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# REPORT

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# ON

### THE

## FUNDAMENTAL STUDIES ON THE SYNTHESIS OF

HEAT-RESISTANT POLYMERS

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## THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

WASHINGTON, D.C.

### PERFORMED

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DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA 46556

PROGRESS REPORT NUMBER 6

ON THE

FUNDAMENTAL STUDIES ON THE SYNTHESIS OF

### HEAT-RESISTANT POLYMERS

### THE SYNTHESIS AND EVALUATION OF POLYMERIC

1

# SCHIFF BASES BY BIS-SCHIFF BASE EXCHANGE REACTIONS

PERFORMED

UNDER

NASA GRANT NsG339

BY

G. F. D'ALELIO

### PRINCIPAL INVESTIGATOR

DEPARTMENT OF CHEMISTRY

UNIVERSITY OF NOTRE DAME

NOTRE DAME, INDIANA 46556

SEPTEMBER 15, 1965

#### FOREWORD

This report is a summary report of the researches performed under NASA Grant NsG339 for the period 31 January 1965 to 15 September 1965 on the synthesis of heat-resistant polymers. The technical aspect of this grant is administered by Mr. Bernard Achhammer, Office of Advanced Research and Technology, NASA Headquarters, Washington, D.C. 20546.

The research under this grant is being conducted in the Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556 under the technical direction of Professor G. F. D'Alelio, principal investigator.

This report covers studies performed by G. F. D'Alelio and J. Crivello.

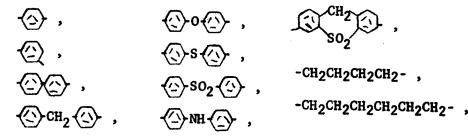
Date September 15, 1965

lelio Signed G.F. D'Alelio

Principal Investigator

#### