, n-C_3H_7OH
23.0		C_4H_5Cl
25.3	25.8	CH_3CCl=$CHCH_3$, $(CH_2Cl)_2$
27.2		C_6-species ?
28.4		C_6H_6
29.6	31.3	?

a Material identification is given in Table IV.

b Retention time in minutes.

TABLE XVII

GAS CHROMATOGRAPHY RESULTS FOR

STAGNATION BURNER TEST PERFORMED ON NEOPRENE COMPOSITION 3A[a]

-23°C Frac[b] r.t	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
	1.9	1.8	CO_2
	2.6	2.3	?
	3.4	3.0	C_2H_4
		3.8	C_2H_6
5.0	4.9	5.0	?, H_2S
6.0	6.2		H_2O, HCl
		6.8	COS
		8.2	C_3H_6
		8.7	C_3H_8, SO_2
		9.1	CH_3Cl
	9.9		CH_3OH
10.9	11.2	11.4	CH_3CHO, CH_2=CHCl ?
	12.6		RSH ?
	13.3	13.6	?, C_4-ene
14.1		14.4	?, C_2H_5Cl
16.2			CH_2=CHCHO ?
		16.8	?
	17.2	17.2	$(CH_3)_2CO$
	18.5	18.4	CS_2, i-C_3H_7OH ?
		19.3	C_5-species ?
19.8		19.9	n-C_3H_7OH, CH_3COOH
	22.8	22.9	C_4H_5Cl
26.4	25.5	25.5	$(CH_2Cl)_2$
		27.2	C_6H_6

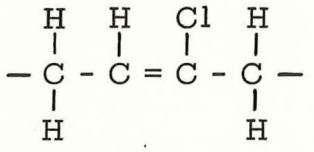
a Material identification is given in Table IV.

b Retention time in minutes.

of the flow-through system only hydrogen chloride and the residues were determined and these data are included together with experimental details in Table XVIII. In Tables XIX and XX are compiled the mg/g quantities of all the products determined in the sealed system and stagnation burner investigations, respectively.

Before proceeding with the discussion of the results it should be mentioned that the gas chromatograph was operated only up to 180°C (see Section 3.1.2) and due to this some materials were not eluted and the retention times for peaks beyond 20 min are different from those given in Table II.

In the sealed tube studies the four compositions afforded substantial residues with uncured neoprene yielding the least and composition 3A yielding the most. Based on TGA curves all the values should have been around 70-75%. Yet one has to remember that in the sealed tube the material is at temperature for a period of time (30 min) whereas in the TGA system it reaches this temperature at a particular rate (10°C/min). Accordingly, if at this temperature range the rate of decomposition is rapid, the values found under steady conditions will show a greater weight loss which was found to be the case. The low oxygen consumption is in agreement with the found high residues. The sample size for the uncured gum, which should require the largest amount of oxygen for complete decomposition, was calculated for the sealed tube tests on the basis of neoprene composition:



MW = 88.53

Accordingly on complete oxidation 1 mole of C_4H_5Cl would give: 1 mole HCl, 2 moles H_2O, and 4 moles CO_2. Each mole of neoprene requires thus 5 moles of oxygen for complete combustion. It is noteworthy that in the case of neoprene gum only 14% of the required oxygen was used. The vacuum line

TABLE XVIII

EXPERIMENTAL DATA AND RESULTS FOR FLOW-THROUGH SYSTEM DEGRADATIONS OF NEOPRENE COMPOSITIONS[a]

Sample Ident[b]	Sample Wt mg	Residue		Cl^- found, as mg/g HCl	
		mg	%[c]	by titration	with ion specific electrode
"Uncured"	501.9	163.0	32.5	343.3	232.5
"Cured"	979.6	672.6	68.7	189.4	94.5
4A	497.2	61.9	12.5	133.1	93.5
3A	519.3	322.3	62.1	67.8	62.2

a All decompositions performed with an air flow rate of 2 SCFH, sample at 390°C, air at 300°C, duration 30 min.

b Material identification is given in Table IV.

c Percent of the weight of the starting material.

TABLE XIX

PRODUCTS OF NEOPRENE COMPOSITIONS[a]

(SEALED TUBE STUDIES)

Products	"Uncured" mg/g	"Cured" mg/g	4A mg/g	3A mg/g
CO	13.2	6.19	19.1	7.35
CH_4	2.15	1.04	0.72	1.16
HCl	311.9	200.0	109.8	64.7
CO_2	16.1	104.4	137.5	26.6
SO_2	-	0.54	0.32	0.69
COS	-	-	-	0.03
CS_2	-	0.84	0.50	2.12
H_2S	-	0.11	0.22	0.31
C_xH_y[b]	3.52	3.38	4.35	2.27
C_6H_6	1.41	0.25	0.11	0.63
$C_6H_5CH_3$	0.69	T	T	0.04
CH_3Cl	0.39	0.22	1.08	0.57
C_2H_3Cl	0.36	-	0.07	1.98
C_2H_5Cl	1.13	0.79	0.54	1.28
$(CH_2Cl)_2$	0.54	-	-	3.08
C_4H_5Cl	6.30	2.27	1.73	0.71
C_4H_7Cl	0.62	-	-	-
CH_3OH	-	-	0.04	0.19
C_2H_5OH	-	-	-	0.30
i-C_3H_7OH	-	-	-	0.06
n-C_3H_7OH	0.27	?	-	-
CH_3CHO	-	0.04	0.04	2.61
$(CH_3)_2CO$	0.07	0.07	0.04	0.49
HCOOH	-	-	0.07	0.08
CH_3COOH	2.39	-	-	-

a Material identification is given in Table IV.

b C_xH_y denotes hydrocarbons C_2 through C_4.

TABLE XX

PRODUCTS OF NEOPRENE COMPOSITIONS [a]

(STAGNATION BURNER STUDIES)

Products	"Uncured" mg/g	"Cured" mg/g	4A mg/g	3A mg/g
HCl	300.3	181.1	99.4	44.9
CO_2	48.0	1160	1050	32.7
SO_2	0.95	6.36	5.74	0.55
COS	-	0.04	0.03	0.17
CS_2	-	0.01	0.01	0.54
H_2S	0.05	0.20	0.06	0.65
C_xH_y [b]	3.53	7.44	4.60	1.91
C_6H_6	1.42	0.02	0.10	0.29
CH_3Cl	0.51	0.43	0.37	0.28
C_2H_3Cl	0.38	-	0.78	-
C_2H_5Cl	0.55	0.75	0.78	0.48
$(CH_2Cl)_2$	0.31	-	0.04	3.32
C_4H_5Cl	4.14	0.26	0.16	0.83
C_4H_7Cl	4.07	-	-	-
CH_3OH	-	0.26	-	0.42
C_2H_5OH	-	-	1.50	-
i-C_3H_7OH	-	0.05	-	-
n-C_3H_7OH	-	T	0.17	0.04
CH_3CHO	-	-	0.08	5.29
$(CH_3)_2CO$	0.06	0.01	0.39	0.99
HCOOH	-	-	T	-
CH_3COOH	0.02	0.01	0.16	0.80

a Material identification is given in Table IV.

b C_xH_y denotes hydrocarbons C_2 through C_4.

fractionation proved to be fairly effective in material separation, in particular regarding the -196°C fractions which in most instances consisted mainly of CO_2 and HCl (this is in particular true for the sealed system studies). It should be explained that in the sealed tube degradations the hydrogen chloride analyses are reliable, whereas in the case of the stagnation burner values found are significantly lower (compare Table VI) due to the interaction of HCl with the metal surfaces.

Under the more drastic conditions found in the stagnation burner compared to the sealed tube, oxidation occurred to a higher degree resulting in the increased production of carbon dioxide and water. The water caused the retention of hydrogen chloride in the less volatile fractions; consequently in some instances no hydrogen chloride was found in the -196°C fraction. Interestingly enough in the case of composition 4A (the stagnation burner experiment, Table XX) although much less hydrogen sulfide was formed than hydrogen chloride, only hydrogen sulfide was found in the -196°C fraction showing clearly that due to the lesser affinity of hydrogen sulfide for water it survived in the gaseous phase. The total H_2S content reported could be very well low, since sulfide ion is hard to measure in low concentrations in the aqueous solutions (the values given in Tables XIX and XX pertain to the gas phase only). This finding indicates that hydrogen sulfide presents a greater toxicity hazard than hydrogen chloride at locations removed from the disaster area since it can be transported for a distance without condensing or reacting. The facile condensation of hydrogen chloride due to its affinity for water and thus its strongly diminished concentration only a short distance from the site of production has been shown also by the work of O'Mara [10], whereas the condensation of HCl on particulate matter was described by Stone et al [11].

To illustrate the composition of the different fractions two representative infrared spectra are presented in Figures 12 and 13. The infrared spectrum of the -196°C fraction of the known cured neoprene (see Figure 12) shows the presence of hydrogen chloride (fine line absorption 3.45 - 3.65μ); carbon dioxide (4.32, 13.47, 13.87, 14.95μ); carbonyl sulfide (4.82, 4.85μ); sulfur dioxide (7.26, 7.32, 7.40μ); chloroprene (10.25, 10.83, 11.37μ) and methyl chloride (13.68μ). The infrared spectrum (see Figure 13) of the -78°C fraction obtained from the sealed tube degradation of uncured neoprene exhibits bands indicative of aromatic species (3.27μ), aliphatic species (3.4 - 3.55μ), aldehydes (3.65μ), carbonyl (~ 5.7μ), ethanol (7.2, 8.1, 9.45μ), 1,2-dichloro-ethane (13.48μ), toluene (13.7 and 14.4μ), and benzene (14.85μ).

In the discussion of TGA data it was pointed out that known cured neoprene and material 4A exhibited closely related TGA curves. The nature and relative concentration of volatiles formed, in conjunction with the occurrence of glow tend to support this observation. Based on the hydrogen chloride analyses and the chloroprene found (see Table XIX) it would appear that material 4A contains less neoprene than the known cured sample. In Tables XIX and XX a number of sulfur containing species is reported, namely SO_2 (TLV, 5 ppm), COS, CS_2 (TLV, 20 ppm), and H_2S (TLV, 10 ppm). These substances are derived from the curing agents and the polymerization initiators, which explains the formation of 0.95 mg/g of SO_2 from uncured neoprene gum. No mercaptans are given since none was definitely identified; however, based on mass spectral analysis (peaks at m/e 47, 81, 96) of the gas chromatographic peaks with retention times of ~ 12.5 min it can be safely deduced that these were formed. In view of their high toxicity (CH_3SH, TLV , 0.5 ppm) additional investigations to determine the nature of the materials formed and their quantity will have to be conducted in the future. The sealed system presents a less severe environment than the stagnation burner, as was discussed earlier (see Section 3.1.1), thus it is not surprising that relatively flammable compounds such as carbon disulfide have been found

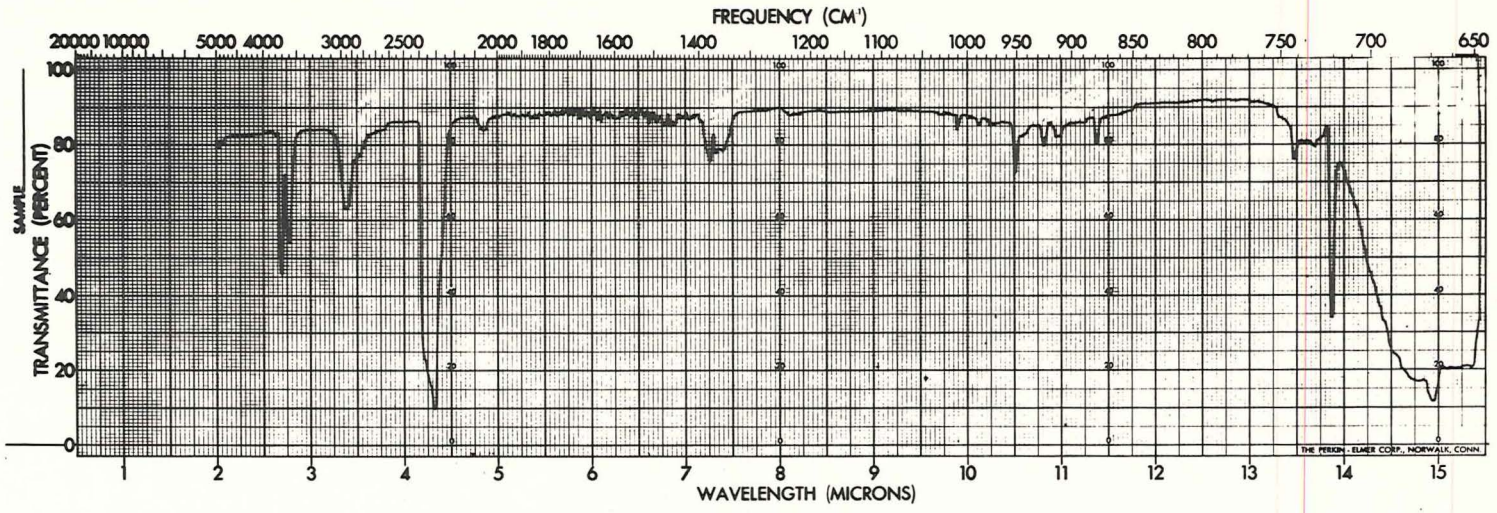


Fig. 12. Infrared Spectrum of -196°C Fraction
Stagnation Burner Treatment of Cured Neoprene (gas, p = 323 mm)

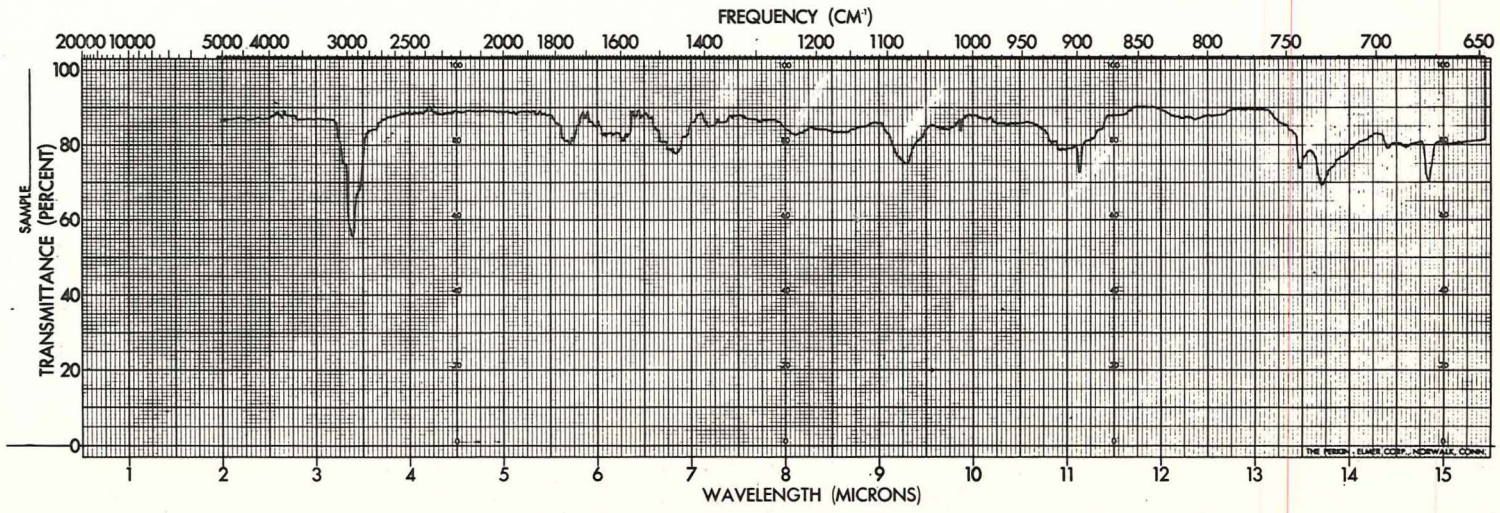


Fig. 13. Infrared Spectrum of -78°C Fraction
Sealed Tube Treatment of Uncured Neoprene (gas, p ~ 22 mm)

amongst the sealed tube products in significantly higher quantities than in the stagnation burner investigations, whereas the opposite was found for sulfur dioxide and carbonyl sulfide. The more drastic nature of the stagnation burner treatment is also reflected in the occurrence of glow and in the destruction of materials such as e.g., chloroprene (TLV, 25 ppm). This is apparent from comparing the values given in Tables XIX and XX for three of the materials (uncured neoprene, known cured neoprene and composition 4A); however, there is not much difference between the sealed system and stagnation burner data for material 3A. This is in agreement with the amounts of residues found for the two experiments. Material 3A is a composite sample of neoprene and a polyester reinforcement. The presence of a polyester, which is most likely based on ethylene glycol, is reflected in the relatively high acetaldehyde content, which is to be expected based on the literature.[1] The infrared spectra of the -78 and -23°C fractions, showed the presence of acetaldehyde. The room temperature involatiles of material 3A, showed in the infrared spectrum (see Figure 14), the presence of mono- and/or disubstituted aromatic species (6.2, 6.35, 6.55, 6.6, 13.7μ), carboxyl groups (3.75, 3.94, 6.9, 7.8μ), and aliphatic linkages (3.42, 3.50μ). The room temperature involatiles obtained from the stagnation burner treatment of uncured neoprene exhibited the infrared spectrum shown in Figure 15. No aldehyde or carboxyl moieties seem to be present; aliphatics (3.43 and 3.50μ) and monosubstituted aromatics appear to be the main components. The presence of aromatics is not surprising since both benzene and toluene were found in the volatiles (see Tables XIX and XX); in addition, in the mass spectra of the -78 and -23°C fractions xylenes (m/e,106, 91), substituted benzenes (m/e, 105, 120), substitutednaphthalenes (m/e, 141, 142, 115), chlorinated toluenes (m/e, 139, 141, 117), substituted phenols (m/e, 122), styrenes (m/e, 104, 103), phenyl acetylene (m/e, 102, 76, 103), possibly benzyl mercaptan (m/e, 124), and possibly benzyl chloride (m/e, 126) were found.

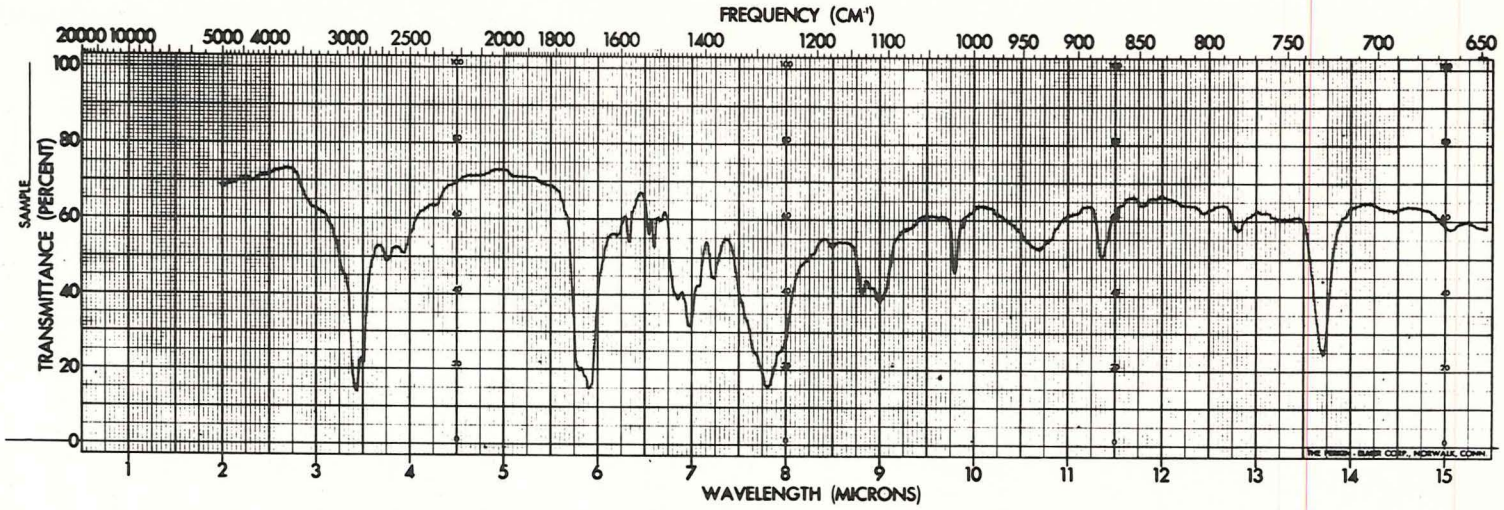


Fig. 14. Infrared Spectrum of Room Temperature Involatile Oils
Stagnation Burner Treatment of Neoprene Composition 3A (liquid film)

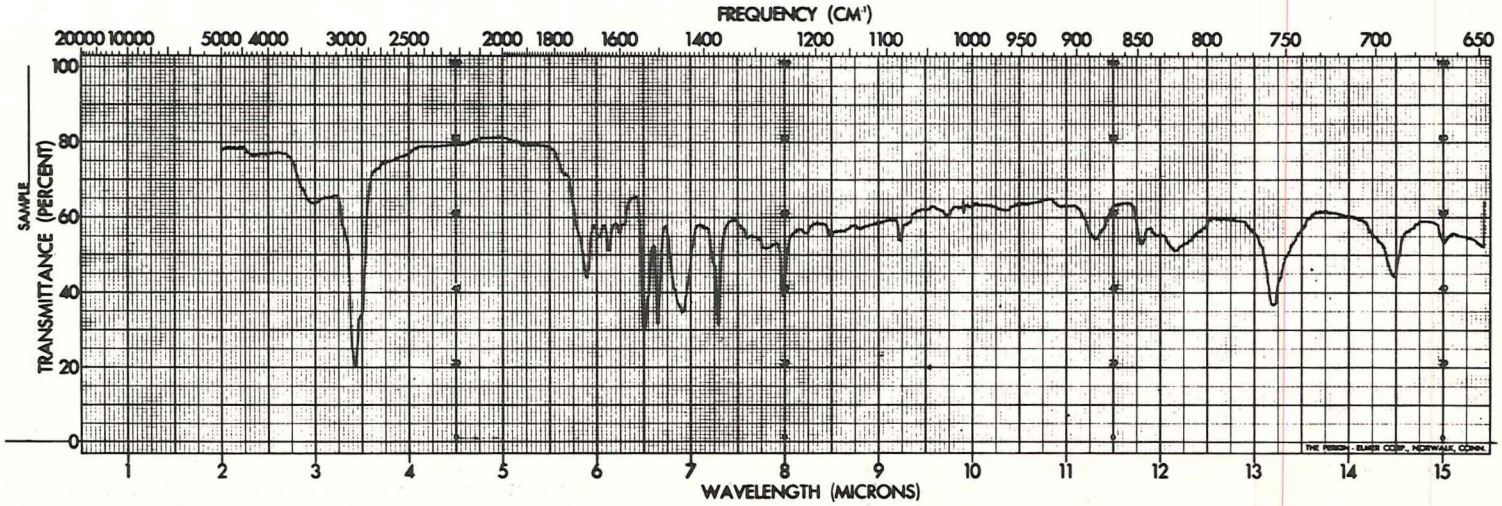


Fig. 15. Infrared Spectrum of Room Temperature Involatile Oils
Stagnation Burner Treatment of Uncured Neoprene (liquid film)

Benzyl chloride (TLV, 5 ppm) has been reported by Boettner[12] to be formed from polyvinyl chloride compositions; thus it is quite reasonable to expect it to be formed from neoprenes. Tables XIX and XX do not include the hydrocarbons which were formed, but not quantitated. Based on mass spectral data these were present in high concentrations, in particular highly unsaturated species as evidenced by high peaks at (m/e 67, 55, 56, 41, 39, etc.).

3.3 POLYVINYL CHLORIDE COMPOSITIONS

Polyvinyl chloride compositions are widely employed in underground operations due to their flame resistance and low cost. These applications, among others, include hose conduits, ventilation pipe, and brattice cloth. In the latter case polyvinyl chloride is usually employed as a laminate in conjunction with nylon or another fiber which provides the strength and tear resistance required for the given end use.

In the current study six polyvinyl chloride compositions were investigated; these are listed in Table XXI. Thermogravimetric analyses were conducted to compare the thermal behavior of "pure" polyvinyl chloride resin with that of the studied compositions and to examine the feasibility of using TGA curves as an efficient method of differentation between polyvinyl chloride compositions and other materials used in mines. The curves are presented in Figures 16-20. All the curves are fairly similar, the main exception being the one obtained from composition 6A (see Figure 17). The main feature of all these curves is the rapid weight loss beyond 250^{o}C due to hydrogen chloride evolution. In Table XXII are presented the comparisons between TGA data (weight loss, first peak) and hydrogen chloride values found in the sealed system and stagnation burner tests. As was noted previously (see Section 3.2) the hydrogen chloride found in the stagnation burner tests was always lower than in the sealed tube due to the apparatus itself. Assuming the sealed tube value to correspond closely to that of the actual hydrogen chloride evolution it is apparent that only in the case of the "pure" resin does the first

TABLE XXI

LIST OF POLYVINYL CHLORIDE COMPOSITIONS STUDIED

Material	Origin	Material Description
Polyvinyl chloride "pure" resin	Air Force Materials Laboratory	Polyvinyl chloride resin manufactured by U.S. Rubber Company; pressed into pellets
Polyvinyl chloride-nylon composition 6A	Bureau of Mines	Brattice cloth #1800y composed of nylon scrim laminated with thin PVC layer; manufactured by C. R. Daniels
Polyvinyl chloride composition 7A	Bureau of Mines	Hose conduit, O'Koseal 200 type THW or MTW; composed of PVC; manufactured by O'Konite Cable (subsidiary of LTV)
Polyvinyl chloride-nylon composition 13A	Bureau of Mines	Reinforced plastic fabric rip-proof #75 clear III, nylon reinforced PVC; manufactured by Griffolyn Company, Inc.
Polyvinyl chloride nylon composition 9B	Manufacturer	#3 nylon (Glasstex) (composition, PVC-Antimony Trioxide ?); manufactured by Johnston-Morehouse-Dickey Company
Polyvinyl chloride composition 10B	Manufacturer	#4 plastic 15Y (appearance, solid yellow plastic) (composition, PVC-Antimony Trioxide ?) manufactured by Johnston-Morehouse-Dickey Company

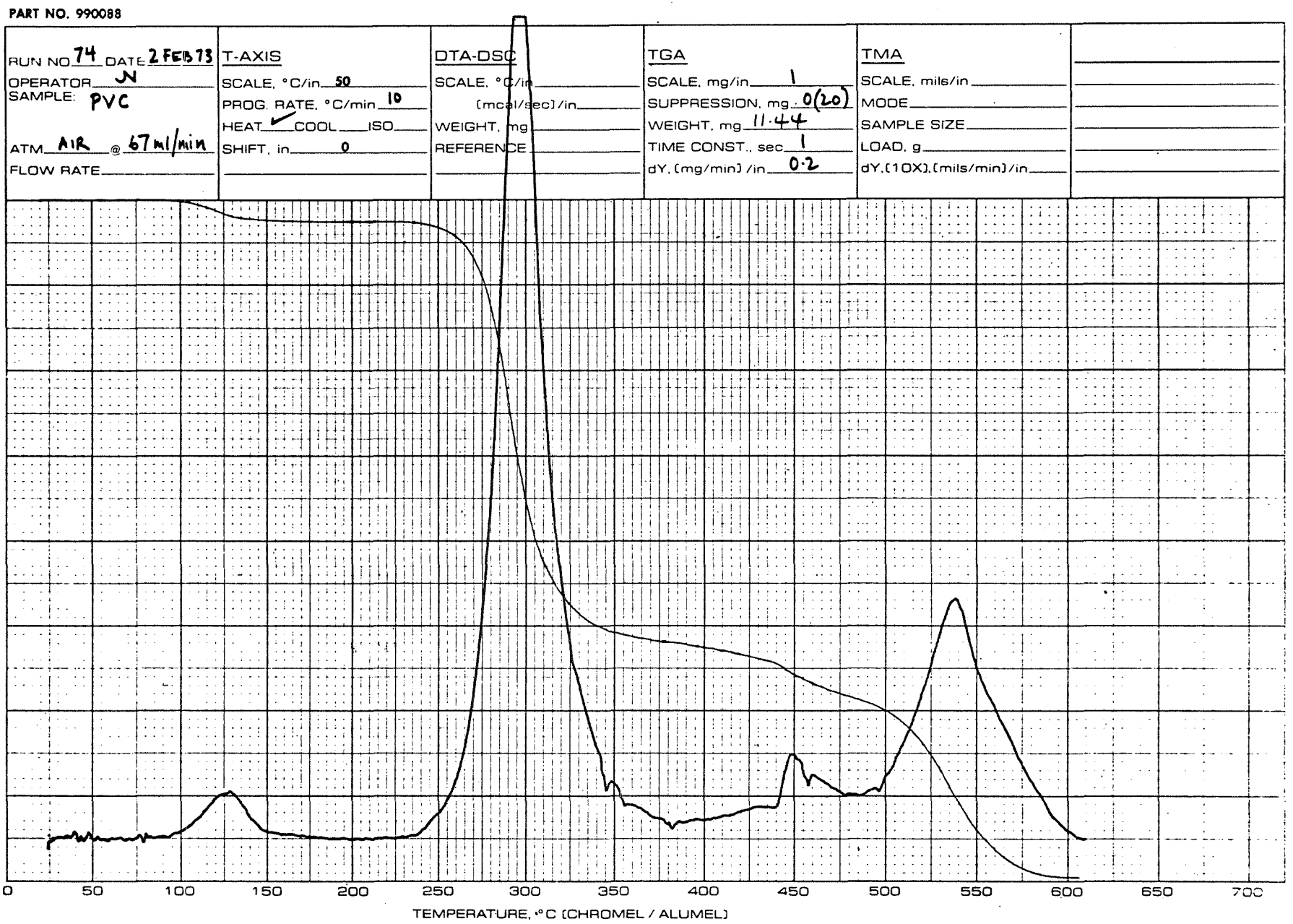


Figure 16

TGA of "Pure" Polyvinyl Chloride Resin

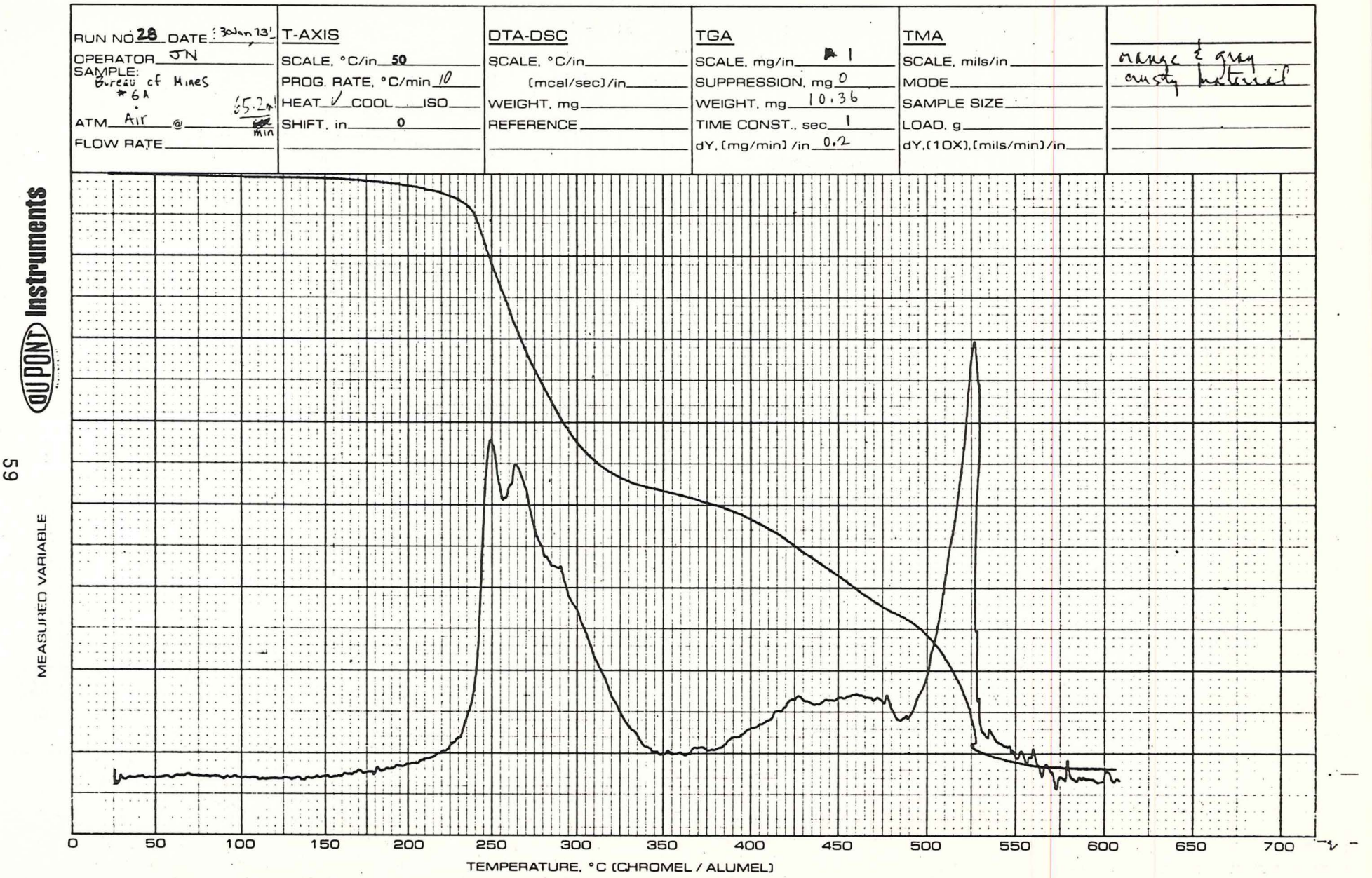


Figure 17

TGA of Polyvinyl Chloride Composition 6A

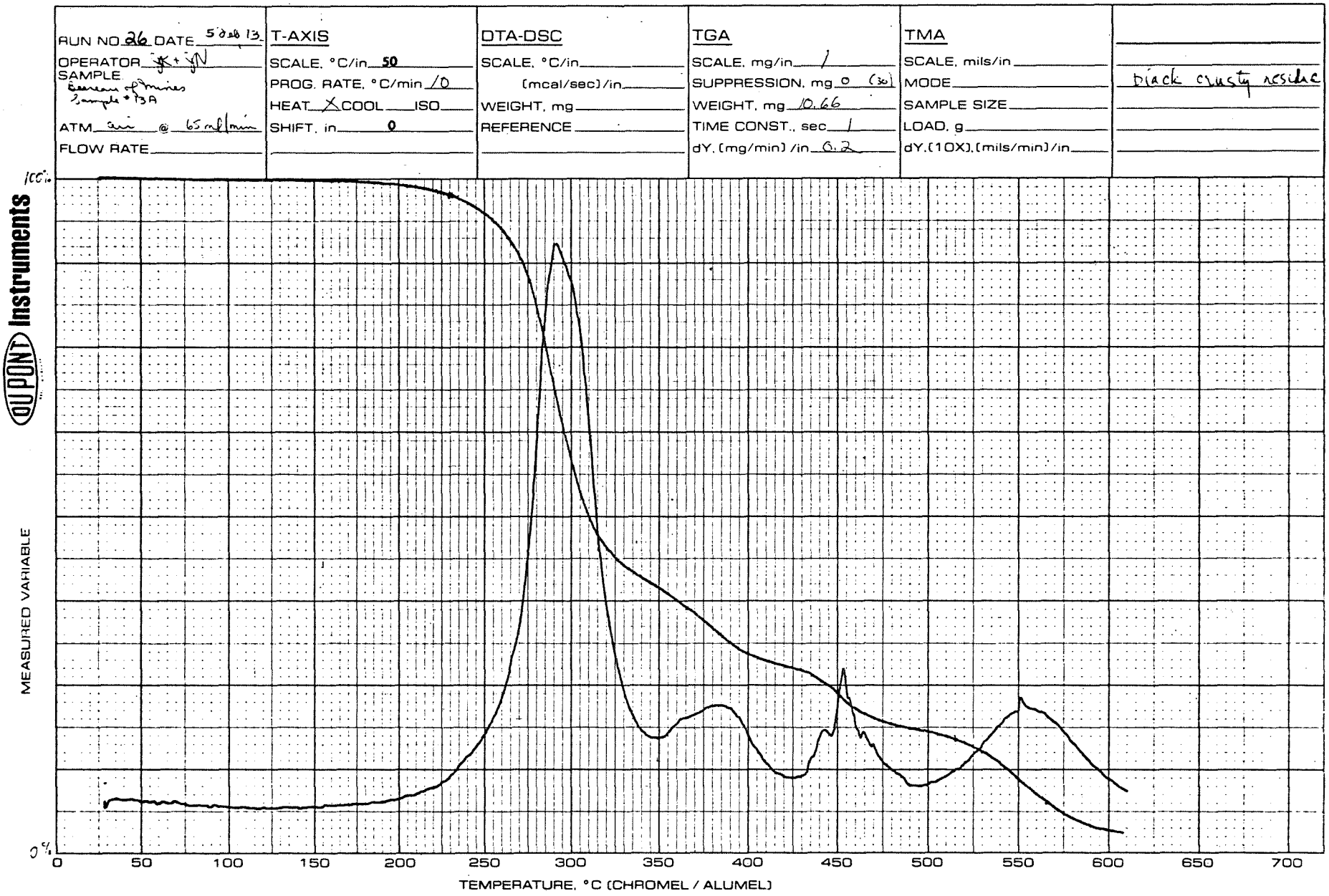


Figure 18

TGA of Polyvinyl Chloride Composition 13A

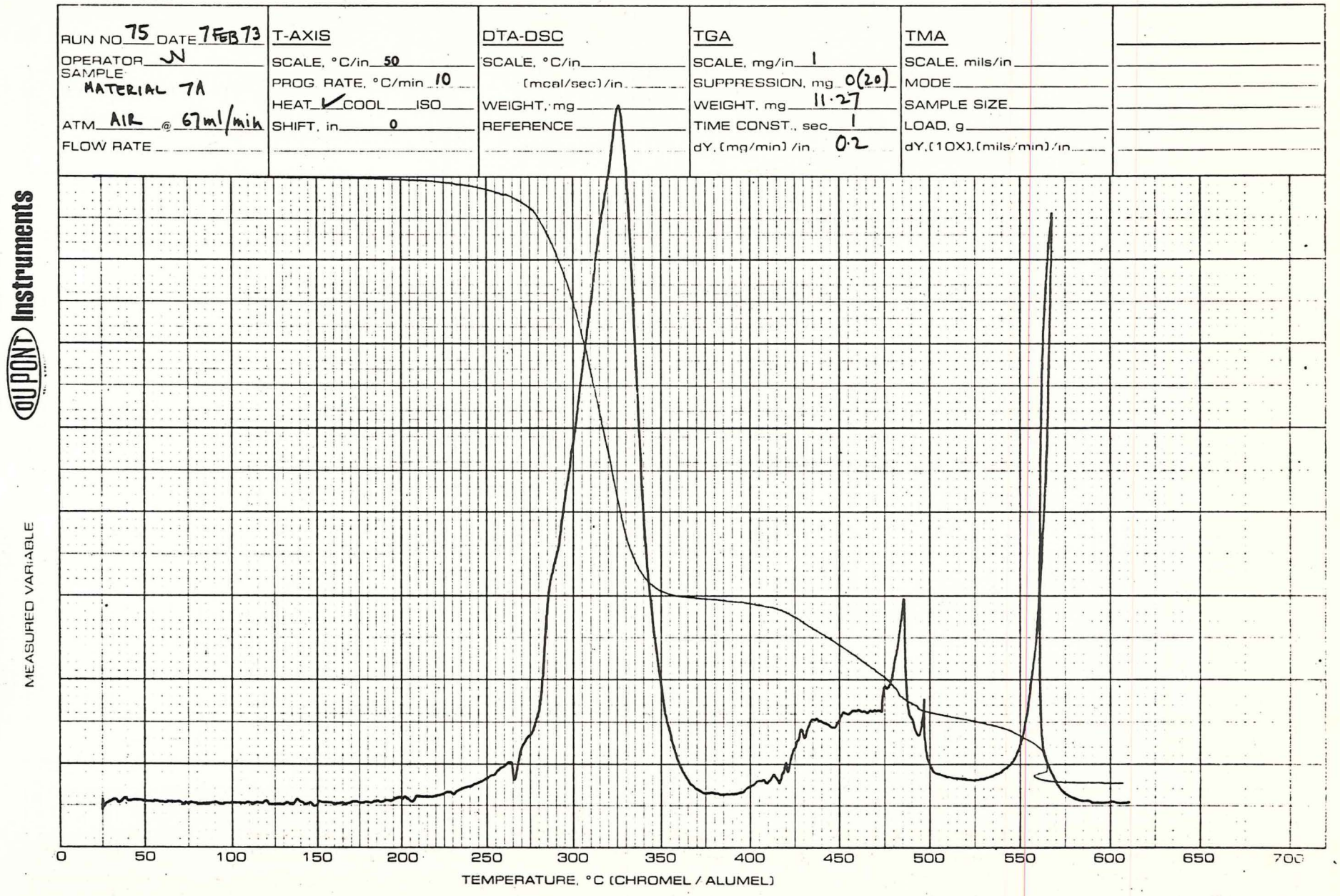


Figure 19

TGA of Polyvinyl Chloride Composition 7A

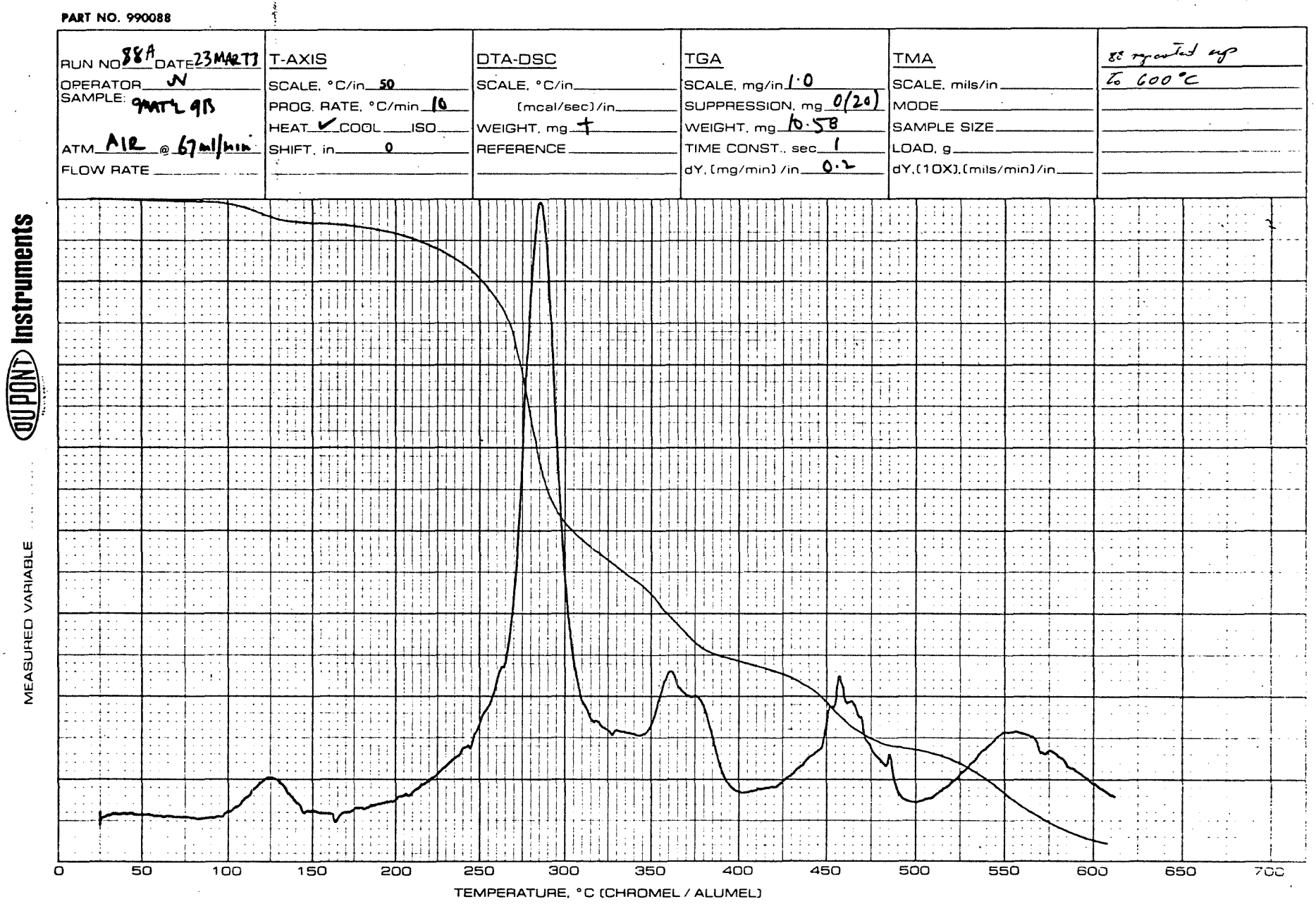


Figure 20

TGA of Polyvinyl Chloride Composition 9B

TABLE XXII

COMPARISON OF CHLORINE CONTENT VALUES

AS OBTAINED BY DIFFERENT MEANS FOR PVC

COMPOSITIONS

HCl FORMATION

Sample	HCl Found, %		Weight Loss, % TGA	Theory %
	Sealed System	Stagnation Burner		
"PVC"	55.1	42.1	58.7	58.34
6A	17.4	16.9	37.5	-
7A	26.4	14.7	50.0	-
13A	25.4	18.4	53.7	-
9B	20.6	15.5	43.5	-

peak correspond to hydrogen chloride evolved. In all the other instances the values are too high by ca a factor of two. This shows clearly that other processes, in addition to hydrogen chloride evolution, which are caused by the other ingredients present in polyvinyl chloride containing compositions, result in the observed weight loss. This was not the case in neoprene formulations wherein the first TGA weight loss reflected fairly truly the hydrogen chloride evolved (not the theoretical hydrogen chloride content).

The thermal and thermal oxidative behavior of polyvinyl chloride compositions has been studied very extensively; some of the work has been reviewed under the past contract [1] and the more recent review by Wagner [13] provides additional information.

Under this program the polyvinyl compositions listed in Table XXI were subjected to thermal oxidative degradations using the sealed system and stagnation burner arrangements. In Tables XXIII and XXIV are given the experimental details and product distribution for the sealed tube studies whereas in Table XXV are summarized the experimental details for stagnation burner tests.

TABLE XXIII

EXPERIMENTAL DATA

FOR SEALED TUBE DEGRADATIONS OF PVC COMPOSITIONS

Sample Ident[a]	Tube V ml	Initial P mm	Final P mm	Reac Temp °C	Sample Wt mg	Residue		Weight Loss mg	Oxygen Consumed		Total Products	
						mg	%[b]		mg	%[c]	mg[d]	%[e]
PVC	2047	503.3	585.3	368	611	201	32.9	410	46.1	12.3	402.1	88.1
6A	2047	507.1	529.9	370	637	243	38.1	394	35.9	9.5	187.9	43.7
13A	2045	495.8	548.9	369	628	231	36.8	397	25.4	4.0	267.8	63.4
7A	2047	505.2	548.9	368	632	224	35.4	408	16.1	4.3	282.8	66.7
9B	2045	507.1	540.2	371	625	188	30.1	437	52.2	14.2	328.1	67.1
10B	2045	511.7	559.9	375	640	250	39.2	390	52.9	14.0	311.9	70.5

a Material identification is given in Table XXI.

b Percent 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 sides of the tube.

c Percent of oxygen available.

d Includes the HCl found in the residue and in the bottom of the reaction flask.

e Percent of total products expected based on sample weight loss and oxygen consumed.

TABLE XXIV

PRODUCT DISTRIBUTION FOR SEALED TUBE

DEGRADATIONS OF PVC COMPOSITIONS

Sample Ident[a]	Noncondensibles					Condensibles								
	Total mmol[b]	CO		CH_4		Total mg	-196°C Frac		-78°C Frac		-23°C Frac		R.T.[d] Frac	
		mg	%[c]	mg	%[c]		mg	%[c]	mg	%[c]	mg	%[c]	mg	%[c]
PVC	54.71	12.0	23.6	0.49	0.08	388.0	329.5	53.9	38.5	6.3	12.7	2.1	7.3	1.2
6A	55.82	3.1	0.5	0.13	0.02	165.1	105.8	16.6	27.3	4.3	0.2	0.03	31.8	5.0
13A	54.33	3.2	0.3	0.34	0.05	262.8	193.3	30.8	41.2	6.6	23.7	3.8	4.6	0.7
7A	55.28	3.6	0.6	0.35	0.06	278.3	184.8	29.2	23.8	3.8	14.9	2.4	54.8	8.7
9B	55.23	5.6	0.9	0.53	0.08	314.7	144.0	23.0	52.6	8.4	41.1	6.6	77.0	2.3
10B	55.54	3.7	0.6	1.24	0.19	305.7	210.3	32.9	72.3	11.3	22.1	3.5	1.0	0.2

a Material identification is given in Table XXI.

b This is mainly air.

c Percent of the weight of the starting material.

d Room temperature.

TABLE XXV

SUMMARY OF EXPERIMENTAL DATA FOR STAGNATION

BURNER EXPERIMENTS PERFORMED ON PVC COMPOSITIONS

Sample Ident[a]	Gas Temp °C	Block Temp °C	Sample Wt mg	Residue		-196°C Frac		-78°C Frac		-23°C Frac		R.T.[c] Frac	
				mg	%[b]	mg	%[b]	mg	%[b]	mg	%[b]	mg	%[b]
PVC	398	394	968	344	35.5	327.4	33.8	52.8	5.5	363.8	37.6	64.6	6.7
6A	406	394	1035	373	36.0	123.5	11.9	29.5	2.9	322.3	31.1	192.2	18.6
13A	407	402	1038	363	34.9	149.1	14.4	59.6	5.8	341.7	32.9	159.2	15.3
7A	407	402	1230	433	35.2	130.0	10.6	29.5	2.4	242.1	19.7	174.4	14.2
9B	403	401	1002	265	26.5	114.0	11.4	55.2	5.5	159.8	16.0	209.2	20.9

a Material identification is given in Table XXI.

b Percent of the weight of the starting material.

c Room temperature.

The results of the gas chromatographic analyses for both of these decomposition procedures are presented in Tables XXVI to XXXVI. Examining these data and comparing the final product compilations listed in Tables XXXVII and XXXVIII it is apparent that no large differences exist between the results of the sealed system and the stagnation burner tests. Even the amounts of residues correspond fairly closely and agree exceptionally well with the TGA values at the given temperatures. This is not surprising since in no instance was glow observed. It should be mentioned that once glow or combustion occurs the product mix changes drastically as was evidenced in the neoprene investigations (see Section 3.2) and as will become apparent later from the wood studies (see Section 3.5). The vacuum line fractionation was again found very effective in these studies of PVC compositions. The -196°C fraction consisted mainly of hydrogen chloride. In the case of the "pure" resin it amounted to above 90%. In other instances the value varied from the high seventies up to 90%. A typical infrared spectrum of a -196°C fraction (stagnation burner degradation of material 13A) is depicted in Figure 21 showing the presence of CH moieties (3.36, 3.42μ) hydrogen chloride (fine structure at 3.5 - 3.7μ), carbon dioxide (4.27, 13.86, 14.93μ), ethyl chloride (7.68, 7.80μ), CH_3OH (9.70μ), ethylene (10.5μ), and methyl chloride (13.65μ). The -78°C fractions usually consisted of organic materials admixed with the aqueous solution of hydrogen chloride. In the case of the "pure" resin the major organic component was benzene with just traces of other materials. However the other compositions afforded a variety of products. This is apparent from the infrared spectrum given in Figure 22 (-78°C fraction from the sealed tube decomposition of material 13A). Benzene is still the main component (3.28, 3.32, 5.1, 5.5, 5.55, 6.67, 6.72, 14.55, 14.87, 15.93μ) admixed with carbonyl compounds (5.70μ), possibly esters (8.0μ), $>CH=CH_2$ unsaturates (10.05, 10.95μ) and toluene (13.70μ). The presence of vinyl groups in conjunction with the absorption in the 8-9μ region would tend to indicate the presence of acrylates.

TABLE XXVI

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON "PURE" PVC [a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
			3.0	C_2H_4
			5.6	HCHO ?
6.1	5.9	6.2	6.2	H_2O, HCl
			9.0	CH_3Cl
		10.3		CH_3OH
11.6		11.5		C_2H_3Cl, CH_3CHO
12.8	12.4		12.8	RSH ?
13.5		13.3		$HCOOCH_3$?
		13.9	13.8	C_2H_5Cl, C_2H_5OH
14.6	15.0		14.5	C_4-species ?
16.4	16.7	16.3		CH_2=CHCHO ?
17.4	17.4	17.3	17.0	$(CH_3)_2CO$, i-C_3H_7OH
			18.1	?
		18.5	18.8	CH_3COOH, n-C_3H_7OH
		22.9		C_4H_5Cl
29.1	26.2	28.5	29.3	C_6H_6
30.5				?

a Material identification is given in Table XXI.

b Room temperature.

c Retention time in minutes.

TABLE XXVII

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON PVC COMPOSITION 6A[a]

R.T.[b] Frac[c] r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
		3.1	C_2H_4
		3.8	C_2H_6
6.1	6.1	6.3	H_2O, HCl
		8.3	C_3H_6
		8.8	C_3H_8, SO_2 ?
		9.2	CH_3Cl
11.7			CH_3CHO
12.9	13.3		?
13.5		13.9	C_2H_5OH, C_4-ene
		14.4	C_2H_5Cl, C_4-species ?
14.8		14.7	?
	16.4	16.0	HCOOH, ?
17.4	17.2	17.4	$(CH_3)_2CO$, CH_2=CHCHO ?
	19.9	19.8	n-C_3H_7OH, CH_3COOH
		20.1	?
	23.2		C_4H_5Cl
		26.1	C_6H_{10}
	28.3	28.5	C_6H_6

a Material identification is given in Table XXI.

b Room temperature.

c Retention time in minutes.

TABLE XXVIII

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON PVC COMPOSITION 13A[a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
			1.8	CO_2
			3.0	C_2H_4
			3.8	C_2H_6
		4.3		HCHO ?
6.2	5.9	5.8	6.0	H_2O, HCl
			8.2	C_3H_6
			8.7	C_3H_8, SO_2
		9.1	9.1	CH_3Cl
11.5				CH_3CHO
	12.7		12.8	RSH ?
			13.8	C_4-ene, C_2H_5OH
14.5	14.5	14.5	14.5	C_2H_5OH, C_2H_5Cl
16.9				$(CH_3)_2CO$?, CH_2=CHCHO ?
	18.3	18.3		i-C_3H_7OH, $HCOOC_2H_5$
		18.9	18.9	CS_2 ?
19.3	19.2	19.6	19.5	n-C_3H_7OH, CH_3COOH
		20.1		C_5-species ?
23.1	23.2			C_4H_5Cl
	24.2			C_6-species ?
	27.0	25.6	26.1	$(CH_2Cl)_2$
28.7	28.7	28.3	29.1	C_6H_6

a Material identification is given in Table XXI.

b Room temperature.

c Retention time in minutes.

TABLE XXIX

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON PVC COMPOSITION 7A[a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
			1.8	CO_2
			2.9	C_2H_4
			3.6	C_2H_6
5.8	5.8	5.7	6.0	HCl, H_2O
			7.9	C_3H_6
			8.4	C_3H_8
			8.8	CH_3Cl
		9.8		CH_3OH
	11.5		11.4	CH_3CHO, C_2H_3Cl
		12.4	12.4	RSH ?
			13.0	$HCOOCH_3$?
			13.4	C_4-ene
		14.2	14.0	C_2H_5Cl ?, C_2H_5OH
16.8		16.9	16.6	$(CH_3)_2CO$, CH_2=CHCHO ?
	17.5	17.5	17.6	i-C_3H_7OH, $HCOOC_2H_5$?
			18.4	CS_2
		19.4	19.2	n-C_3H_7OH, CH_3COOH
	19.8			CH_3COOH
20.2	20.6			C_5-species ?
		21.8		$CH_3COC_2H_5$?
	23.2	22.9		C_6-species ?
			24.0	?
		25.7		$(CH_2Cl)_2$?
28.3		27.4	27.6	C_6H_6

a Material identification is given in Table XXI.

b Room temperature.

c Retention time in minutes.

TABLE XXX

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON PVC COMPOSITION 9B[a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
			1.8	CO_2
			2.8	C_2H_4
			3.6	C_2H_6
5.2				HCHO ?
5.9	5.9	6.0	5.9	H_2O, HCl
			7.9	C_3H_6
			8.4	C_3H_8, SO_2
			8.9	CH_3Cl
		9.9		CH_3OH
12.6				?
13.9		13.2	13.5	C_2H_5OH, C_4-ene, $HCOOCH_3$?
			14.0	C_2H_5Cl
			14.3	?
15.7		15.7		HCOOH
	16.9	16.9	17.1	$(CH_3)_2CO$, CH_2=CHCHO ?
18.5	18.5	18.4	18.5	i-C_3H_7OH, CH_3COOCH_3 ?
		18.8		?
19.0	19.0	19.2	19.1	n-C_3H_7OH, CH_3COOH
		19.9	19.8	C_5-species ?, isoprene
20.7	20.7	20.6	20.7	C_4-species (oxygenated) ?
		22.8		$CH_3COC_2H_5$?
	23.9	23.7		C_6-species ?
24.7	24.5	25.5	25.8	C_6-species ?
	28.1	28.3	29.0	C_6H_6
		29.9		?
		31.8		?
		33.2		$C_6H_5CH_3$?

a Material identification is given in Table XXI.

b Room temperature.

c Retention time in minutes.

TABLE XXXI

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON PVC COMPOSITION 10B[a]

-23°C Frac r.t.[b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
		2.9	C_2H_4
		3.7	C_2H_6
5.8	5.8	5.9	H_2O, HCl
		8.0	C_3H_6
		8.5	C_3H_8, SO_2
	9.0	9.0	CH_3Cl
	9.9		CH_3OH
		11.6	CH_3CHO
	12.5	12.6	RSH ?
	13.2		$HCOOCH_3$?
	13.7	13.6	C_4-ene, C_2H_5OH
14.2	14.2	14.2	?, C_2H_5Cl
15.5	15.6		HCOOH
16.2			?
17.0	17.0	16.7	$(CH_3)_2CO$, CH_2=CHCHO ?
18.3	18.3		i-C_3H_7OH, CH_3COOCH_3 ?
	18.9	18.7	C_5-species ?
19.3	19.3	19.3	n-C_3H_7OH, CH_3COOH
	20.8		?
	22.9		$CH_3COC_2H_5$?
24.0	23.6		C_6-species ? C_4H_5Cl
	25.5	26.1	?
	28.0	28.3	C_6H_6

a Material identification is given in Table XXI.

b Retention time in minutes.

TABLE XXXII

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON "PURE" PVC [a]

$-23^{\circ}C$ Frac r.t. [b]	$-78^{\circ}C$ Frac r.t.	$-196^{\circ}C$ Frac r.t.	Peak Identification
1.9	1.9	1.9	CO_2
		3.0	C_2H_4
		3.9	C_2H_6
6.2	6.4	6.2	H_2O, HCl
		8.3	C_3H_6
		8.8	C_3H_8, SO_2
		9.2	CH_3Cl
	11.6	11.7	CH_3CHO, C_2H_3Cl
	12.8	12.8	RSH ?
		14.5	C_4-species, C_2H_5Cl ?
	15.4		HCOOH
		16.4	CH_2=CHCHO ?
	17.1		$(CH_3)_2CO$
	19.6		n-C_3H_7OH, CH_3COOH
28.8	27.6	29.0	C_6H_6
	28.8		?

a Material identification is given in Table XXI.

b Retention time in minutes.

TABLE XXXIII

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON PVC COMPOSITION 6A[a]

-23°C Frac[b] r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
		2.3	?
		3.0	C_2H_4
		3.6	C_2H_6
6.0	5.9	5.9	H_2O, HCl
		6.7	COS
		7.9	C_3H_6
9.0		8.8	CH_3Cl
12.6			RSH ?
		13.4	C_4-ene
		14.0	C_2H_5Cl, C_2H_5OH
		14.3	C_4-species ?
	16.9		$(CH_3)_2CO$, CH_2=CHCHO ?
	17.6	18.4	i-C_3H_7OH
19.0	18.8	18.8	C_5-species ?
	19.7	19.6	n-C_3H_7OH, CH_3COOH
20.9	21.4		C_4-species (oxygenated) ?
23.5	23.6		C_6-species ?
		25.5	C_6H_{10}
	26.5		?
	28.2	27.9	C_6H_6
	31.0		?

a Material identification is given in Table XXI.

b Retention time in minutes.

TABLE XXXIV

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON PVC COMPOSITION 13A[a]

-23°C Frac r.t.[b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
1.9	1.8	1.9	CO_2
		3.0	C_2H_4
		3.7	C_2H_6
5.7	5.8	5.5	H_2O, HCl
		8.1	C_3H_6
		8.6	C_3H_8, SO_2
	8.8	9.0	CH_3Cl
	9.7		CH_3OH
11.3	11.2		CH_3CHO
		11.6	C_2H_3Cl
	12.4		RSH ?
13.1	13.0		$HCOOCH_3$?
		13.6	C_4-ene
14.6	14.0		C_2H_5OH
	14.2	14.4	C_2H_5Cl
	16.9		$(CH_3)_2CO$, CH_2=CHCHO ?
17.9	17.9		i-C_3H_7OH, $HCOOC_2H_5$
	18.8	18.7	CH_3COOCH_3 ?
19.4	19.5	19.2	n-C_3H_7OH, CH_3COOH
	20.8	19.9	C_5-species ?
	22.5		$CH_3COC_2H_5$?
	23.4		C_6-species ?
	24.8		C_6-species ?
	26.0	25.8	?
28.4	27.8	28.8	C_6H_6

a Material identification is given in Table XXI.

b Retention time in minutes.

TABLE XXXV

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON PVC COMPOSITION 7A[a]

-23°C Frac[b] r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
1.9	1.9	1.8	CO_2
		3.0	C_2H_4
		3.7	C_2H_6
5.8	5.9	6.2	HCl, H_2O
		8.0	C_3H_6
		8.5	C_3H_8
8.7	8.8	9.0	CH_3Cl
	10.2		CH_3OH
		11.7	CH_3CHO ?
12.3	12.4	12.7	RSH ?
		13.4	$HCOOCH_3$?
		13.7	C_4-ene
14.1	14.2	14.2	C_2H_5OH, C_2H_5Cl
		14.6	C_2H_5Cl ?
16.9	17.3	17.8	$(CH_3)_2CO$, CH_2=CHCHO ?
18.0	18.1		i-C_3H_7OH, $HCOOC_2H_5$
18.6	18.7	18.6	C_5-species ?
19.6	19.4	19.6	n-C_3H_7OH, CH_3COOH
	22.6		$CH_3COC_2H_5$?, C_3H_7CHO ?
27.7	27.2	28.2	C_6H_6

a Material identification is given in Table XXI.

b Retention time in minutes

TABLE XXXVI

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON PVC COMPOSITION 9B [a]

-23°C Frac r.t. [b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
		3.0	C_2H_4
		3.8	C_2H_6
5.8	5.8	6.1	HCl, H_2O
		8.2	C_3H_6
		8.7	C_3H_8
9.0	9.0	9.1	CH_3Cl
12.5	12.6		?
		13.7	C_4-ene
		14.2	C_2H_5Cl
		14.5	C_2H_5OH ?
	17.3		$(CH_3)_2CO$?, CH_2=CHCHO ?
		18.6	i-C_3H_7OH ?
19.2	19.3	19.0	CH_3COOH, n-C_3H_7OH
		19.6	Isoprene
	21.8		$CH_3COC_2H_5$?
		22.5	?
	22.9	23.0	C_6H_{12}
24.5	23.9	24.6	C_6H_6
	29.2		C_7-species ?
	31.2		$C_6H_5CH_3$
	34.5		?
	36.6		4-Methyl cyclohexanone ?
	40.0		$C_6H_{13}Cl$

a Material identification is given in Table XXI.

b Retention time in minutes.

TABLE XXXVII

PRODUCTS OF PVC COMPOSITIONS[a]

(SEALED TUBE STUDIES)

Products	PVC mg/g	6A mg/g	13A mg/g	7A mg/g	9B mg/g	10B mg/g
CO	19.7	4.84	5.02	5.65	8.91	5.83
CH_4	0.80	0.20	0.54	0.55	0.85	1.94
HCl	550.6	174.2	253.7	263.5	205.8	300.0
CO_2	12.1	29.1	18.1	19.0	32.4	33.7
SO_2	0.38	0.25	0.37	-	-	0.22
COS	-	0.16	-	-	-	-
CS_2	-	-	-	0.36	-	-
C_xH_y[b]	1.51	1.71	6.14	2.87	2.18	4.52
Isoprene	-	-	-	-	0.66	-
C_6H_6	47.5	5.12	26.7	25.4	35.8	19.5
C_6H_{12}	-	1.05	-	-	-	-
$C_6H_5CH_3$	0.61	0.57	1.51	0.84	0.42	0.58
$C_6H_4(CH_3)_2$	0.08	0.03	0.08	0.11	0.02	0.02
CH_3Cl	0.44	3.75	3.19	T	0.72	0.48
C_2H_3Cl	0.05	-	-	0.05	-	-
C_2H_5Cl	0.03	1.10	20.7	T	0.34	0.33
$(CH_2Cl)_2$	0.10	-	0.81	-	-	-
C_4H_5Cl	0.56	0.02	0.19	-	-	0.31
$C_6H_{13}Cl$	0.10	0.16	-	0.11	0.35	-
$C_6H_5CH_2Cl$	0.03	-	-	T	-	-
CH_3OH	0.03	0.03	0.05	0.06	0.05	0.06
C_2H_5OH	0.02	T	1.10	0.28	4.88	0.66
n-C_3H_7OH	0.03	0.23	0.43	0.02	1.18	1.11
i-C_3H_7OH	0.07	-	T	0.08	0.40	0.16
HCHO	?	?	?	?	?	0.06
CH_3CHO	0.13	T	0.02	0.09	-	0.02
$(CH_3)_2CO$	0.07	0.64	0.03	1.44	2.82	1.36
HCOOH	-	T	-	-	0.16	0.13
CH_3COOH	0.06	0.23	0.30	0.03	0.72	0.50

a Material identification is given in Table XXI.

b C_xH_y denotes hydrocarbons C_2 through C_4.

TABLE XXXVIII

PRODUCTS OF PVC COMPOSITIONS[a]

(STAGNATION BURNER STUDIES)

Products	PVC mg/g	6A mg/g	13A mg/g	7A mg/g	9B mg/g
HCl	421.4	168.6	184.4	146.9	155.4
CO_2	49.2	23.2	22.6	31.6	24.0
SO_2	0.23	0.12	0.40	-	-
COS	-	0.11	-	-	-
C_xH_y[b]	1.92	0.65	3.03	0.90	0.33
C_6H_6	39.4	16.0	33.3	17.6	32.0
C_6H_{12}	-	0.73	-	-	-
$C_6H_5CH_3$	0.40	0.48	0.02	0.09	0.50
$C_6H_4(CH_3)_2$	0.20	0.02	T	T	T
CH_3Cl	0.36	3.31	2.49	0.51	0.13
C_2H_3Cl	-	0.16	0.15	-	-
C_2H_5Cl	T	0.50	12.4	0.24	0.03
$C_6H_{13}Cl$	-	-	0.05	-	2.11
$C_6H_5CH_2Cl$	-	0.01	-	-	-
CH_3OH	0.01	0.03	0.04	0.03	0.04
C_2H_5OH	-	T	7.22	0.38	0.05
n-C_3H_7OH	T	0.04	0.48	T	T
i-C_3H_7OH	0.01	0.02	0.06	0.01	T
HCHO	?	?	?	?	?
CH_3CHO	0.16	-	0.77	-	-
$(CH_3)_2CO$	0.01	0.15	0.59	1.26	0.02
HCOOH	0.10	-	-	-	-
CH_3COOH	0.01	0.04	0.47	0.38	0.14
$HCOOC_2H_5$	-	-	0.56	0.02	-
4-Methylcyclo-hexanone	-	-	-	-	2.08

a Material identification is given in Table XXI.

b C_xH_y denotes hydrocarbons C_2 through C_4.

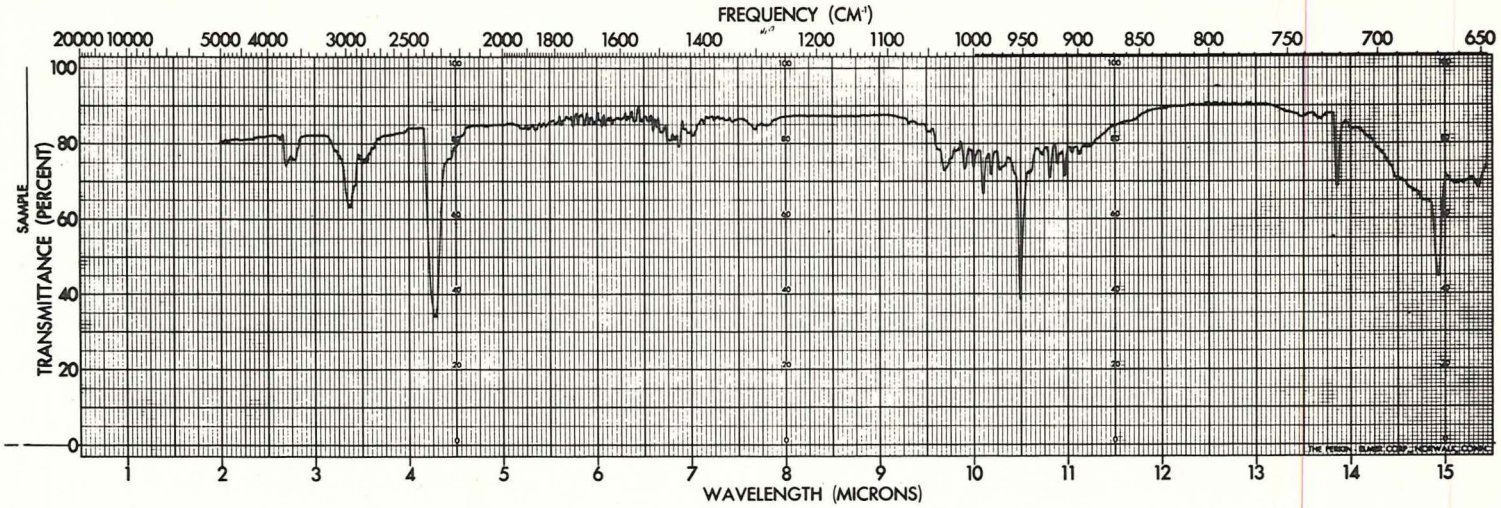


Fig. 21. Infrared Spectrum of -196°C Fraction
Stagnation Burner Treatment of PVC Composition 13A (gas, p = 140 mm)

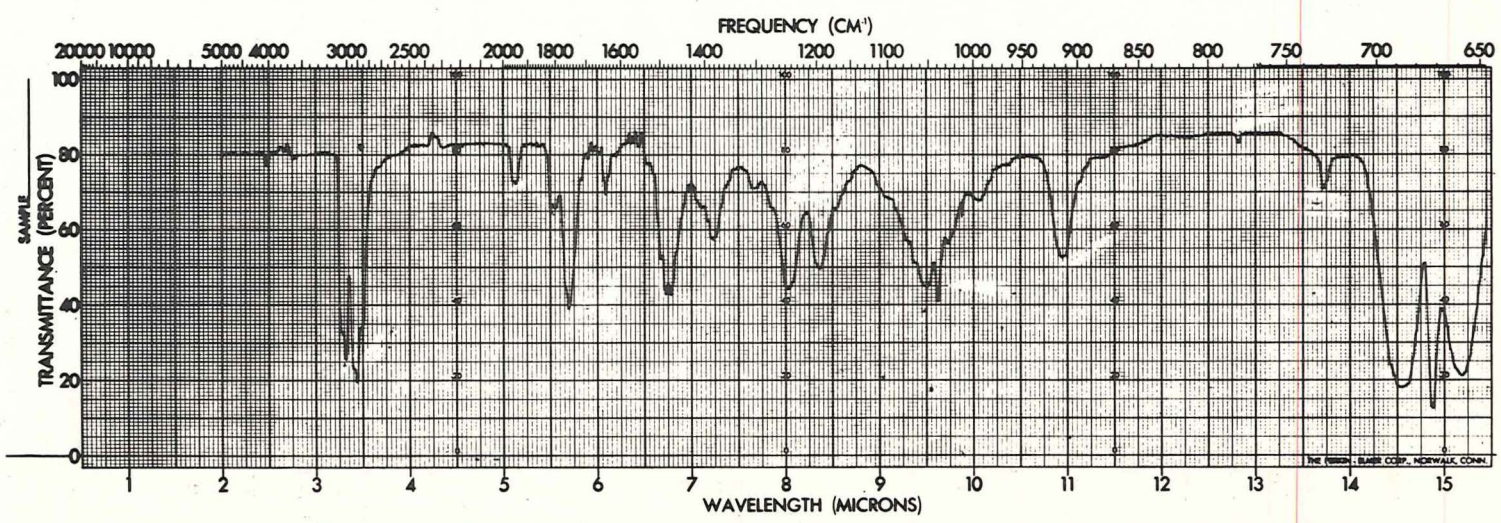


Fig. 22. Infrared Spectrum of -78°C Fraction
Sealed Tube Treatment of PVC Composition 13A (gas, p ~46 mm)

Material 6A, a polyvinyl chloride composition presented an even more complicated product mix which could be anticipated based on the TGA results (see Figure 17). Benzene no longer was the main hydrocarbon produced as evidenced by infrared, mass spectral and gas chromatographic analyses. Actually the benzene found was lower than would be deduced from the evolved hydrogen chloride (basing the amount of PVC present in the original material on hydrogen chloride formed). On the other hand, methyl chloride produced was about an order of magnitude higher than in the "pure" PVC. The mass spectral analyses of the -78°C fraction indicate that the organic portion is composed largely of C_6 skeleton derived compounds both cyclic and linear (m/e, 112, 84, 83, 82, 69, 70, etc., but mainly 55, 56, and 41). This finding in conjunction with the presence of carbonyls in all except the -196°C fraction, would tend to indicate that possibly nylon-66 was the nylon component of this brattice cloth. It should be added that under the somewhat more drastic stagnation burner conditions a portion of the C_6 compounds was transformed into benzene (compare Tables XXXVII and XXXVIII). Based on mass spectral evidence, materials such as tolualdehyde (m/e = 119, 120) appear to have been also produced together with higher aromatics (napthalenes), C_3- and C_4-substituted benzenes and possibly chlorinated aromatics (m/e, 155, 140, 126, 120, 119, 118). The m/e, 126 peak has been ascribed to benzyl chloride (TLV, 1 ppm). This compound was also found by Boettner et al[12] on thermal oxidative degradation of polyvinyl chloride compositions. All these materials seemed to be present in very small quantities, at least in the volatile fractions. Examination of the products that are relatively involatile at room temperature is necessary to ascertain the formation of these types of species.

In the case of the sealed tube experiments the -23°C and room temperature fractions were composed essentially of water as shown by gas chromatography and infrared spectroscopy; however in the room temperature fraction, the presence of carbonyls could be noted by absorptions in the 5.6 - 6.1μ region. These fractions did contain alcohols of which ethanol and C_3 alcohols were identified. There were most likely higher alcohols

also present as shown by the high m/e = 31 peak in the mass spectra, however these were not identified nor were the species responsible for the carbonyl absorption.

The oils and deposits found on the sides of the finger of the sealed system and the room temperature involatile oils in the stagnation burner investigations were found to consist in the case of the polyvinyl chloride compositions, mostly of phthalate esters and phthalic anhydride (TLV, 2 ppm), admixed in certain instances with what appeared to be lactams and/or amides (this was especially evident in material 9B). The lactams and amides are most likely derived from the nylon constituent of these compositions. The production of caprolactam from nylon-6 was disclosed by Smith.[14] The surprising aspect of the current investigation is the lack of detection of amines among the volatiles. On the other hand in the presence of the hydrogen chloride these would be expected to form the involatile hydrochloride salts which nevertheless dissociate at elevated temperatures. Thus, although no amines were detected amongst the sealed tube or the stagnation burner products, this does not mean that in an actual situation of oxidative thermal decomposition of e.g., nylon reinforced brattice cloth, the primary decomposition products HCl (TLV, 5 ppm) and amines (e.g., methyl amine, ethyl amine, TLV, 10 ppm) cannot pose a hazard. It is obvious that amine hydrochloride formation is a rate and concentration controlled process and the procedures employed under this program favored the salt formation, whereas in reality dangerously high concentrations of these toxic materials may exist for considerable lengths of times and at relatively far distances from the point of their formation.

As was discussed above in the majority of instances the oily involatiles were found to consist of a mixture of phthalate esters and phthalic anhydride. A typical spectrum is shown in Figure 23 (involatile stagnation burner products from material 6A) (phthalic anhydride 5.4, 5.57, 5.63μ; dioctyl phthalate 5.77, 7.75, 8.9, 9.3, 13.4μ). Interestingly, in the case

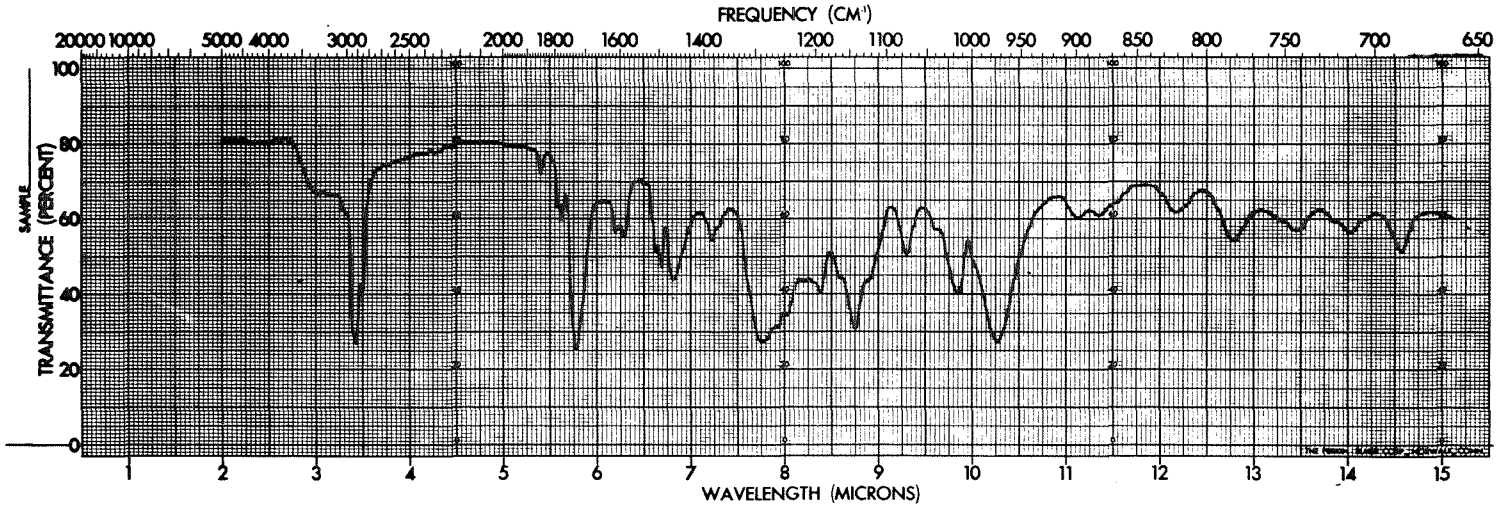


Fig. 23. Infrared Spectrum of Room Temperature Involatile Oils
Stagnation Burner Treatment of PVC Composition 6A (liquid film)

of materials 7A and 9B relatively large quantities of phthalic anhydride were formed as evidenced by the precipitation of white crystals on the walls of the sealed system bulb which were identified by infrared spectrum, melting point, and mixed melting point and found to consist of pure phthalic anhydride. Yet, under the stagnation burner conditions only dioctyl phthalate was obtained. This would tend to indicate that in the dynamic system the plasticizer evaporates mostly unchanged and is immediately swept out of the reaction zone, whereas in the quiescent system, being exposed to heat treatment for a considerable period of time, it undergoes oxidation to phthalic anhydride and other products. Phthalate esters are used extensively as plasticizers in polyvinyl chloride formulations.[15] Their thermal degradations have been studied by Hagen[16], and Wagner[13], in his review mentions the production of phthalic anhydride from polyvinyl chloride materials decomposition.

Other findings of the present investigations are evident from the data given in Tables XXVI through XXXVIII. Among others it is apparent, in particular with respect to compositions 7A and 13A, that production of chlorinated organic species is not necessarily dependent upon the material's polyvinyl chloride content (assuming that the quantity of hydrogen chloride corresponds to the polyvinyl chloride content and that no other chlorinated compounds are present). As can be seen material 7A, which obviously contains less PVC than "pure" PVC resin, produces definitely larger quantities of ethyl chloride than the "pure" resin. Other examples are the increased production of methyl chloride from materials 6A and 13A and of chlorohexane from material 9B when these quantities are compared to those formed from "pure" PVC. Thus one could speculate that it is the environment within the given material, i.e., the nature of the other "composite" ingredients which determines, at least to some extent, the type of products formed. Consequently, the data obtained from a given "pure" composition insofar as the nature and relative product concentration is concerned can be used as a guideline but not as an

absolute measure regarding the expected production of individual species from a composite.

A large amount of controversy exists regarding the formation of hydrogen cyanide from nylons or polyamide type of material. It is noteworthy that we have observed traces of hydrogen cyanide (TLV, 10 ppm) in the -196°C fraction of materials 6A and 9B as shown by the infrared absorption at 14.05μ. Both of these compositions contain nylon.

In none of the analyses have we been able to identify unequivocally the presence of formaldehyde (TLV, 2 ppm) and acrolein (TLV, 0.1 ppm). Yet, based on definite identification of formic acid and its esters and the observation of m/e, 30 in the mass spectra (assuming that this is not derived from amines, NO, or N_2O) we feel certain that formaldehyde is formed. However, as will become apparent later, its quantitation is not easy (see Section 3.5). Regarding acrolein, in a number of the gas chromatographic analyses peaks at retention times of 16 - 16.5 min were observed, yet these were too small to allow unambiguous identification due to the rather commonplace breakdown pattern of acrolein. Isolation of the C_3 alcohols and of acetone would indicate that acrolein is also formed.

In a number of instances we have observed sulfur dioxide, which originates most likely from sulfur containing antioxidants and/or polymerization initiators. The presence of sulfur containing materials is further indicated by the presence of what appear to be mercaptans (gas chromatographic peaks at ca 12.5 min). This postulation is based on the mass spectral pattern, e.g., peaks at m/e 47, 81, 96. It should be noted that these materials were also observed among the neoprene derived volatiles.

If one considers polyvinyl chloride compositions, the main toxic species at the temperatures involved in the current investigations is undoubtedly hydrogen chloride; however, other components which cannot be ignored are benzene, phthalates, the aldehydes and carbon monoxide. The latter, as can be seen from the sealed tube data, does not really pose a great danger.

Based on TLV values benzene (TLV, 25 ppm) which is produced in a larger quantity than carbon monoxide (TLV, 50 ppm) has to be rated as a greater hazard.

3.4 URETHANE RIGID FOAMS

Urethane rigid foams have been finding increasing use in the mines as dust suppression and wall sealing agents in view of their case of application, low density, and reasonable cost.

Under this program three or rather two urethane foam systems listed in Table XXXIX were subjected to the sealed system oxidative thermal degradation.

TABLE XXXIX

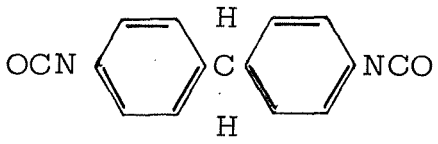
LIST OF INVESTIGATED URETHANE RIGID FOAMS

Material	Origin	Material Description
Polyurethane rigid foam system composition 1B	Manufacturer	Resin component - CCl_3F 22%; polyols, amines, catalyst 78%. Activator component - CCl_3F 5%, isocyanate polymeric, MDI type 94%; manufactured by Callery Chemical Company
Polyurethane rigid foam system composition 2B	Manufacturer	Same as preceding
Polyurethane rigid foam system composition 16A	Bureau of Mines	Urethane-isocyanurate #4 foam; manufactured by Callery Chemical Company

In view of their low density and the size limitations imposed by the stagnation burner gap the sample sizes feasible for the stagnation burner test were considered of too low weight to afford meaningful results. Accordingly no stagnation burner experiments were conducted.

Two of the above materials, 1B and 2B, were obtained directly from Callery Chemical Company; the material 16A was obtained from the Bureau of Mines. The materials 1B and 2B exhibited different physical appearances, although the shipment of three foam samples was accompanied by one data sheet only for the resin and activator systems. Based on the attached data the activator consisted of 5% of Freon-11 ($CFCl_3$) and 94% of isocyanate (polymeric, MDI Type), whereas the resin consisted of 78% of polyols, amines and catalyst and 22% of Freon-11. No details were given in which ratio the activator and resin were combined and how these were cured to produce the resulting rigid foam system. No information was obtained as to the nature and relative quantities of polyols or amines. Regarding the rigid foam received from the Bureau of Mines, the only information available was that it was manufactured by Callery Chemical Company.

Examining the thermogravimetric curves of the two materials received from Callery Chemical Company (see Figures 24 and 25) it is apparent that these are basically identical. The analyses of the products of the thermal oxidative tests further support this. The material 16A exhibited a somewhat similar, yet nevertheless definitely different TGA curve (see Figure 26). Bachus [17, 18] and Einhorn [19], among others, published TGA curves of MDI (4,4'-diphenyl methane diisocyanate) based urethane foams



MDI

in the majority of which the decomposition onset occurred in the vicinity of 200°C, whereas materials 16A, 1B and 2B exhibit a decomposition onset around 100°C. Thus it can be deduced that the materials tested under this program are thermally less stable than those usually encountered. On the other hand, Bachus et al [17] did note that the DTA curves of the foams studied by them showed an endotherm at 85°C due to $CFCl_3$ evolution. Since the nature of the ingredients of materials 16A, 1B and 2 B are not known with the exception of the partial data given for compositions 1B and 2B regarding the blowing agent and the type of isocyanate, it is hard to draw any meaningful conclusions.

PART NO. 990088

RUN NO. 93 DATE 25 APR 73	T-AXIS	DTA-DSC	TGA	TMA
OPERATOR N	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 0.5	SCALE, mils/in
SAMPLE MAT'L 1B	PROG. RATE, °C/min 10	(mcal/sec)/in	SUPPRESSION, mg 0(20)	MODE
	HEAT ✓ COOL ISO	WEIGHT, mg	WEIGHT, mg 5.68	SAMPLE SIZE
ATM AIR @ 67 ml/min	SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g
FLOW RATE			dY, (mg/min) /in 0.2	dY, (10X), (mils/min) /in

DUPONT Instruments

MEASURED VARIABLE

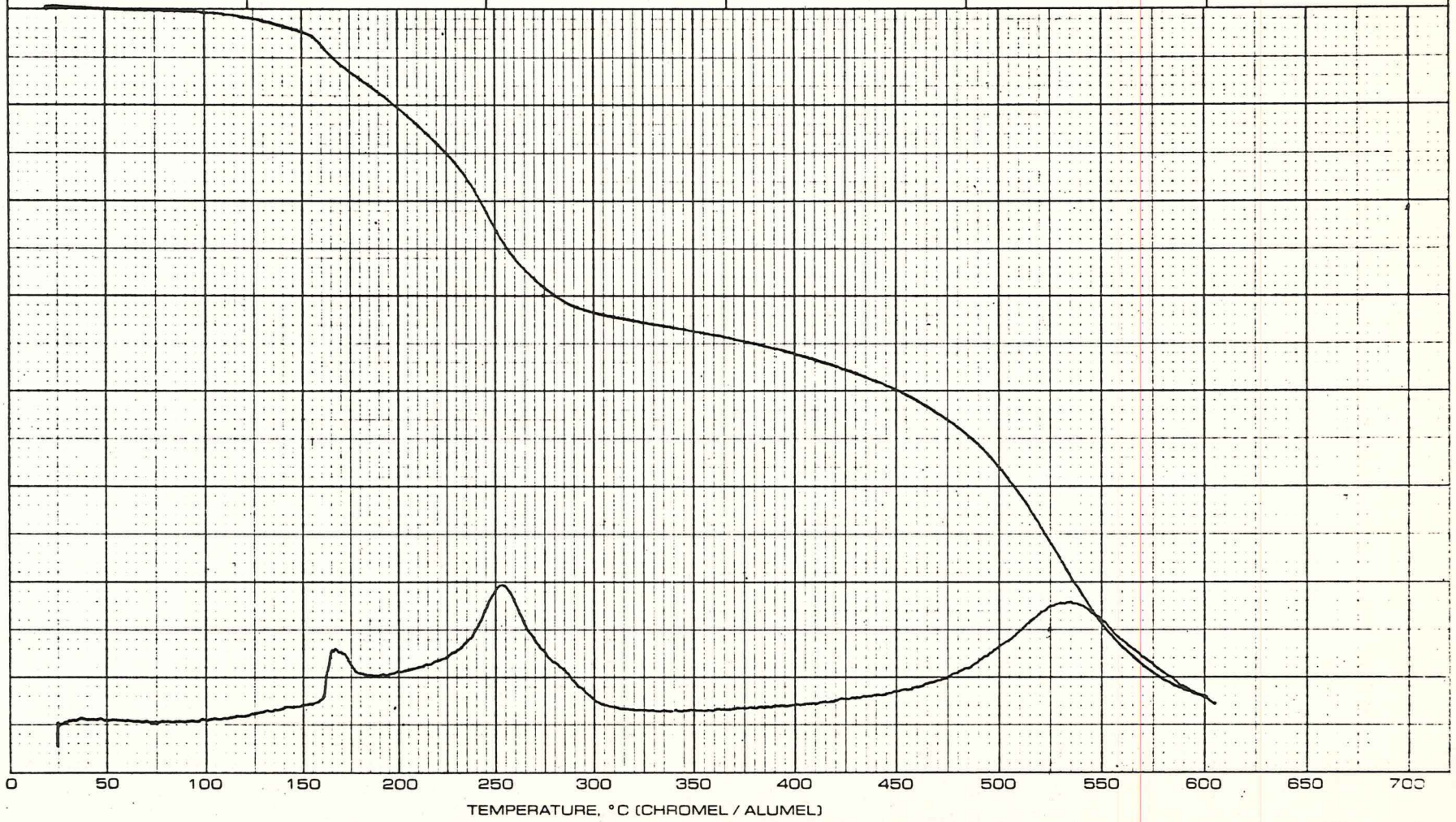


Figure 24

TGA of Urethane Foam Material 1B

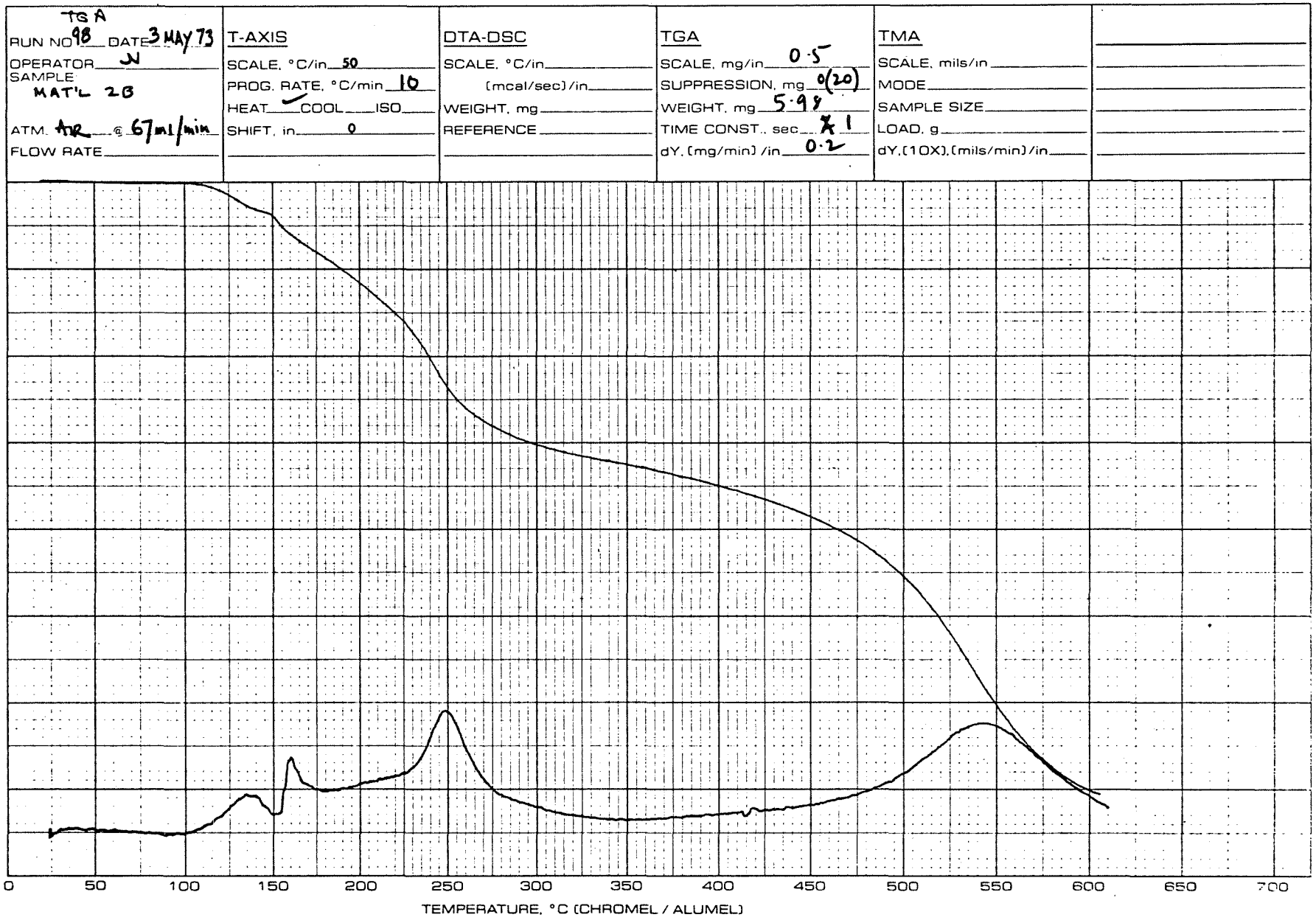


Figure 25

TGA of Urethane Foam Material 2B

PART NO. 990088

RUN NO. 94 DATE 30 Apr 73	T-AXIS	DTA-DSC	TGA	TMA
OPERATOR W	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 0.5	SCALE, mils/in
SAMPLE: MAT'L 16A	PROG. RATE, °C/min 10	(mcal/sec)/in	SUPPRESSION, mg 0(20)	MODE
ATM AIR @ 67ml/min	HEAT ✓ COOL ISO	WEIGHT, mg	WEIGHT, mg 6.01	SAMPLE SIZE
FLOW RATE	SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g
			dY, (mg/min) /in 0.2	dY, (10X), (mils/min)/in

DUPONT Instruments

MEASURED VARIABLE

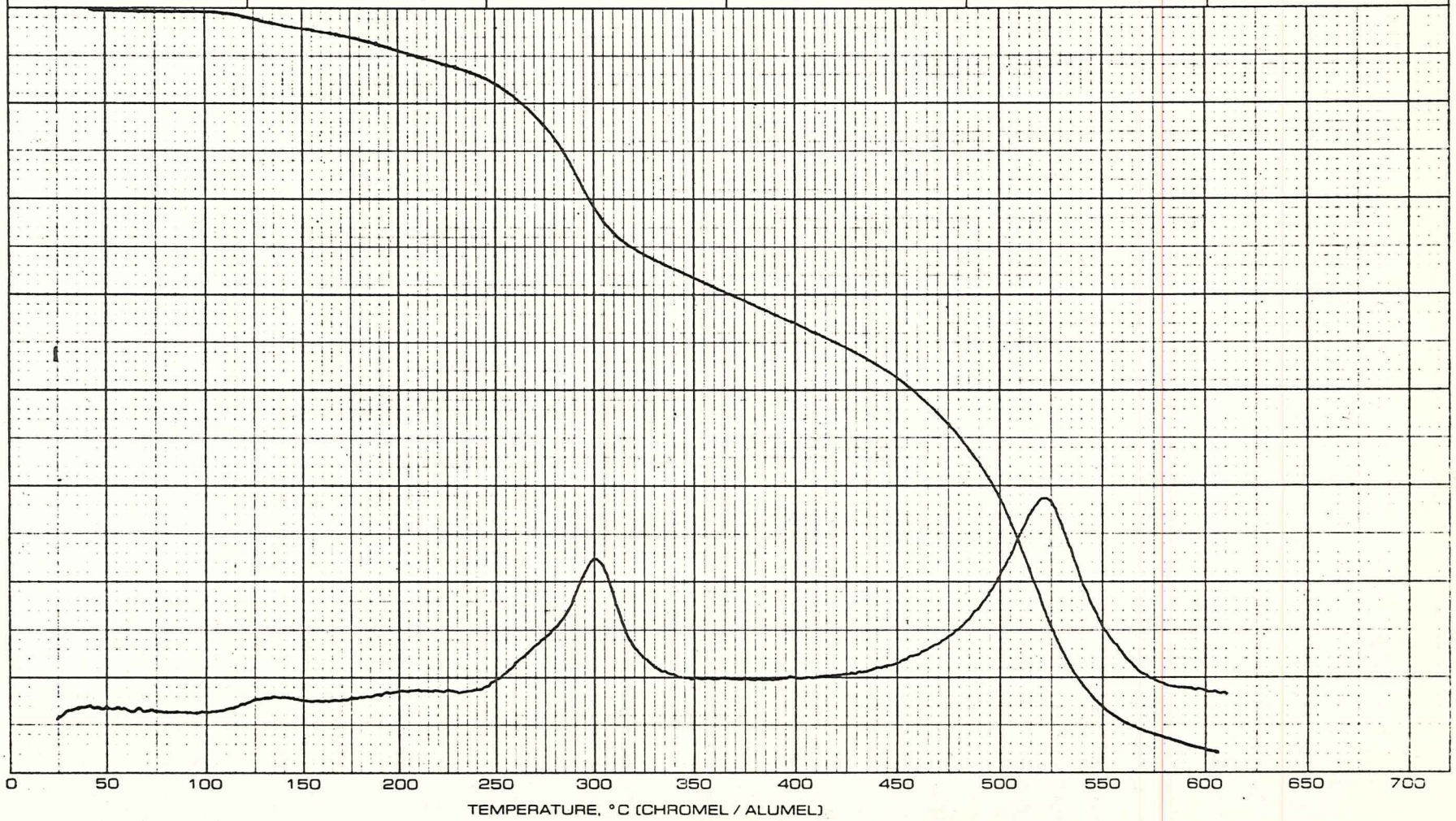


Figure 26

TGA of Urethane Foam Material 16A

The experimental details of urethane foam sealed tube studies are summarized in Table XL whereas the product distribution is presented in Table XLI and the results of the gas chromatographic analyses are given in Tables XLII - XLIV. As was noted above based on the analytical data, namely gas chromatograms (see Tables XLII and XLIII) infrared and mass spectra, obtained for the volatiles formed on oxidative thermal degradation of materials 1B and 2B it is obvious that these are essentially identical compositions. The discrepancies in the actual quantities of individual products formed which are given in Table XLV, can be explained partly by different batches of materials, i.e., depending on the cure and/or speed of ingredient mixing the amount of retained blowing agent will vary. The large discrepancy in the hydrogen chloride content is due to the method of analysis since in the sample 1B a portion of the condensible volatiles was condensed onto sodium hydroxide solution whereas in the case of material 2B pure water was used. It would appear that dehydrohalogenation of chlorine containing species by the alkaline medium is responsible for the relatively high chloride content observed (2.32 versus 0.585%). In the case of sample 1B the variation in the ammonia value is most likely due to the fact that the fraction from material 1B was allowed to stand for several days prior to analysis and the low ammonia (0.31% versus 1.07%) content may thus be the result of product loss. It should be noted that the ammonia was determined by acid titration of a portion of the $-196^{\circ}C$ fraction which was condensed onto water. Since based on infrared spectroscopy (see Figure 28) some ammonia was also present in the other fractions the value given in Table XLV (for material 2B) must be too low, although not significantly so. The vacuum line fractionations, of the volatiles produced from foams 1B and 2B, were found to be very effective in species separation. Thus the $-196^{\circ}C$ fractions consisted mainly of carbon dioxide, Freon-11 ($CFCl_3$), some $CHCl_2F$, ammonia, ethyl chloride and C_2-C_4 hydrocarbons admixed with traces of other chlorinated species, acetone and what appeared to be a carbodiimide and possibly a trace of hydrogen cyanide. In Figure 27 is presented the infrared spectrum of the $-196^{\circ}C$ fraction of material 1B. The presence of CO_2 is shown by absorptions at 4.32, 13.91, and 14.98μ; NH_3 at 3.01, 6.14, 10.35, and 10.74μ; $CFCl_3$ at 9.20 and 11.85μ; $CFCl_2H$ at 8.05, 8.13, and 12.53μ;

TABLE XL

EXPERIMENTAL DATA

FOR SEALED TUBE DEGRADATION OF URETHANE RIGID FOAMS

Sample[a] Ident.	Tube V ml	Initial P mm	Final P mm	React. Temp. °C	Sample Wt mg	Residue		Weight Loss mg	Oxygen Consumed		Total Products	
						mg	%[b]		mg	%[c]	mg[d]	%[e]
1B	2047	510.8	523.9	365	287	32	11.3	255	10.8	2.9	126.0	47.4
2B	2047	507.2	524.5	370	272	50	18.2	222	12.5	3.3	113.5	48.3
16A	2045	502.9	505.9	370	276	148	53.5	128	64.6	17.4	122.2	63.4

a Material identification is given in Table XXXIX.

b Percent 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.

c Percent of oxygen available.

d Includes the HCl found in the residue and in the bottom of the reaction flask.

e Percent of the total products expected based on sample weight loss and oxygen consumed.

TABLE XLI

PRODUCT DISTRIBUTION FOR SEALED TUBE DEGRADATION OF URETHANE RIGID FOAMS

Sample[a] Ident.	Noncondensibles					Condensibles								
	Total[b] mmol	CO		CH_4		Total mg	$-196^{\circ}C$ Frac		$-78^{\circ}C$ Frac		$-23^{\circ}C$ Frac		R.T.[d] Frac	
		mg	%[c]	mg	%[c]		mg	%[c]	mg	%[c]	mg	%[c]	mg	%[c]
1B	55.93	-	-	0.46	0.16	122.1	77.0	26.8	19.5	6.8	5.6	1.9	20.0	7.0
2B	55.92	-	-	0.26	0.10	112.2	63.4	23.3	25.0	9.2	20.2	7.4	3.6	1.3
16A	54.82	9.52	3.5	0.65	0.24	107.7	56.3	20.4	38.4	13.9	12.1	4.4	0.9	0.3

a Material identification is given in Table XXXIX.

b This is mainly air.

c Percent of the weight of the starting material.

d Room temperature.

TABLE XLII

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON URETHANE RIGID FOAM 1B [a]

R.T. [b] Frac r.t. [c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	1.8	CO_2
			3.0	C_2H_4
			3.7	C_2H_6
5.8	5.8	6.0		HCl, H_2O
			8.1	C_3H_6
			8.6	C_3H_8
			9.0	CH_3Cl
			11.6	C_2H_3Cl
			14.4	C_2H_5Cl
		14.7		C_2H_5OH
			15.0	$CHFCl_2$?
		17.3	17.1	$(CH_3)_2CO$, $CFCl_3$
17.6	17.5	17.6		i-C_3H_7OH
			18.9	CH_2Cl-CH=CH_2
		19.2		n-C_3H_7OH
			19.6	C_5 species ?
	19.8	19.8		CH_3COOH
		21.7		$CH_3COC_2H_5$
		22.1		?
		23.1	23.2	CH_2Cl-CH_2Cl
23.6	23.5	23.7		CH_2Cl-CH_2OH
	24.8	24.6	24.6	C_6H_6
26.7	26.6	26.5		1-chloro-2-propanol, 1,4-dioxane
	27.5			?

a Material identification is given in Table XXXIX.

b Room temperature.

c Retention time in minutes.

TABLE XLIII

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON URETHANE RIGID FOAM 2B [a]

-23°C Frac r.t. [b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
	1.9	1.8	CO_2
		3.0	C_2H_4
		3.7	C_2H_6
		4.6	NH_3
5.8	6.1	6.1	H_2O, HCl
		8.2	C_3H_6
		8.6	C_3H_8
		9.1	CH_3Cl
		11.7	C_2H_3Cl
		13.7	C_4-ene
	14.5	14.5	C_2H_5OH, C_2H_5Cl
		15.1	$CHFCl_2$?
	15.9		HCOOH
	17.2	17.1	$(CH_3)_2CO$, $CFCl_3$
17.4			i-C_3H_7OH
	18.8		n-C_3H_7OH ?
		19.0	CH_2Cl-CH=CH_2
		19.6	C_5 species ?
	20.2		CH_3COOH
	21.6		$CH_3COC_2H_5$
	22.8	23.3	CH_2Cl-CH_2Cl
23.6	23.3		CH_2Cl-CH_2OH
	24.6		C_6H_6
26.6	26.3		1-chloro-2-propanol, 1,4-dioxane

a Material identification is given in Table XXXIX.

b Retention time in minutes.

TABLE XLIV

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON URETHANE RIGID FOAM 16A[a]

-23°C Frac r.t.[b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.85	CO_2
		3.01	C_2H_4
		3.76	C_2H_6
5.8	6.0	6.50	HCl, H_2O
		8.27	C_3H_6
		9.20	CH_3Cl
	10.3		CH_3OH
	11.4	11.78	CH_3CHO, C_2H_3Cl
		13.02	CH_3Br
	14.6	14.65	?, C_2H_5Cl
		15.74	C_2H_3Br
	15.9		HCOOH, CH_3CN ?
	17.0		$(CH_3)_2CO$
		17.41	$CFCl_3$
	17.7		i-C_3H_7OH
		18.24	C_2H_5Br
	18.8		n-C_3H_7OH
	19.0	19.06	3-Chloropropene
19.6	19.5		CH_3COOH
	20.0		$CHCl_2$-CH_3 ?
	21.5		$CH_3COC_2H_5$
	22.1		?
		23.05	?
	23.0		CH_2Cl-CH_2Cl
23.3	23.6		C_6H_6
	24.5		CH_2Cl-CH_2OH
25.8	26.1		1,4-Dioxane
26.1	26.4		1-Chloro-2-propanol
27.6	27.3		CH_2Cl-CH_2Br
	27.9		Sorbaldehyde ?
	30.5		Toluene
31.3	32.0		CH_2Br-CH_2Br

a Material identification is given in Table XXXIX.

b Retention time in minutes.

TABLE XLV

PRODUCTS OF URETHANE RIGID FOAMS[a]

(SEALED TUBE STUDIES)

Products	Material 1B mg/g	Material 2B mg/g	Material 16A mg/g
CO	-	-	34.5
CH_4	1.60	0.96	2.36
HCl	23.2	5.85	17.3
NH_3	3.17	10.7	-
HCN	T	T	T
CO_2	144.2	148.7	191.5
C_xH_y [b]	1.81	3.90	2.18
C_6H_6	2.92	0.77	0.18
$C_6H_5CH_3$	0.21	0.18	0.30
CH_3Cl	1.08	1.03	0.22
C_2H_3Cl	0.28	0.22	0.22
C_2H_5Cl	11.70	7.43	0.07
CH_2Cl-CH_2Cl	40.0	52.0	17.7
$CH_2Cl-CH=CH_2$	0.87	0.51	0.23
C_6H_5Cl	0.14	0.04	-
CH_2Cl-CH_2Br	-	-	26.0
CH_3Br	-	-	1.85
C_2H_3Br	-	-	0.51
C_2H_5Br	-	-	3.12
CH_2Br-CH_2Br	-	-	12.5
$CFCl_3$	89.2	56.0	9.25
$CHFCl_2$	1.63	0.92	-
CH_3OH	0.02	0.07	0.44
C_2H_5OH	0.42	0.77	-
$i-C_3H_7OH$	0.07	0.07	T
$n-C_3H_7OH$	0.03	-	T
CH_2Cl-CH_2OH	1.29	1.10	0.03
$CH_2Cl-CHOH-CH_3$	0.94	2.91	3.41
CH_3CHO	-	-	0.15
Sorbaldehyde	-	-	1.04
$(CH_3)_2CO$	2.37	1.54	14.4
$CH_3COC_2H_5$	0.50	0.74	0.16
1,4-Dioxane	0.14	0.18	1.67
HCOOH	-	0.06	0.04
CH_3COOH	0.02	0.39	1.52
$C_6H_5NH_2$	58.6	66.9	-
p-Toluidine	10.3	7.4	-
p-Phenylenediamine	?	Yes	-
2,4-Toluenediamine	?	Yes	-

a Material identification is given in Table XXXIX.

b C_xH_y denotes hydrocarbons C_2 through C_4

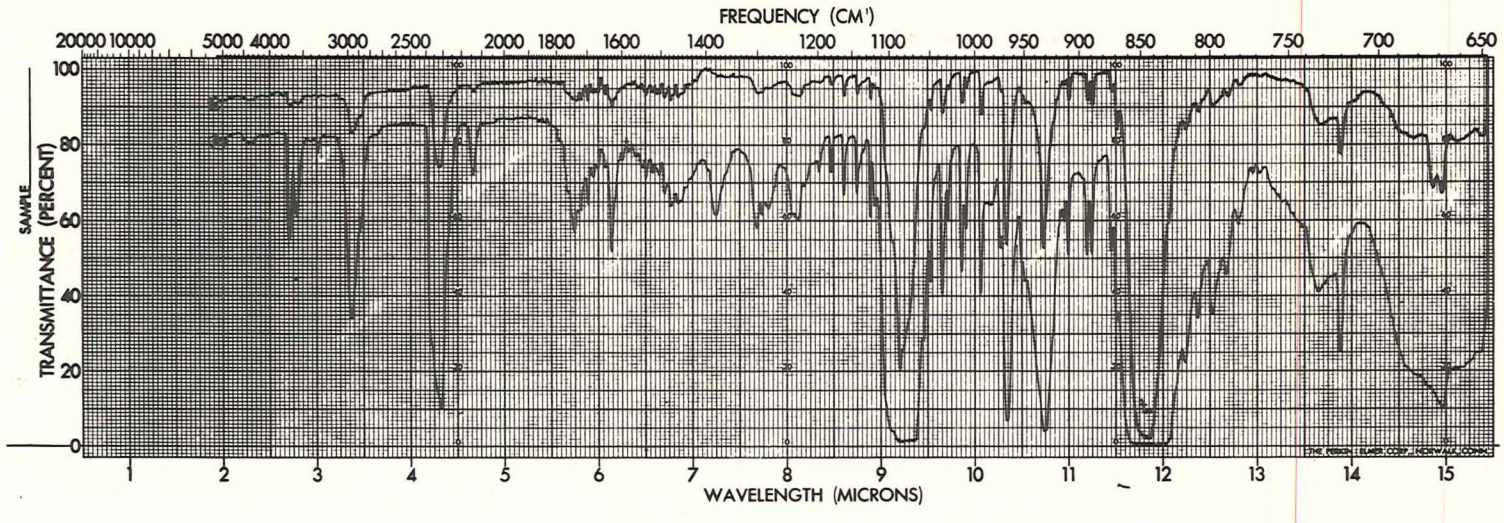


Fig. 27. Infrared Spectrum of -196°C Fraction
Sealed Tube Treatment of Urethane Foam 1B (gas, p = 261, 34 mm)

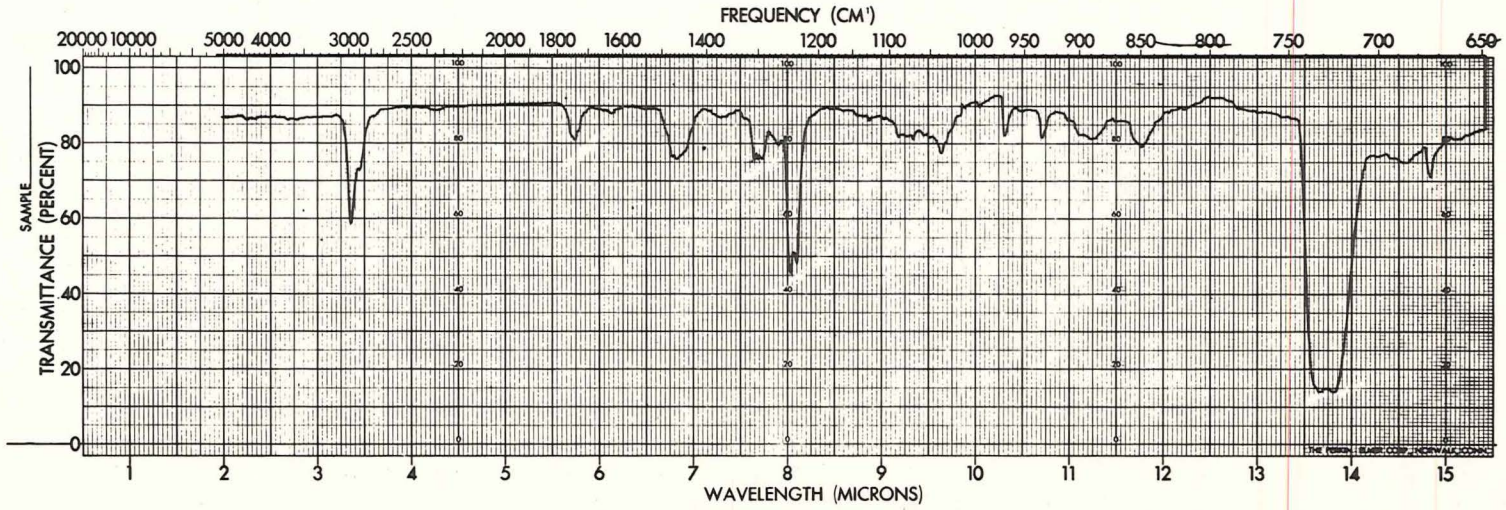


Fig. 28. Infrared Spectrum of -78°C Fraction
Sealed Tube Treatment of Urethane Foam 1B (gas, p ~ 40 mm)

C_2H_5Cl at 7.67, 7.74, 7.80μ; C_6H_6 at 14.86μ; 1,2-dichloroethane at 13.65μ; aliphatic CH at 3.37 - 3.55μ and a carbodiimide moiety at 4.66μ. The formation of carbodiimide linkages is not surprising and has been proposed as a decomposition path of isocyanates by a number of investigators [17, 19, 20];

$$2 \sim\!\!\sim N\text{-}C{=}O \longrightarrow \sim\!\!\sim N{=}C{=}N \sim\!\!\sim + CO_2$$

Yet based on Bachus [17] considerations the production of carbodiimide bonds would be expected to result in involatile compounds found mainly in the residues; consequently finding this type of structures in the -196°C fraction is rather surprising. The isocyanate band occurs usually at about 4.4μ and due to the high content of carbon dioxide in the -196°C fractions (Figure 27) it would be masked by the CO_2 absorption. However the mass spectrum did not show any isocyanate present.

The -78°C fractions of materials 1B and 2B consisted essentially of water and 1,2-dichloroethane admixed with small quantities of other species the most interesting of these being the chlorinated alcohols namely chloroethanol (TLV, 5 ppm) and chloropropanol. It should be mentioned that the vapor phase of the -78°C fraction was composed mainly of 1,2-dichloroethane admixed with traces of ammonia and benzene which is apparent from Figure 28.

The -23°C fractions consisted of almost pure aniline (TLV, 5 ppm) admixed with small amounts of p-toluidine and possibly an isocyanate (band at 4.35μ) as shown by the infrared spectrum presented in Figure 29. In the mass spectra of the -23°C and room temperature fractions of material 2B, p-phenylenediamine (peaks at m/e 108 and 80) and toluene diamine (peak at m/e 121 and 122) were detected. The mass spectra of these fractions indicated also the presence of substituted aromatics, peaks at m/e 133, 148, and 77. The finding of the aromatic amines is in agreement with the results reported by Takeuchi, Tsuge and Okumoto [21] who also detected these compounds in their pyrolysis studies of flexible urethane foams. These authors claim to have found several nitriles in their decomposition products, but we were unable to detect any in our investigations. It should be mentioned that Ball and Boettner [22] and

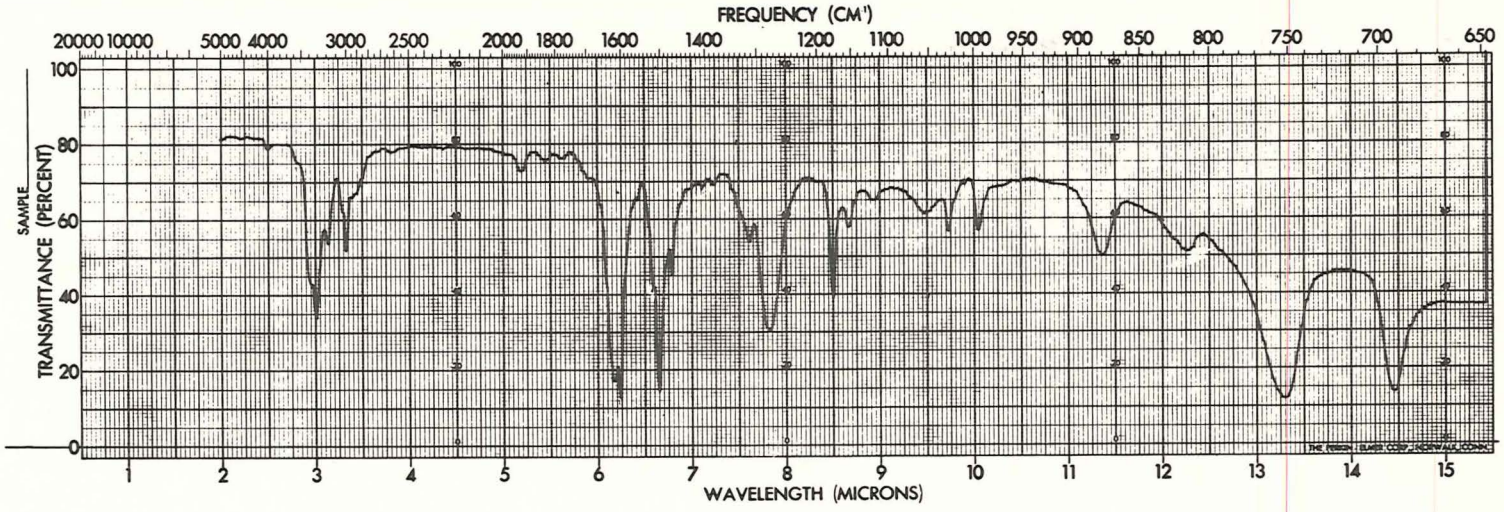


Fig. 29. Infrared Spectrum of -23°C Fraction
Sealed Tube Treatment of Urethane Foam 2B (liquid film)

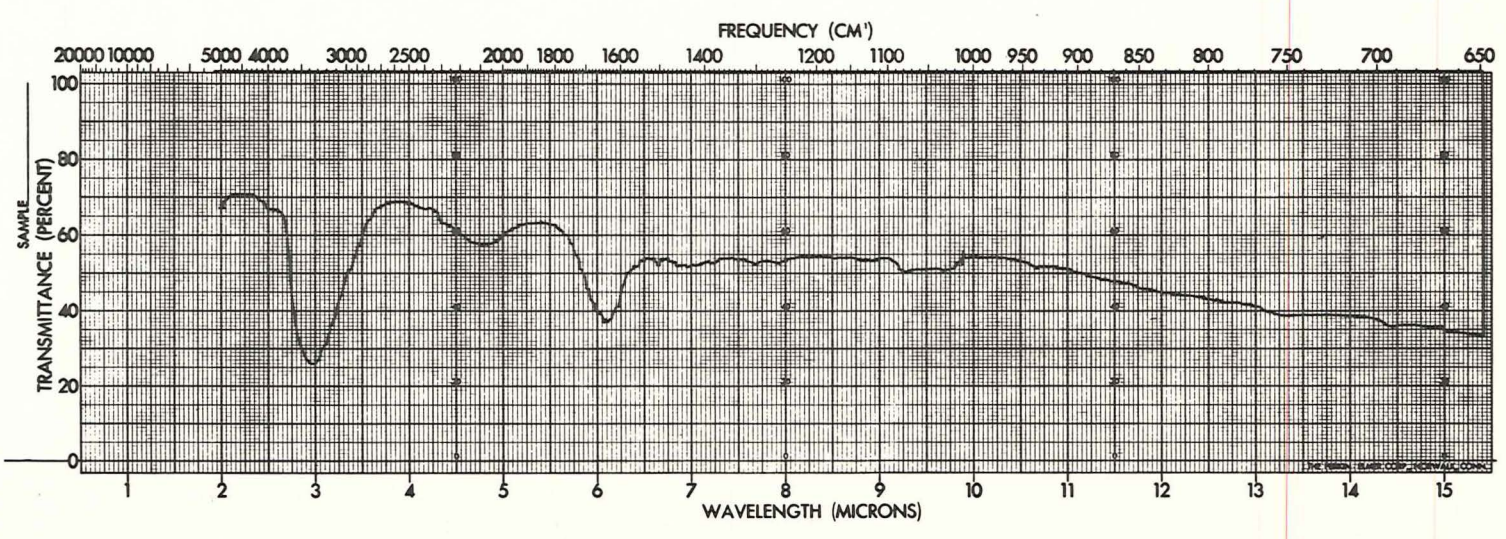


Fig. 30. Infrared Spectrum of -78°C Fraction
Sealed Tube Treatment of Urethane Foam 2B (liquid film)

Boettner, Ball and Weiss[12] also indicate the possible presence of aniline in their combustion of urethane materials; they did not however identify it positively. In Figure 30 is given the infrared spectrum of the liquid portion of the -78°C fraction. The band of importance here in addition to the bands due to water (3μ, 6.1μ), is the absorption at 4.75μ which would appear to be derived from CN^- ion. All the aqueous phases of materials 1B, 2B, and 16A in the room temperature, -23 and -78°C fractions exhibited this band, yet we were unable to determine the cyanide ion quantitatively using Liebig's titration (silver nitrate, potassium iodide). The controversy about the production of hydrogen cyanide from urethanes was discussed previously[1]; the recent work[12, 22-24] seems to indicate clearly that hydrogen cyanide is definitely formed. Ball and Boettner[22] claim that hydrogen cyanide production is lower at higher heating rates whereas the opposite is advocated by Schmitt[23], yet a publication by Paabo and Comeford[25] fails to mention the production of HCN altogether.

The oily residues left in the finger of the sealed tube after the decomposition of materials 1B and 2B exhibited the spectrum shown in Figure 31. Based on the work of Bachus et al[17] the absorption in the 6.0 - 6.2μ region is consistent with the spectrum of benzophenone and/or benzhydrol which could be formed by oxidation of the methylene bridge of the polymeric isocyanate.

Material 16A, as can be seen from the experimental and analytical data compiled in Tables XL, XLI, XLIV and in particular Table XLV represents an entirely different foam system from compositions 1B and 2B. The most striking differences are that material 16A contains brominated species and that no ammonia and no aniline were detected. This does not mean that none was formed; however, if formed, it was produced in trace quantities only. No hydrogen halides (HCl and/or HBr) were detected in the volatile condensibles. The only hydrogen halide found was in the involatile residues (see Figure 32). Titration for base showed absence of free base indicating either

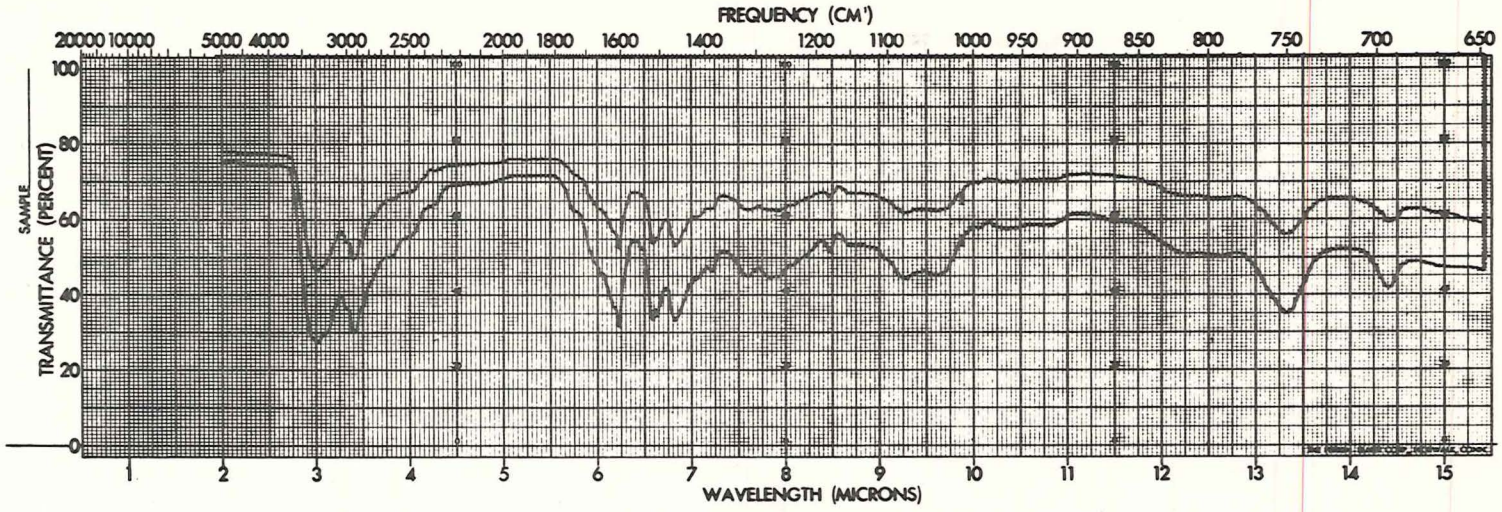


Fig. 31. Infrared Spectrum of Involatile Oil
Sealed Tube Treatment of Urethane Foam 2B (liquid film)

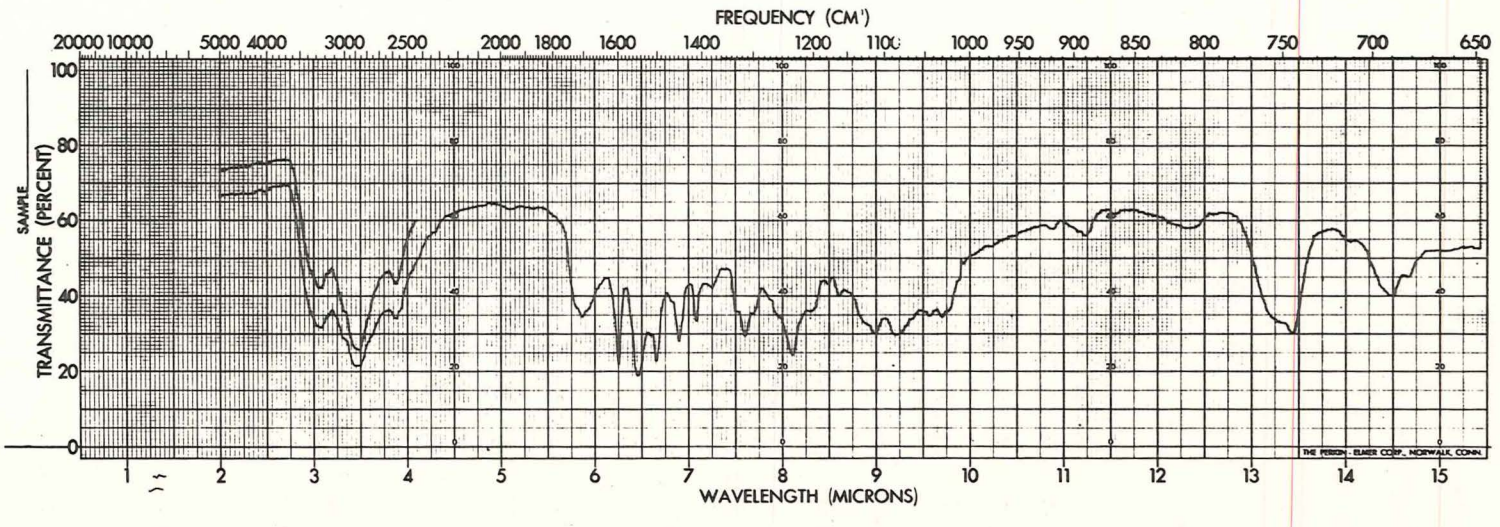


Fig. 32. Infrared Spectrum of Involatile Oil
Sealed Tube Treatment of Urethane Foam 16A (liquid film)

that all the bases (amines) present were in the form of salts or that the organic bases (amines) were insoluble in water. Again relying on infrared spectral evidence it would appear that both of these assumptions are basically correct, inasmuch as the infrared spectrum of the room temperature involatiles revealed the presence of aromatic amines, possibly amine salts and carbonyls (3.0μ, NH and OH; 3.4-3.5μ, aliphatic C-H stretch; 3.87μ NH^+; 5.85μ carbonyl; 6.5μ -NH amide II band; 7.05μ aliphatic N-C amine; 7.6μ NH; 13.25, 13.45, 14.5μ substituted aromatics).

The -196^{o}C fraction exhibited a completely different infrared spectrum from that obtained from materials 1B and 2B (compare Figures 33 and 27). The infrared spectrum depicted in Figure 33 shows the presence of carbon dioxide (4.32, 13.91, and 14.98μ), acetone (5.75, 8.10, 8.18, 8.25μ), Freon-11 (9.20, 11.85μ) ethylene (10.5μ), propylene 10.95μ and hydrogen cyanide 14.02μ.

When comparing the types and the quantities of volatile halogenated products formed upon oxidative thermal degradation (excluding the blowing agents employed) it would appear that these originate in all three foam samples from one common ingredient. The only difference between foams 1B and 2B on the one hand and foam 16A on the other is, that in foam 16A this common ingredient contains bromine in addition to chlorine. This becomes particularly apparent (see Table XLV) when the quantities of 1,2-dichloroethane formed from foams 1B and 2B are compared with the quantities of 1,2-dichloro-, 1-chloro-2-bromo-, and 1,2-dibromoethane produced during decomposition of foam 16A.

As noted previously the lack of detection of amino compounds and ammonia in material 16A cannot be explained and any postulations would be purely speculation since the nature of the ingredients used in the foam formation is totally unknown.

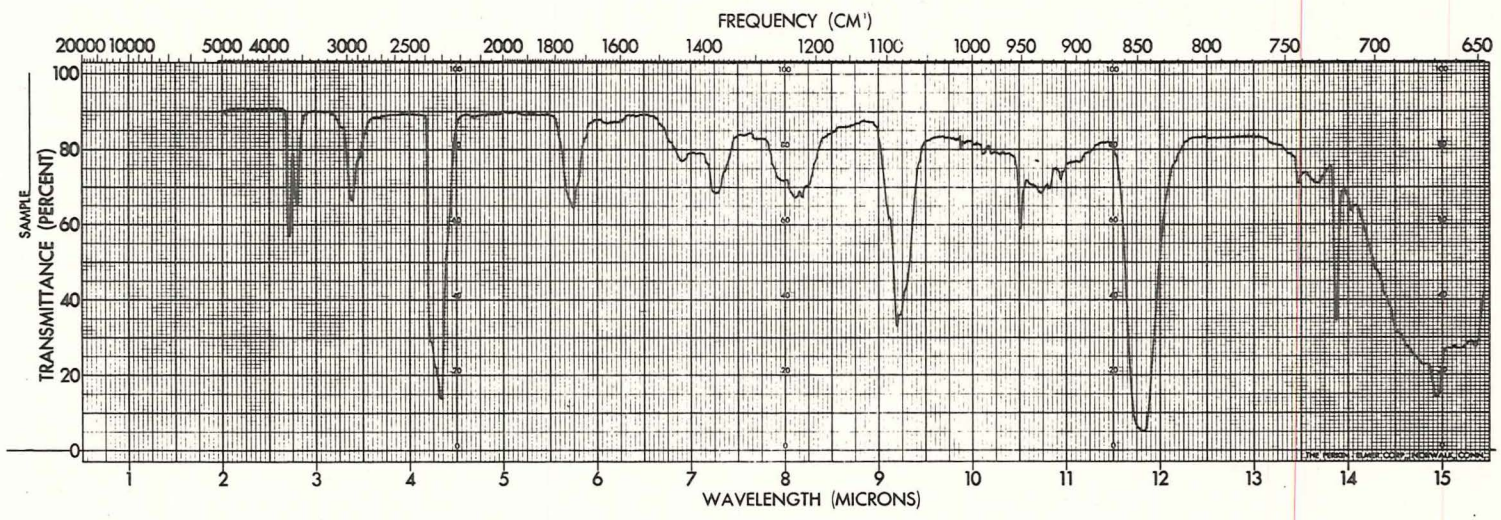


Fig. 33. Infrared Spectrum of -196°C Fraction
Sealed Tube Treatment of Urethane Foam 16A (gas, p = 274 mm)

In summary, for all three foams tested carbon dioxide is the major decomposition product followed by the blowing agents and in the case of composition 1B and 2B aniline. All three materials produced significant quantities of chlorinated hydrocarbons. The formation of the chlorinated alcohols was unexpected.

Another aspect worth noting is the detection of $CHFCl_2$. This finding could mean that either impure $CFCl_3$ was originally employed or that $CFCl_3$ did participate in the oxidative thermal degradation process. The latter would seem to be a more plausible explanation, in particular since the content of $CFCl_3$ was very high.

3.5 WOODS

Wood is used extensively in mines as structural material. For this type of an application the wood has to be made flame retardant and must be treated against rot and decay. The objective of this portion of the study was to determine the effects of these treatments on the nature and relative concentration of the products formed on thermal oxidative decomposition.

The woods studied were untreated and variously impregnated samples of standard southern yellow pine; these are listed in Table XLVI. Two samples of untreated pine were tested since the originally obtained specimen (material 1D) appeared to be contaminated as shown by the presence of chloride ion (see Tables LX and LXI) and by its TGA curve (see Figure 39) which is different from that of what is believed to be a "virgin" standard southern yellow pine (see Figure 40).

Before proceeding with the presentation and discussion of the experimental results it would seem advantageous to provide some background information. Under the previous contract a literature survey of cellulosic materials was compiled [1]; however, it was not specifically directed toward woods and no mention was made of impregnations and treatments of woods. Wood is composed of cellulose, lignin, hemicellulose, resins, tannins, fats,

TABLE XLVI

LIST OF PINE SAMPLES STUDIED

Material	Origin	Material Description
Untreated pine sample 1D	Bureau of Mines	Standard southern yellow pine
Untreated pine sample 6D	Bureau of Mines	Standard southern yellow pine
Treated pine sample 2D	Bureau of Mines	Standard southern yellow pine treated with oil-borne preservative (pentachloro-phenol); 0.37 lbs/ft^3; impregnation by Koppers Company
Treated pine sample 3D	Bureau of Mines	Standard southern yellow pine treated with creosote (coal tar distillate); 10.6 lbs/ft^3; impregnation by Koppers Company
Treated pine sample 4D	Bureau of Mines	Standard southern yellow pine treated with fire retardant type-C, Minalith ($(NH_4)_2HPO_4$, 10%; $(NH_4)_2SO_4$, 60% $Na_2B_4O_7$, 10%; H_3BO_3, 20%): 0.4 lbs/ft^3; impregnation by Koppers Company
Treated pine sample 5D	Bureau of Mines	Standard southern yellow pine treated with water-borne preservative-CCA (CrO_3, CuO, As_2O_5); 0.40 lbs/ft^3; impregnation by Koppers Company

waxes, and some coloring matter [26-28] and it is the degradation of all these constituents that leads to the variety of chemicals observed on pyrolysis of wood. A large number of investigations have been published and reviewed pertaining to wood degradation [29,30]. Of these probably the most useful and most inclusive is the compilation by the Canadian Wood Council [30]. The work done by Lipska [31,32] and others [33], to mention just a few, although pertaining only to cellulose is nevertheless of direct application to wood studies since wood consists largely of cellulose. Regarding the effect of preservatives and flame retardants on wood's thermal oxidative behavior and the nature and relative concentration of volatiles the data in the literature are more limited. The extent of penetration is usually of the order of 3/4 - 1" depending both on the type of wood, its water content and the method of impregnation. A number of theories have been advanced for the action of flame retardants in woods; to summarize briefly the current belief is that a flame retardant influences the mechanism of decomposition, lowers the temperature of decomposition onset and increases the char yield. Byrne et al [33] state that an effective flame retardant must act at temperatures below that at which cellulose would normally pyrolyze. Our results support these stipulations, as will become apparent later. The action of the preservatives on the thermal oxidative behavior of wood would depend on the nature of the agent or agents and the method of application (aqueous or oil). In actual practice the wood will have to be treated both with preservatives and with fire retardants. The treatments applied to the pine samples listed in Table XLVI can thus be viewed to a certain extent as model studies.

To determine the effect of both the preservatives and flame retardants on the thermal oxidative behavior, DTA and TGA investigations were carried out. To establish the nature and relative material concentration sealed system and stagnation burner tests were performed.

The DTA curves are presented in Figures 34-38. They show in general three processes in which heat is either consumed or produced by the sample: a) an endotherm at ~ 120°C present in all five samples which is most likely caused by evaporation of water (drying) and/or formation of water via dehydration (e.g., -CHOH- $\longrightarrow$ $-C\lessgtr + H_2O$), b) a very gentle reaction exotherm, which may indicate slow oxidation and/or simultaneous oxidation and dehydration, and c) a final sharp exotherm, which definitely points to oxidative decomposition. It is apparent that untreated pine (Figure 34), creosote treated pine (Figure 36) and CCA treated pine (Figure 38) exhibit very similar DTA curves, with the exception that the final steep reaction exotherm for CCA treated pine occurs ~ 22°C lower (~333°C) than for the other two materials (~ 355°C). It is also apparent that pentachlorophenol treated pine exhibits a DTA curve (Figure 35) significantly different from that of untreated pine (Figure 34) since there appears an additional endotherm at ~ 280°C which could very well be associated with the sublimation (evaporation) of some of the impregnant. The fire retardant, Minalith, treatment (Figure 37) of pine obviously has the most profound effect on the wood decomposition processes. This DTA curve shows two additional reaction endotherms which could very well be due to impregnant decomposition and/or evaporation; furthermore, the onset of the final steep reaction exotherm starts here as low as 250°C compared to 355°C for untreated pine. Such a lowering of the decomposition temperature would be expected for an efficient flame retarding action according to Byrne et al.[33]

It should be mentioned at this stage that the DTA curves tend to show exotherms much lower than would be expected from heat of combustion values and from calculations of standard bond energies. This is due to the failure of the DTA method to measure accurately the heat produced by oxidation of gaseous degradation products and also due to incomplete combustion. Yet, based on the DTA curves one can at least get an idea of the

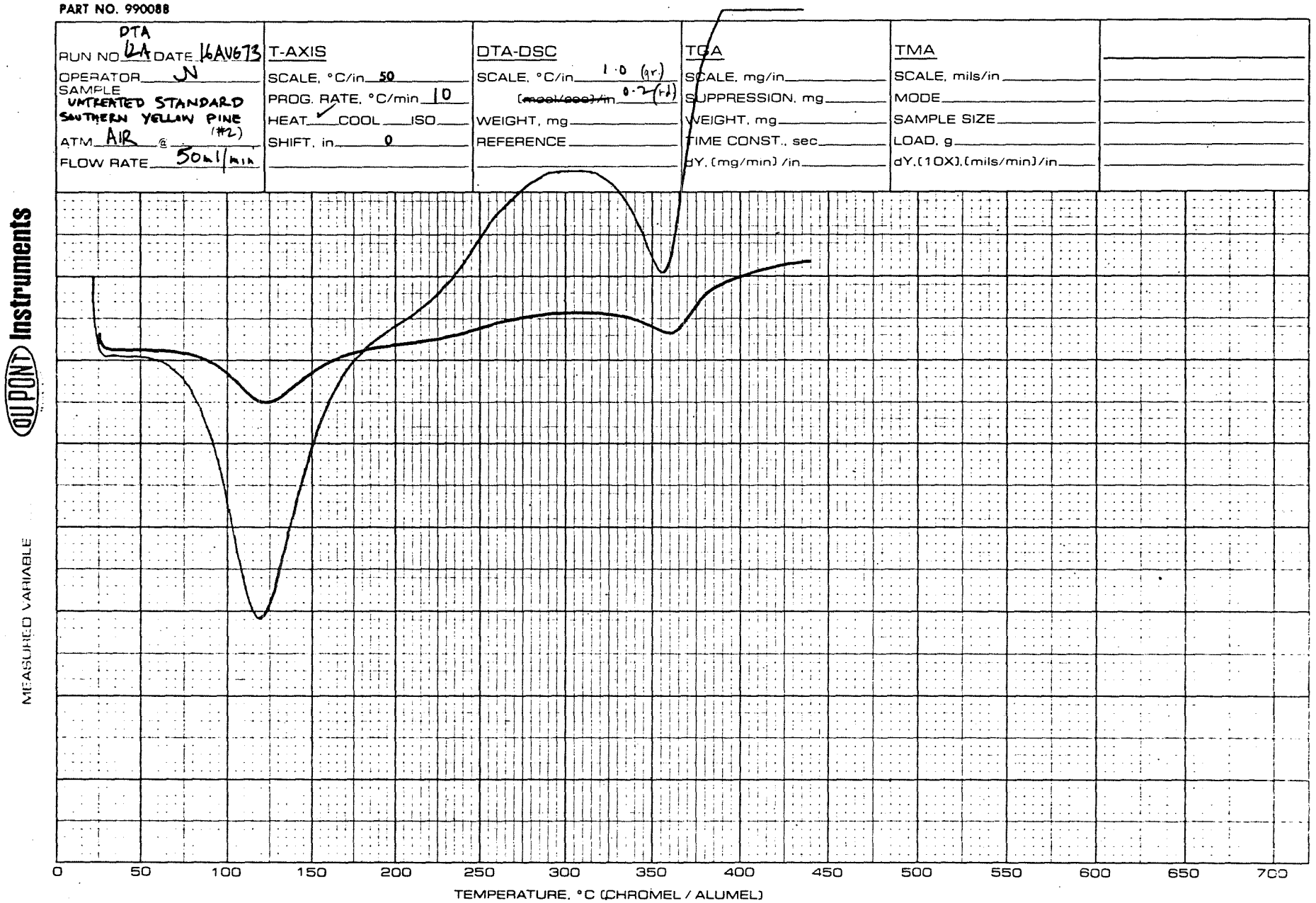


Figure 34

DTA of Untreated Standard Southern Yellow Pine (Material 6D)

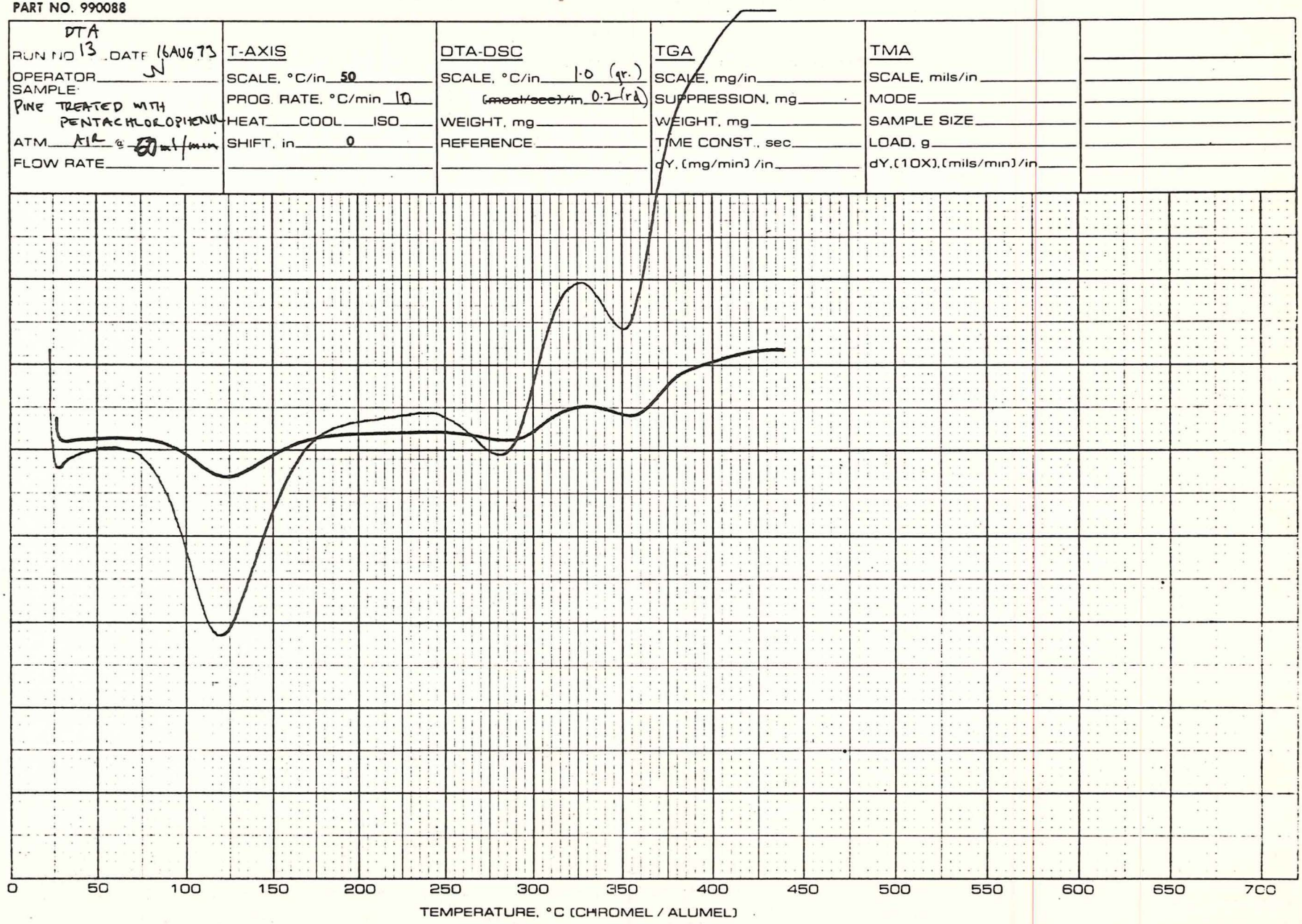


Figure 35

DTA of Pentachlorophenol Treated Standard Southern Yellow Pine (Material 2D)

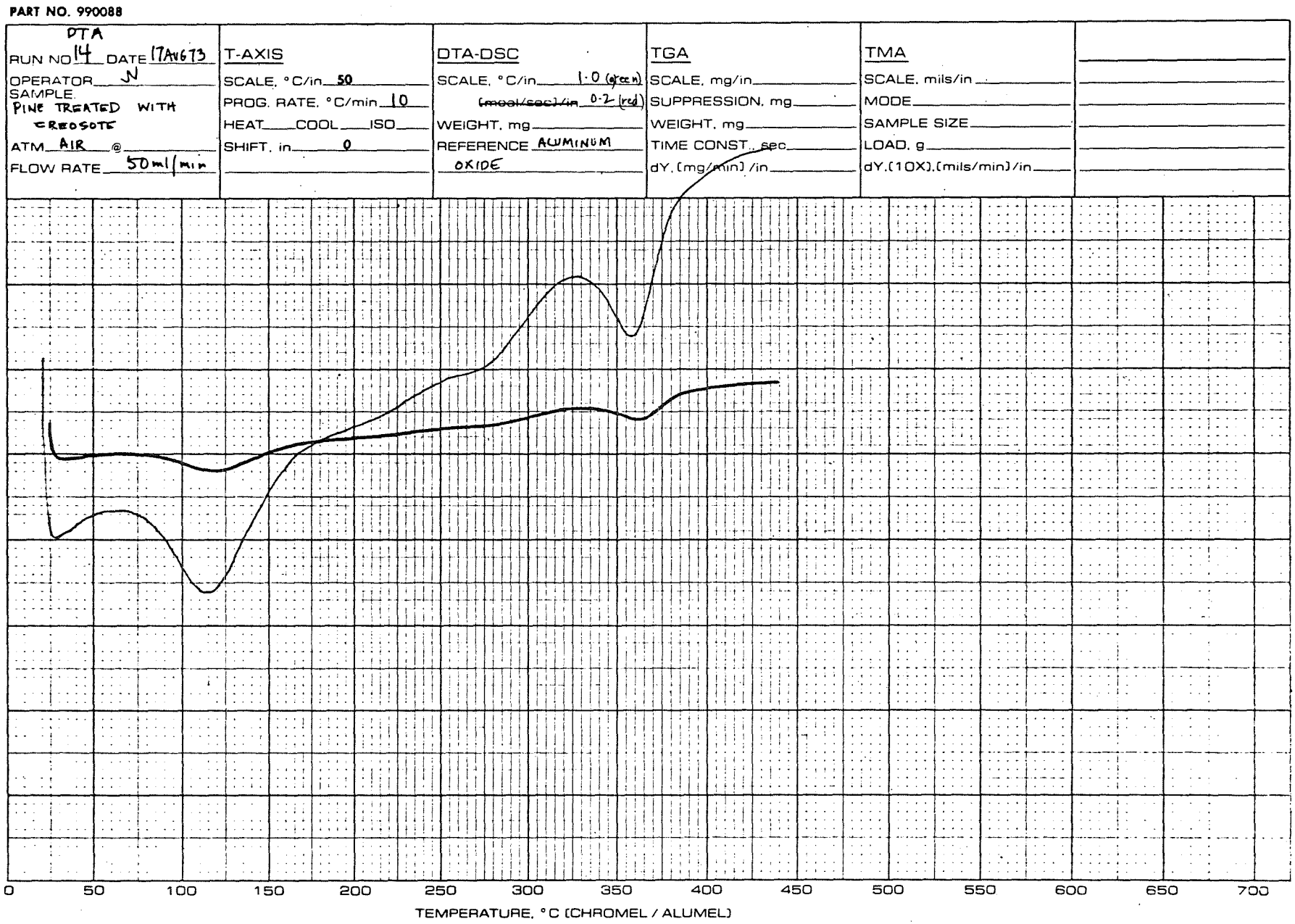


Figure 36

DTA of Creosote Treated Standard Southern Yellow Pine (Material 3D)

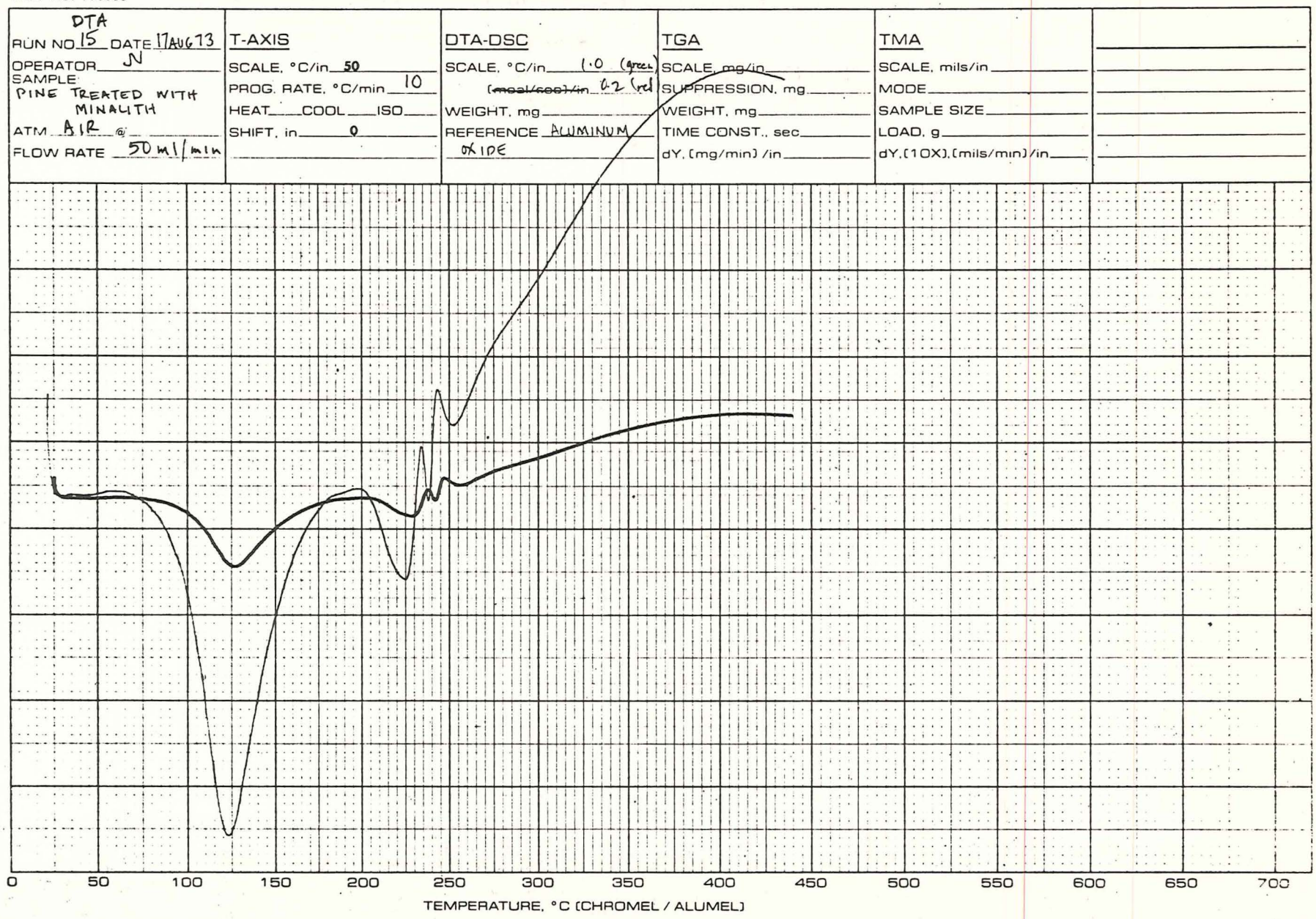


Figure 37

DTA of Minalith Treated Standard Southern Yellow Pine (Material 4D)

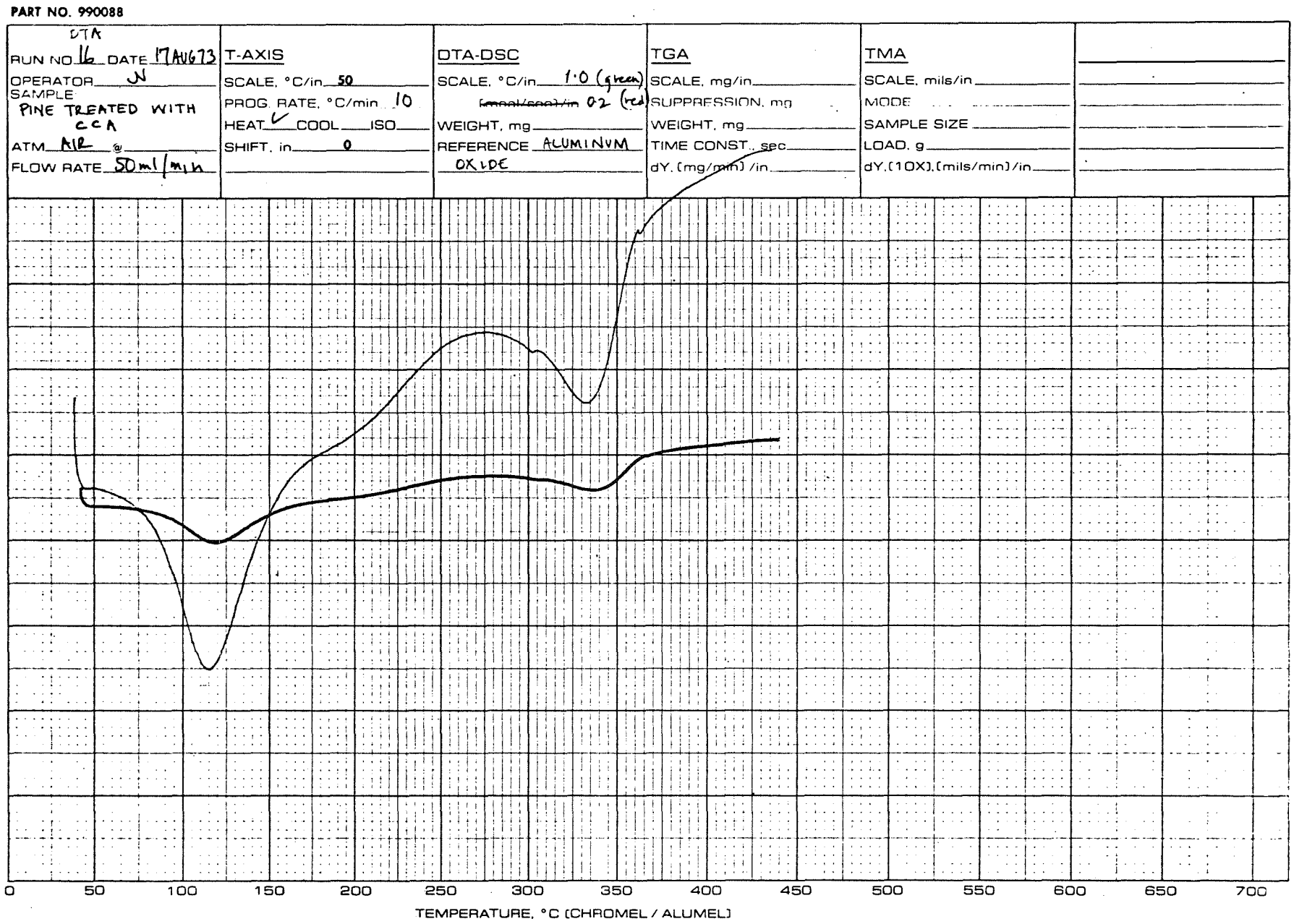


Figure 38

DTA of CCA Treated Standard Southern Yellow Pine (Material 5D)

general effect of a particular additive on the thermal behavior of a given material such as wood.

In Figures 39-44 are presented the TGA curves of the various pine samples. It should be noted that the "untreated", yet apparently contaminated pine (Figure 39, sample 1D) exhibited a definitely different TGA from that of truly untreated pine (Figure 40, material 4D). Comparison of the six curves shows clearly that in the case of Minalith treated pine (see Figure 43) no rapid material loss occurs beyond 270°C which points to the absence of combustion. Furthermore at 400°C the char yield is about 44% which is in a rough agreement with the 40% obtained in the stagnation burner treatment. The lower stagnation burner value can be explained by the longer residence time there at the temperature as compared to the TGA conditions. The almost complete material loss in the case of the CCA treated pine, found in the stagnation burner test, again could have been predicted from the TGA curve (see Figure 44). The absence of glow in the case of creosote impregnated pine and the low residue obtained from the pentachlorophenol treated sample is not indicated either by TGA or the DTA data. Thus it is obvious that no one method can provide all the necessary information to predict a thermal behavior of a composition.

The actual thermal oxidative tests were performed using a quiescent (sealed tube) and a dynamic (stagnation burner) system. The experimental details of the sealed tube studies are summarized in Table XLVII whereas the product distribution is given in Table XLVIII. In Tables XLIV-LIII are compiled the results of the gas chromatographic analyses.

The vacuum line fractionations did provide a considerable degree of material separation and thus have grossly simplified the gas chromatographic analyses. The gas chromatographic conditions used have been amply described in Section 3.1.2; it should be added however that in the case of the wood products the analyses were carried out using programming at 8°C/min from 50 to 220°C. The experimental details of the stagnation

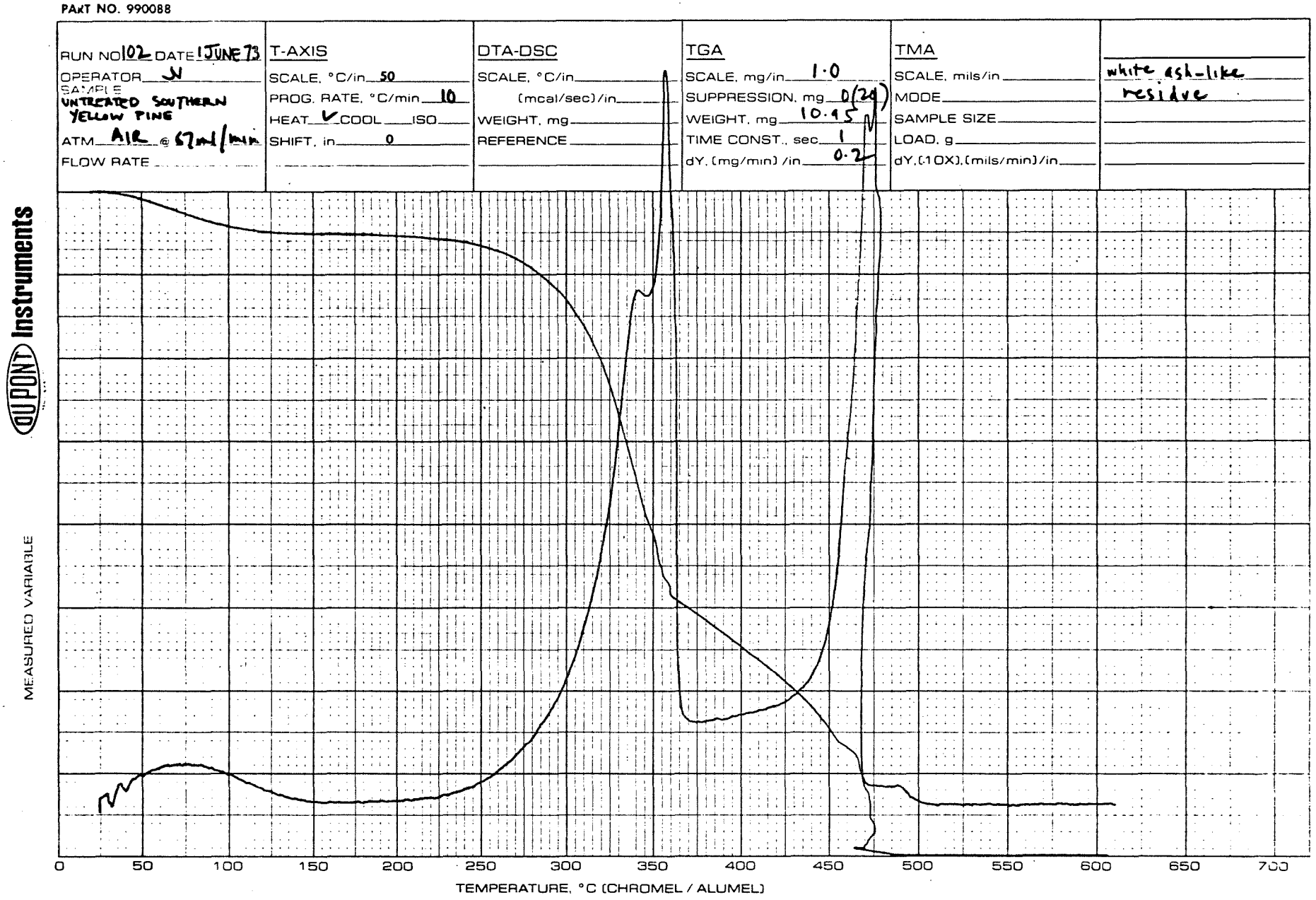


Figure 39

TGA of "Untreated" Southern Yellow Pine (Material 1D)

PART NO. 990088

RUN NO 120A DATE 6 AUG 73	T-AXIS	DTA-DSC	TGA	TMA
OPERATOR N	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 1.0	SCALE, mils/in
SAMPLE STANDARD UNTREATED SOUTHERN YELLOW PINE #2	PROG. RATE, °C/min 10	(mcal/sec)/in	SUPPRESSION, mg 0(20)	MODE
ATM AIR @	HEAT ✓ COOL ISO	WEIGHT, mg	WEIGHT, mg 10.85	SAMPLE SIZE
FLOW RATE 67 ml/min	SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g
			dY, (mg/min) /in 0.5	dY, (10X), (mils/min)/in

DU PONT Instruments

MEASURED VARIABLE

0 50 100 150 200 250 300 350 400 450 500 550 600 650 700

TEMPERATURE, °C (CHROMEL / ALUMEL)

Figure 40

TGA of Untreated Standard Southern Yellow Pine (Material 6D)

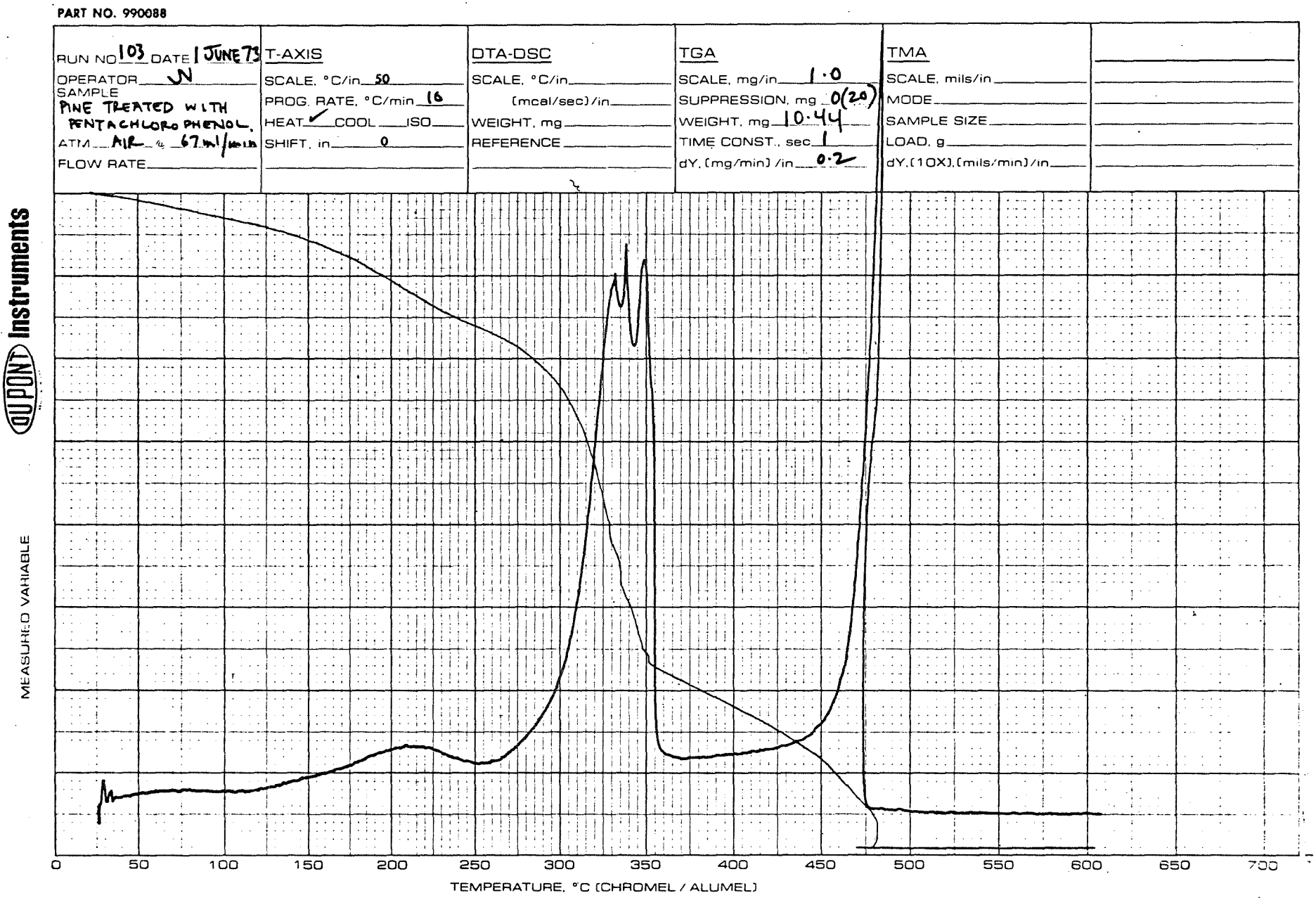


Figure 41

TGA of Pentachlorophenol Treated Standard Southern Yellow Pine (Material 2D)

PART NO. 990088

RUN NO 109 DATE 22 JUNE 73	T-AXIS	DTA-DSC	TGA	TMA	
OPERATOR N	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 1	SCALE, mils/in	1 Lbl increm, fiber-like
SAMPLE: PINE TREATED WITH CREOSOTE	PROG. RATE, °C/min 10	(mcal/sec)/in	SUPPRESSION, mg 0 (20)	MODE	
ATM AIR @ 67 ml/min	HEAT ✓ COOL ISO	WEIGHT, mg	WEIGHT, mg 10.74	SAMPLE SIZE	
FLOW RATE	SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g	
			dY, (mg/min) /in 0.2	dY, (10X), (mils/min)/in	

DU PONT Instruments

MEASURED VARIABLE

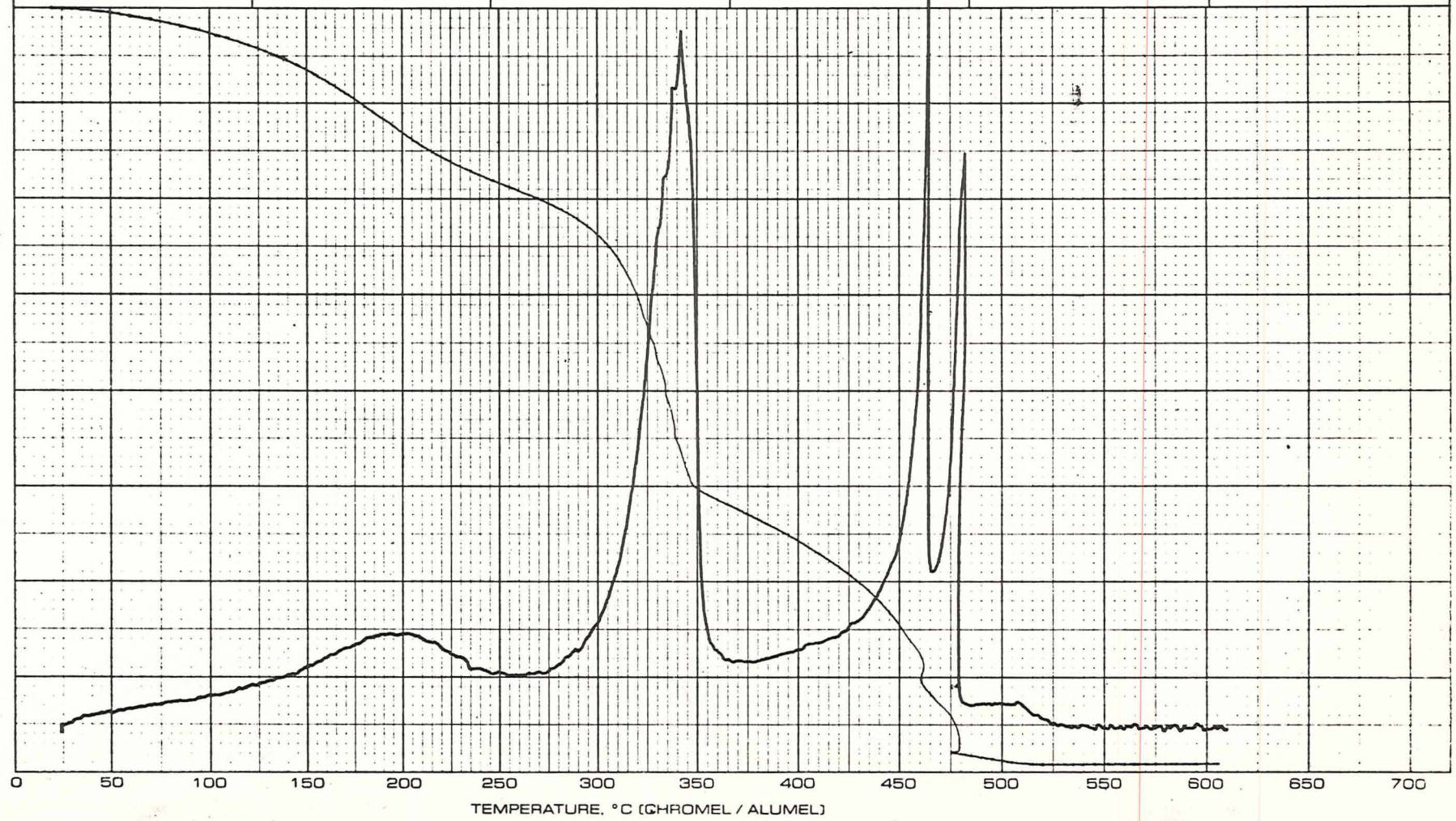


Figure 42

TGA of Creosote Treated Standard Southern Yellow Pine (Material 3D)

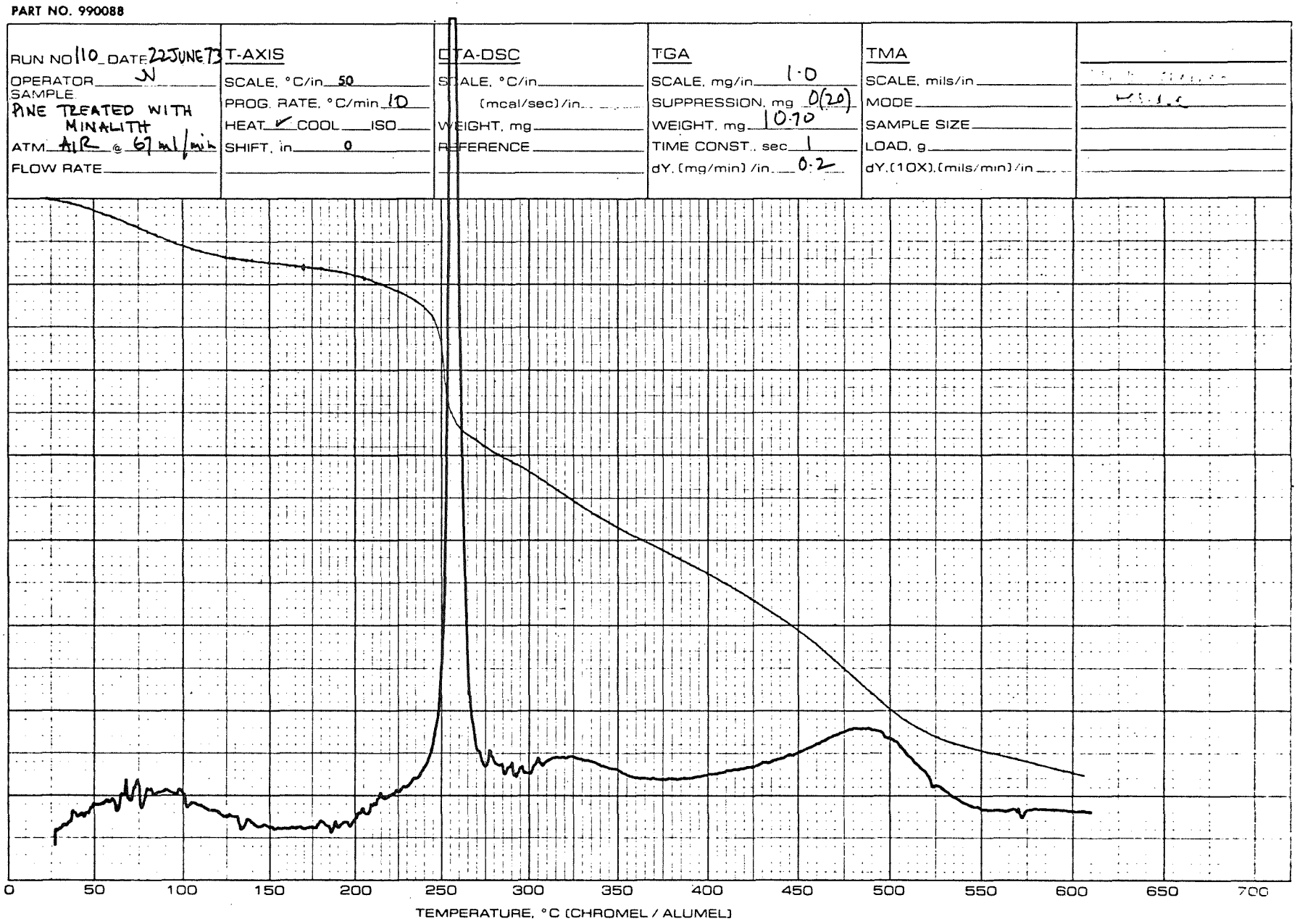


Figure 43

TGA of Minalith Treated Standard Southern Yellow Pine (Material 4D)

PART NO. 990088

RUN NO 119A DATE 23 JULY 73	T-AXIS	DTA-DSC	TGA	TMA	
OPERATOR N	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in 1.0	SCALE, mils/in	
SAMPLE: PINE + CCA	PROG. RATE, °C/min 10	(mcal/sec)/in	SUPPRESSION, mg 0(20)	MODE	
	HEAT ✓ COOL ISO	WEIGHT, mg	WEIGHT, mg 10.92	SAMPLE SIZE	
ATM Air @	SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g	
FLOW RATE 67 ml/min			dY, (mg/min) /in 0.5	dY, (10X), (mils/min) /in	

DUPONT Instruments

MEASURED VARIABLE

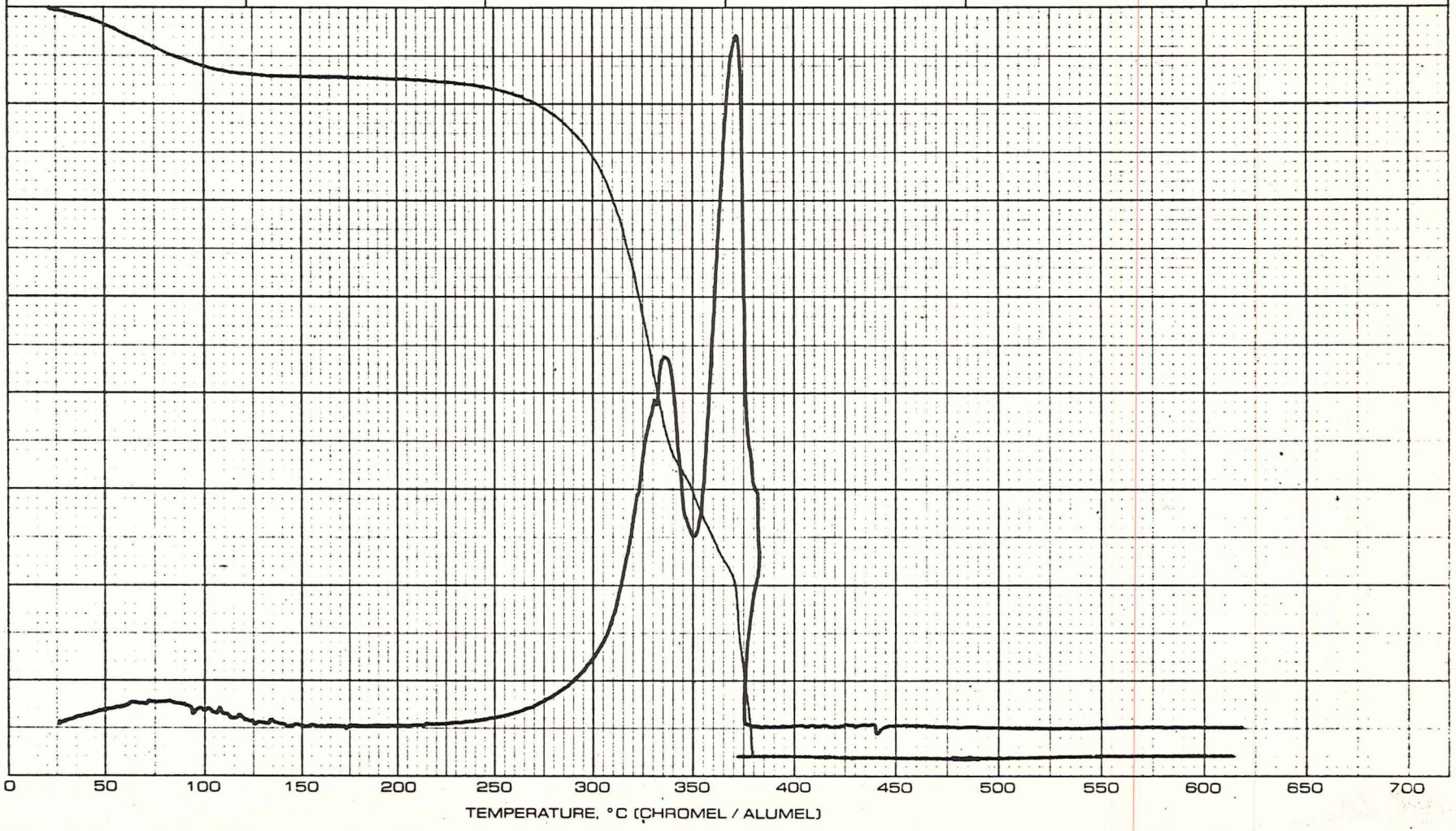


Figure 44

TGA of CCA Treated Standard Southern Yellow Pine (Material 5D)

TABLE XLVII

EXPERIMENTAL DATA

FOR SEALED TUBE DEGRADATIONS OF PINE SAMPLES

Sample Ident [a]	Tube V ml	Initial P mm	Final P mm	React. Temp °C	Sample Wt mg	Solid Residue		Weight Loss mg	Oxygen Consumed		Total Products	
						mg	%[b]		mg	%[c]	mg[d]	%[e]
1D	2047	504.8	536.6	370	615	208	33.8	407	48.0	12.9	342.3	75.2
6D	2045	505.3	536.1	371	597	203	34.0	394	35.5	9.5	290.0	67.6
2D	2045	506.8	538.1	368	625	206	32.9	419	43.2	11.6	280.3	60.6
3D	2047	506.6	532.0	370	630	207	32.8	423	33.3	9.0	263.0	57.7
4D	2045	504.8	530.1	371	603	283	47.0	320	54.0	14.7	297.0	79.4
5D	2045	501.2	528.8	370	605	212	35.0	393	49.0	13.3	321.6	72.8

a Material identification is given in Table XLVI.

b Percent 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.

c Percent of oxygen available.

d Includes the HCl found in the residue and in the bottom of the reaction flask.

e Percent of total products expected based on sample weight loss and oxygen consumed.

TABLE XLVIII

PRODUCT DISTRIBUTION FOR SEALED TUBE DEGRADATION OF PINE SAMPLES

Sample Ident.[a]	Noncondensibles							Condensibles								
	Total mmol[b]	H_2		CO		CH_4		Total	-196^oC Frac		-78^oC Frac		-23^oC Frac		R.T.[d] Frac	
		mg	%[c]	mg	%[c]	mg	%[c]	mg	mg	%[c]	mg	%[c]	mg	%[c]	mg	%[c]
1D	55.68	0.05	0.01	29.6	4.8	1.4	0.2	310.8	79.2	12.9	199.0	32.2	27.3	4.4	5.3	0.9
6D	56.03	0.04	0.01	28.8	4.8	0.5	0.1	260.7	73.3	12.3	173.8	29.1	3.4	0.6	10.2	1.7
2D	55.64	0.08	0.01	28.2	4.5	0.7	0.1	251.1	54.9	8.8	93.3	14.9	91.5	14.6	11.4	1.8
3D	55.60	0.01	T[e]	13.1	2.1	1.8	0.3	248.1	51.5	8.2	176.0	27.9	6.2	1.0	14.4	2.3
4D	54.64	0.01	T	35.1	5.8	0.6	0.1	261.3	63.6	10.5	150.2	24.9	45.7	7.6	1.8	0.3
5D	54.46	0.08	0.01	26.2	4.3	1.4	0.2	293.9	84.2	13.9	139.4	23.1	26.2	4.3	44.1	7.3

a Material identification is given in Table XLVI.

b This is mainly air.

c Percent of the weight of the starting material.

d Room temperature.

e Trace - denotes less than 0.005%.

TABLE XLIX

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON UNTREATED PINE 6D[a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
			1.8	CO_2
			2.9	C_2H_4
			3.7	C_2H_6
		5.5	5.0	HCHO
5.9	5.7	5.9	5.9	H_2O
7.4	7.3			HCHO
			8.1	C_3H_6
			8.6	C_3H_8
10.5	10.5	10.3		CH_3OH
		11.8	11.5	CH_3CHO
		13.6	13.5	Methyl formate
	16.6	17.6	16.7	Acetone, furan, acrolein
		18.8		Methyl acetate
19.5	19.5	19.9		CH_3COOH
		21.0		?
			21.5	2-Methylfuran
22.0	22.7	21.8		Vinyl acetate, methyl ethyl ketone, 2-methylfuran
		22.9		?
24.4	24.2	23.8		C_6H_6
		25.6		$CH_3COC_3H_5$
		26.5		2,5-Dimethylfuran
		27.8		?
29.1	28.9			2,3-Pentanedione
30.7	30.2	31.9		$C_6H_5CH_3$
34.0	33.7	33.8		Furfural
	38.3			?
	40.8			?

a Material identification is given in Table XLVI.

b Room temperature.

c Retention time in minutes

TABLE L

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON TREATED PINE 2D[a]

-23°C Frac[b] r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
		3.0	C_2H_4
		3.8	C_2H_6
5.1	5.1		HCHO
5.8	6.1	6.3	H_2O
		8.3	C_3H_6
		8.8	C_3H_8
	9.4	9.3	CH_3Cl
10.1	10.0		CH_3OH
	11.8	11.7	CH_3CHO
	13.6	13.6	Methyl formate
		13.9	C_4-ene
		14.5	?
		17.1	Furan, acrolein
	17.5	17.4	Acetone
	18.7	18.9	Methyl acetate
		19.5	?
19.6	19.6		CH_3COOH
	21.1	20.9	?
	22.1	21.9	2-Methylfuran, methyl ethyl ketone, vinyl acetate
	23.2		?
	23.7	23.3	C_6H_6
	25.7		$CH_3COC_3H_5$
26.1	26.7		2,5-Dimethylfuran
		28.7	?
	28.8		2,3-Pentanedione
	31.7	31.9	$C_6H_5CH_3$
34.1	34.0		Furfural
	37.0		?
42.0			?

a Material identification is given in Table XLVI.

b Retention time in minutes.

TABLE LI

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON TREATED PINE 3D [a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
			1.9	CO_2
			3.0	C_2H_4
			3.7	C_2H_6
		4.5	4.8	HCHO
5.8	5.6	6.3	5.9	H_2O
7.2	7.0			HCHO
			8.1	C_3H_6
			8.6	C_3H_8
			9.1	CH_3Cl
10.4	10.2	10.1		CH_3OH
11.8	11.6	11.8	11.6	CH_3CHO
		13.6	13.7	Methyl formate
			14.3	C_2H_5Cl
17.5	17.1	17.5	16.9	Furan, acetone, acrolein
			17.7	?
18.5		18.6	18.2	Methyl acetate
19.4	19.5	19.7		CH_3COOH
		20.9		?
			21.6	2-Methylfuran
21.6		21.8		Methyl ethyl ketone, vinyl acetate, 2-methylfuran
		22.4		?
		22.8		?
		23.6		?
23.9	23.8	24.6		C_6H_6
25.5	25.3	25.4		$CH_3COC_3H_5$
		26.4		2,5-Dimethylfuran
28.9	28.8	28.5		2,3-Pentanedione
	30.2	30.7		$C_6H_5CH_3$
33.9	33.6	33.7		Furfural
	38.2	38.5		?
	40.6			?

a Material identification is given in Table XLVI.

b Room temperature.

c Retention time in minutes.

TABLE LII

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE

DEGRADATION PERFORMED ON TREATED PINE 4D[a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
			1.9	CO_2
			4.5	HCN ?
			5.4	HCHO
5.9	5.95	6.2	6.2	H_2O, COS
			9.0	SO_2
9.4		10.2		CH_3OH
		11.8		CH_3CHO
13.6		13.6		Methyl formate
		16.2		HCOOH
			17.1	Furan, acrolein ?
17.6		17.6		Acetone
18.7		18.7		Methyl acetate
		19.6		CH_3COOH
22.0		22.0	21.8	Methyl ethyl ketone, vinyl acetate , 2-methylfuran
		22.8		?
		24.7		C_6H_6
		25.5		$CH_3COC_3H_5$
		26.3		2,5-Dimethylfuran
		31.5		$C_6H_5CH_3$
34.4		34.3		Furfural

a Material identification is given in Table XLVI.

b Room temperature.

c Retention time in minutes.

TABLE LIII

GAS CHROMATOGRAPHY RESULTS FOR SEALED TUBE DEGRADATION PERFORMED ON TREATED PINE 5D [a]

R.T.[b] Frac r.t.[c]	-23°C Frac r.t.	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
			1.9	CO_2
			3.1	C_2H_4
			4.6	?
5.1				HCHO
			5.3	?
			5.5	?
5.6	6.0	6.0	6.6	H_2O
			8.3	C_3H_6
			8.8	C_3H_8
			9.2	CH_3Cl
10.3	10.6	10.5		CH_3OH
11.6		11.8	11.7	CH_3CHO
14.0		13.6		Methyl formate
17.7		17.3	17.0	Acetone, furan, acrolein
18.6		18.7		Methyl acetate
19.6		20.1		CH_3COOH
21.8		21.8	21.6	2-Methylfuran, vinyl acetate, methyl ethyl ketone
		22.6		?
		23.7	24.1	C_6H_6
		24.5		?
		25.2		$CH_3COC_3H_5$
		26.2		2,5-Dimethylfuran
32.0		31.4		$C_6H_5CH_3$
33.8	34.3	34.2		Furfural
36.7				?
39.1				?

a Material identification is given in Table XLVI.

b Room temperature.

c Retention time in minutes.

burner tests are summarized in Table LIV whereas the gas chromatographic separations are given in Tables LV - LIX. The tabulations of the products on a mg/g basis for the sealed tube investigations and for the stagnation burner studies are presented in Tables LX and LXI, respectively. Comparing the experimental data for the two procedures (Tables XLVII and LIV) it is apparent that the stagnation burner, although operated at only 30°C higher temperatures than the sealed system, provides a much more severe environment which is reflected both in the lower residue yields and in the high carbon dioxide content in the volatiles. It could be argued that the sealed system is more related to the TGA environment since the char yields, based on TGA data, correspond closely with those found for the sealed tube studies (i.e., material 1D 33.8 versus 37.5%; material 6D 34.0 versus 31.2%; material 2D 32.9 versus 26%; material 3D 32.8 versus 33.8%; material 4D 47.0 versus 47.2%; material 5D 35 versus 27%).

Before discussing the decomposition products of the individual materials several general points should be made. The main effort under this program was to identify and quantitate the materials of relatively high volatility, accordingly in Tables LX and LXI are not listed phenols, cresols, highly substituted furan derivatives and related species. Furthermore as is apparent from the examination of the gas chromatographic data (Tables XLIX - LIII and LV - LIX), a mumber of peaks were not identified. These were usually very small peaks and no meaningful identification could be obtained using mass spectral analyses. Some of the higher molecular weight compounds were not eluted from the columns, however, from mass spectral evidence we know that compounds such as 2-furyl ethyl ketone (m/e 95, 124), 2-furyl methyl ketone (m/e 95, 110), 5-methyl-2-furaldehyde (m/e 110, 109), dimethylphenol (m/e 122,107), benzofuran (m/e 118, 90), and furfuryl alcohol m/e 97) were formed. The materials of direct interest to this program are the toxic species such as acrolein (TLV, 0.1 ppm) formaldehyde (TLV, 2 ppm),

TABLE LIV

SUMMARY OF EXPERIMENTAL DATA FOR

STAGNATION BURNER EXPERIMENTS PERFORMED ON PINE SAMPLES

Sample Ident.[a]	Gas Temp °C	Block Temp °C	Glow min	Sample Wt mg	Residue		-196°C Frac		-78°C Frac		-23°C Frac		R.T.[c] Frac	
					mg	%[b]	mg	%[b]	mg	%[b]	mg	%[b]	mg	%[b]
1D	401	397	8-15	1020	132	12.9	216.2	21.2	33.4	3.3	655.3	64.3	147.6	14.5
2D	401	397	6-15	1007	34	3.4	249.9	24.8	148.7	14.8	399.3	39.6	202.2	20.1
3D	406	404	no glow	1008	264	26.2	185.5	18.4	77.4	7.7	367.3	36.4	116.2	11.5
4D	399	400	no glow	1018	404	39.7	312.8	30.7	284.1	27.9	385.8	37.9	17.0	1.7
5D	410	404	4-6	1003	14	1.4	616.9	61.5	95.2	9.5	508.2	50.6	144.0	14.4

a Material identification is given in Table XLVI.

b Percent of the weight of the starting material.

c Room temperature.

TABLE LV

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER

TEST PERFORMED ON UNTREATED PINE-1D[a]

-23°C Frac r.t.[b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
	5.1		HCHO
5.8	5.9	6.1	H_2O
10.2	9.9		CH_3OH
	11.6		CH_3CHO
	13.5		Methyl formate; ethyl alcohol ?
	16.8		Furan, acrolein
17.5	17.3		$(CH_3)_2CO$
18.5	18.6		Methyl acetate, n-propanol ?
	19.2		CH_3COOH
	20.8		2-Methylfuran
	21.7		Methyl ethyl ketone, vinyl acetate
	22.9		?
	23.6		C_6H_6
	25.4		$CH_3COC_3H_5$
	26.7		2,5-Dimethylfuran
	28.8		2,3-Pentanedione
	31.8		Toluene
	32.3		?
34.1	34.2		Furfural
37.0			?

a Material identification is given in Table XLVI.

b Retention time in minutes.

TABLE LVI

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON UNTREATED PINE-2D[a]

$-23^{\circ}C$ Frac r.t.[b]	$-78^{\circ}C$ Frac r.t.	Peak Identification
5.8	6.2	H_2O
	10.2	CH_3OH
	11.8	CH_3CHO
	13.5	Methyl formate
	16.8	Acrolein, furan
	17.5	$(CH_3)_2CO$
	18.6	Methyl acetate, n-propanol ?
	19.8	CH_3COOH
	20.9	Methyl ethyl ketone
	21.7	2-Methylfuran, vinyl acetate
	22.8	?
	23.6	?
	24.7	C_6H_6
	25.3	$CH_3COC_3H_5$
	26.3	2,5-Dimethylfuran
	28.2	2,3-Pentanedione
31.6	30.7	Toluene
	33.7	Furfural

a Material identification is given in Table XLVI.

b Retention time in minutes.

TABLE LVII

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON TREATED PINE-3D[a]

-23°C Frac r.t.[b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
		3.1	C_2H_4
		3.8	C_2H_6
		5.7	HCHO ?
5.8	5.6	6.3	H_2O
10.2	10.1		CH_3OH
	11.7		CH_3CHO
	13.6		Methyl formate
	17.4		Acetone, furan, acrolein ?
	18.6		Methyl acetate
20.1	19.7		CH_3COOH
	21.7		Methyl ethyl ketone, vinyl acetate, 2-methylfuran
	22.8		?
	23.6		?
	24.7		C_6H_6
	25.3		$CH_3COC_3H_5$
	26.4		2,5-Dimethylfuran
	29.6		?
	30.6		$C_6H_5CH_3$
34.0	33.9		Furfural
38.0	37.1		?

a Material identification is given in Table XLVI.

b Retention time in minutes.

TABLE LVIII

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON TREATED PINE-4D [a]

-23°C Frac r.t. [b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
	1.9	1.8	CO_2
6.0	6.1	6.2	H_2O
		8.9	SO_2
	10.2		CH_3OH
	11.7		CH_3CHO
	13.6		Methyl formate
	16.1		HCOOH
	17.4		Acetone, furan, acrolein ?
	18.5		Methyl acetate
	20.1		CH_3COOH
	21.8		2-Methylfuran, methyl ethyl ketone, vinyl acetate
	22.9		?
	24.7		C_6H_6
	26.5		2,5-Dimethylfuran
	31.8		$C_6H_5CH_3$
	33.8		Furfural

a Material identification is given in Table XLVI.

b Retention time in minutes.

TABLE LIX

GAS CHROMATOGRAPHY RESULTS FOR STAGNATION BURNER TEST PERFORMED ON TREATED PINE-5D[a]

-23°C Frac r.t.[b]	-78°C Frac r.t.	-196°C Frac r.t.	Peak Identification
		1.9	CO_2
	5.4	5.6	HCHO
5.7	6.1	6.1	H_2O
	7.9		HCHO
	10.2		CH_3OH
	11.8		CH_3CHO
	13.7		Methyl formate
	17.6		Acetone, furan, acrolein ?
	18.7		Methyl acetate
	19.8		CH_3COOH
	21.8		Methyl ethyl ketone, vinyl acetate, 2-methylfuran
	22.6		?
	23.7		?
	24.7		C_6H_6
	25.5		$CH_3COC_3H_5$
	26.4		2,5-Dimethylfuran
	27.8		?
	28.6		2,3-Pentanedione
	32.0		$C_6H_5CH_3$
	34.0		Furfural

a Material identification is given in Table XLVI.

b Retention time in minutes.

TABLE LX

PRODUCTS OF PINE SAMPLES[a]

(SEALED TUBE STUDIES)

Products	Untreated Pine-1D mg/g	Untreated Pine-6D mg/g	Treated Pine-2D mg/g	Treated Pine-3D mg/g	Treated Pine-4D mg/g	Treated Pine-5D mg/g
H_2	0.09	0.07	0.13	0.01	0.01	0.13
CO	48.1	48.3	45.1	20.7	58.1	43.4
CH_4	2.21	0.78	1.18	2.79	0.98	2.30
H_2O	324.8	276.6	268.1	243.1	306.3	320.2
HCl	19.3	-	0.51	-	-	-
HCN	?	?	?	?	0.51	?
CO_2	112.1	115.8	73.8	77.7	88.7	135.4
SO_2	-	-	-	-	15.0	-
COS	-	-	-	-	0.08	-
C_xH_y[b]	0.39	0.85	1.22	1.03	1.04	0.36
C_6H_6	0.57	0.28	0.82	0.92	1.43	0.50
$C_6H_5CH_3$	0.11	0.54	5.64	17.7	0.29	0.25
Xylenes	0.05	0.02	0.18	0.04	-	T
CH_3Cl	-	-	3.41	0.11	-	0.05
C_2H_5Cl	-	-	-	0.03	-	-
CH_3OH	13.8	7.74	5.15	6.48	9.42	7.97
HCHO	1.85	2.38	1.84	1.68	3.64	2.40
CH_3CHO	1.22	1.54	3.57	0.43	0.07	1.21
Furfural	1.56	2.18	3.04	4.32	1.39	4.28
5-Methyl-2-furaldehyde	0.07	0.03	0.01	0.02	-	0.02
Acrolein	0.67	0.62	1.21	0.43	?	0.47
$(CH_3)_2CO$	1.38	3.15	1.77	2.72	2.01	1.49
$CH_3COC_2H_5$	0.44	1.34	0.36	1.19	1.24	0.86
$CH_3COC_3H_5$	2.70	1.83	0.56	2.75	0.02	0.35
2,3-Pentanedione	0.11	0.10	0.29	0.30	-	-
HCOOH	?	?	?	?	0.23	?
CH_3COOH	7.74	7.27	7.68	10.9	-	4.57
Methyl formate	4.24	2.78	5.44	2.32	0.93	0.84
Methyl acetate	2.63	1.84	2.08	1.95	3.96	0.88
Vinyl acetate	2.11	2.28	2.02	1.37	0.08	0.18
Furan	1.15	1.46	2.83	1.13	0.36	1.60
2-Methylfuran	1.19	2.13	1.23	0.32	0.35	2.13
2,5-Dimethylfuran	0.60	0.40	0.27	3.38	0.13	0.84

a Material identification is given in Table XLVI.

b C_xH_y denotes hydrocarbons C_2 through C_4.

TABLE LXI

PRODUCTS OF PINE SAMPLES[a]

(STAGNATION BURNER STUDIES)

Products	Untreated Pine-1D mg/g	Treated Pine-2D mg/g	Treated Pine-3D mg/g	Treated Pine-4D mg/g	Treated Pine-5D mg/g
H_2O	486.2	334.3	224.3	468.5	410.3
HCl	1.46	8.57	-	-	-
CO_2	199.6	226.8	171.8	274.0	590.9
SO_2	-	-	-	22.3	-
COS	-	-	-	0.12	-
HCN	?	?	?	1.32	?
C_xH_y[b]	0.85	1.37	0.59	0.87	1.53
C_6H_6	0.86	0.85	1.61	1.08	0.19
$C_6H_5CH_3$	0.07	20.0	22.0	0.03	0.19
Xylenes	T	T	-	0.03	0.01
CH_3Cl	0.22	0.46	0.30	-	-
CH_3OH	2.78	4.15	3.68	8.81	5.17
HCHO	2.09	0.37	0.71	0.50	9.97
CH_3CHO	2.53	0.84	0.81	0.76	1.12
Furfural	1.09	1.15	2.23	4.85	3.18
5-Methyl-2-furaldehyde	T	T	-	T	-
Acrolein	0.21	0.70	0.59	0.22	0.68
$(CH_3)_2CO$	2.81	2.02	1.80	0.45	1.45
$CH_3COC_2H_5$	0.69	0.15	0.62	0.48	0.70
$CH_3COC_3H_5$	0.71	1.74	1.55	-	0.52
2,3-Pentanedione	T	T	-	-	0.04
HCOOH	?	?	?	0.13	?
CH_3COOH	0.01	0.62	3.04	0.30	2.83
Methyl formate	0.28	1.23	1.12	0.04	0.23
Methyl acetate	0.76	0.96	0.85	0.45	0.18
Vinyl acetate	1.48	1.76	1.90	0.06	0.16
Furan	1.41	0.88	1.26	0.37	0.79
2-Methylfuran	1.05	1.77	1.06	0.06	0.76
2,5-Dimethylfuran	0.79	1.62	0.96	0.03	0.18

a Material identification is given in Table XLVI.

b C_xH_y denotes hydrocarbons C_2 through C_4.

formic acid (TLV, 5 ppm) and furfuryl (TLV, 5 ppm). Unfortunately the values given for the first three compounds in our compilations (see Tables LX - LXI) are probably much lower than the actual values. This is due to strong retention of these products in water and tars and their apparent tendency to associate during condensation, which results in a greatly reduced volatility. Thus it is quite possible that a significant fraction of these chemicals remained in the room temperature involatile oils and tars. This unexpected behavior has been also reported by Byrne et al[33] who found formaldehyde, acetaldehyde and other volatile compounds in the condensate formed at low pressures in a trap kept at temperatures between 20 - 200°C. Depending on the water content of the given fraction we have found the retention time for formaldehyde to vary from 4 to 8 min (based on actual trappings) and we suspect that in a large number of instances it was eluted undetected with the large water peak. Both acrolein and formaldehyde were found in various fractions, which is not surprising in view of the findings of Byrne et al[33]. Comparing Tables LX and LXI it is obvious that the product distribution and the nature of the materials formed is fairly close for the stagnation burner and the sealed system, if one neglects the higher carbon dioxide yields in the stagnation burner studies. Yet it is apparent on close examination that the stagnation burner did provide a more drastic environment, as evidenced by, e.g., the increased production of chloride ion from the pentachlorophenol treated pine as compared to the results of the sealed system. It should be stressed at this point, as it was in Sections 3.2 and 3.3, that the chloride ion values obtained for the stagnation burner tests are always significantly lower than the true or actual chloride ion production due to the reaction of the chloride ion formed with the burner walls and metal connections. No such problem exists in the sealed tube apparatus. Since no carbon monoxide determinations were carried out in the stagnation burner studies no comparison between the two methods can be made insofar as this species is concerned. From the sealed tube studies

(Table LX) it can be said that the creosote treated pine (material 3D) afforded a significantly lower quantity of CO than the untreated woods, whereas the Minalith treated pine (material 4D) formed definitely higher amounts of CO. The small room temperature fraction in the case of material 4D is in agreement with the theories advanced above that flame retardants do act by changing the mechanism of decomposition, i.e., increase in yields of volatiles such as water and CO_2 and decrease in production of tars, an important constituent of which (levoglucosan), is believed to be one of the flammable species.[34]

Insofar as toxic product formation is concerned Minalith treated pine (material 4D) is, on the basis of the products identified and quantitated, the most dangerous of the samples investigated in view of SO_2 (TLV, 5 ppm) formation, definite hydrogen cyanide presence (TLV, 10 ppm), and the increased CO (TLV, 50 ppm) production. Actually in the case of material 4D sulfur dioxide presents the greatest danger. As given in Table XLVI the Minalith treatment includes, among others, ammonium sulfate, yet no ammonia was detected. Since a substantial quantity of SO_2 was found it can be deduced that the sulfate is reduced to sulfur dioxide by ammonia.

The pentachlorophenol and the creosote impregnations are carried out in organic (oil) media; this accounts for the relatively high content of toluene (suggested TLV, 100 ppm) in the volatiles formed.

As was noted in Section 3.1.2 infrared spectroscopy was used quite extensively to identify and reveal the presence of various species. In Figure 45 is presented the infrared spectrum of the -196°C fraction obtained from the sealed tube treatment of material 4D. The infrared spectrum shows the presence of sulfur dioxide(4.01, 7.27, 7.34, 7.42, 8.56, 8.78μ); carbon dioxide (4.31, 13.89, 14.97μ); carbonyl sulfide (4.82, 4.87μ), methyl acetate (5.65, 8.0μ), methanol (9.45, 9.65, 9.90μ), 2-methylfuran (12.6, 13.75μ), furan (13.42μ), and hydrogen cyanide (14.02μ). All the other materials afforded similar -196°C fractions with the only exception that no

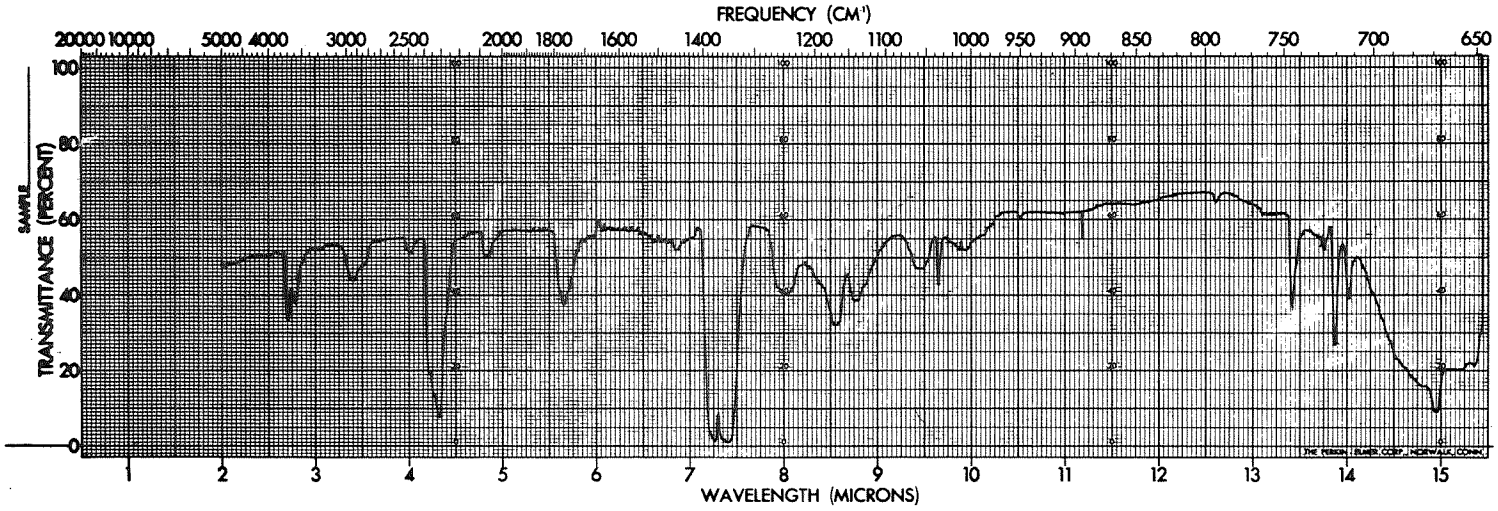


Fig. 45. Infrared Spectrum of -196°C Fraction
Sealed Tube Treatment of Minalith Impregnated Pine (4D) (gas, p = 294 mm)

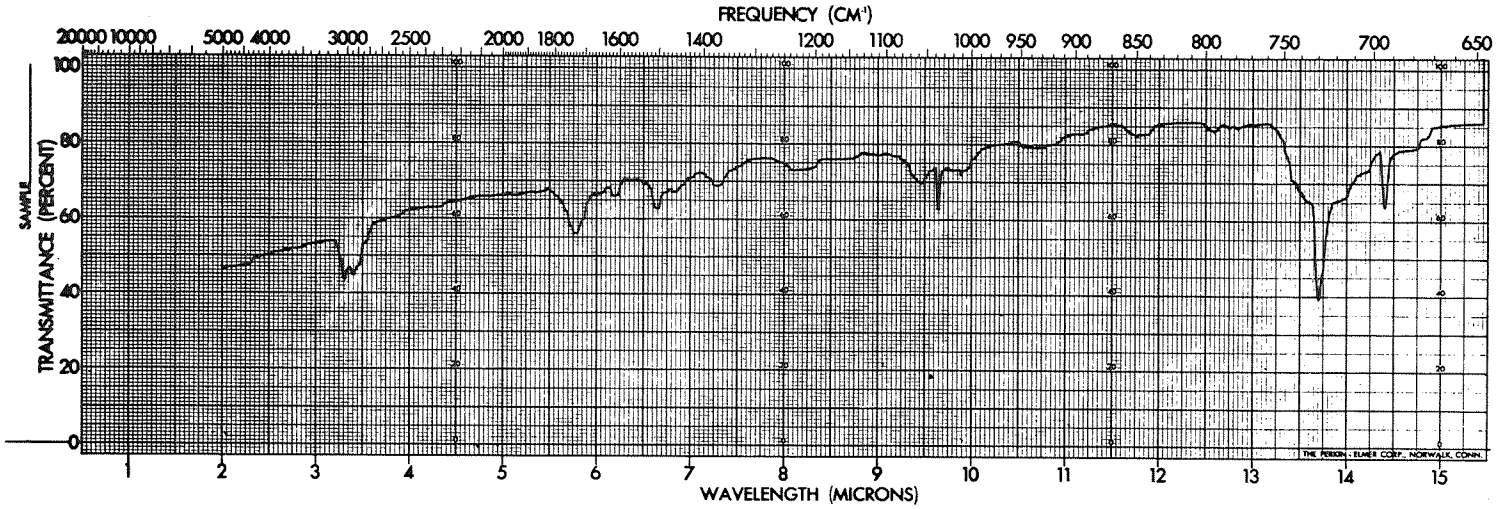


Fig. 46. Infrared Spectrum of -78°C Fraction
Stagnation Burner Treatment of Pentachlorophenol Impregnated Pine (2D) (gas, p = 24 mm)

sulfur dioxide, carbonyl sulfide and hydrogen cyanide bands were observed. Minalith treated pine was the only sample in which HCN was seen in the infrared spectrum. Figure 46 depicts a typical infrared spectrum of the gaseous phase of a -78°C fraction. The particular spectrum presented is that of a fraction derived from pentachlorophenol treated pine. The main constituent here is toluene (3.30, 6.20, 6.65, 13.70, 14.40μ) together with a carbonyl (5.77μ) methanol (9.45, 9.65, 9.90μ) and aliphatic CH (3.40-3.55μ). The liquid portions of the -78°C fractions consisted largely of water admixed with alcohols, acids and carbonyls (ketones, aldehydes). In Figure 47 is given a representative spectrum. The broad bands centered at 3.0 and 6.1μ are due to water. Of interest here is the absorption at 4.75μ, which was also encountered in the liquid portion of the -23°C fractions and which we believe is due to CN^- ion; yet, both the Liebig and the Prussian Blue tests were ambigous, which could be due to small samples sizes. The same problem was found in the urethane rigid foam investigations. Figure 48 shows a typical infrared spectrum of the room temperature involatile oils obtained in the stagnation burner studies. These materials were volatile at 400°C. Surprisingly enough both the treated and untreated pines appeared to afford fairly similar spectra with the exception of Minalith treated pine where hardly any tars were formed. The significance of this observation was discussed earlier.

To summarize briefly the findings of the wood investigations, it can be said that the Minalith treatment did affect most significantly the thermal oxidative behavior of the pine. The most important here is the lowered decomposition onset, the increased production of carbon monoxide (in the sealed system; no CO data have been obtained for the stagnation burner work), formation of substantial quantities of sulfur dioxide, and some hydrogen cyanide, absence of glow, increased char yield and strongly decreased tar production. The pentachlorophenol and creosote treatments resulted, among

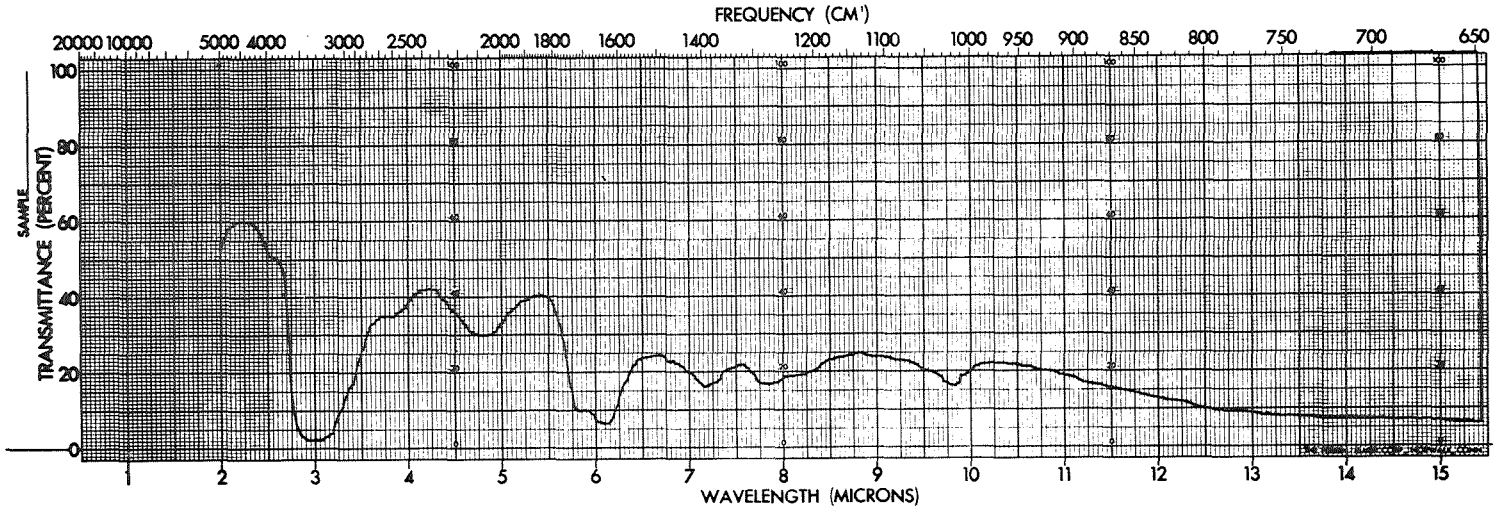


Fig. 47. Infrared Spectrum of -78°C Fraction
Sealed Tube Treatment of Pentachlorophenol Impregnated Pine (2D) (liquid film)

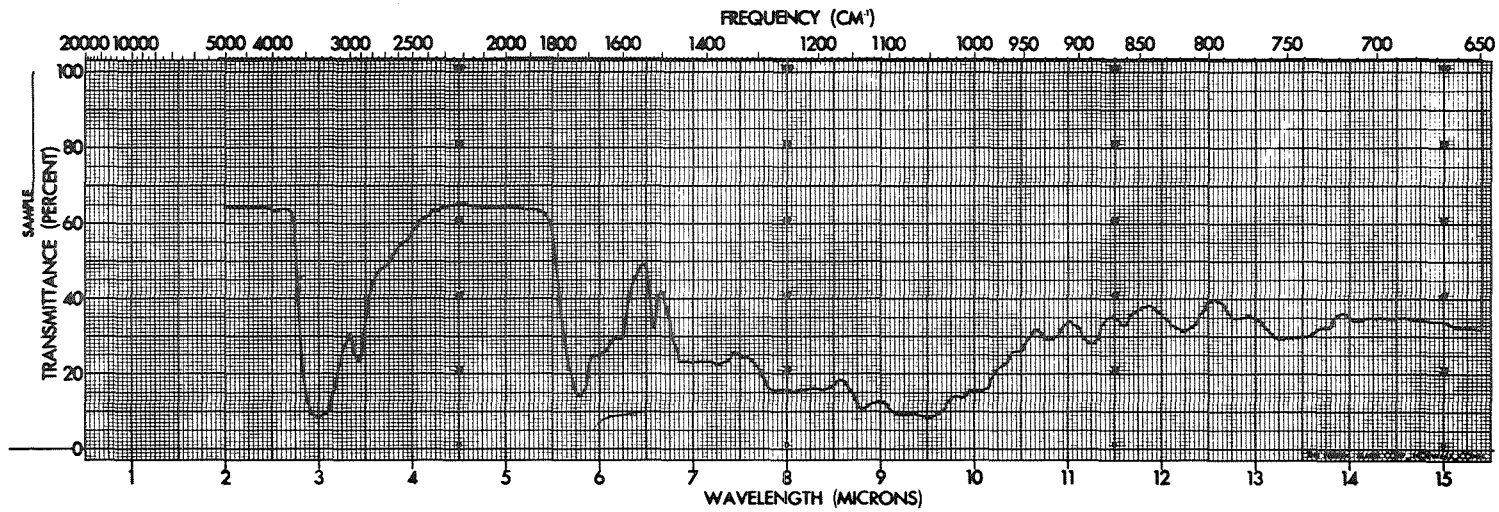


Fig. 48. Infrared Spectrum of Room Temperature Involatile Oils
Stagnation Burner Treatment of Creosote Impregnated Pine (3D) (liquid film)

others, in an increased toluene content of the volatiles, most likely caused by the oil impregnation medium. The CCA treatment resulted in the highest carbon dioxide production of all the samples both in the sealed tube and stagnation burner investigations; this is most apparent in the latter case. Another aspect of importance is the relatively high concentration of formaldehyde found among the oxidative thermal decomposition products.

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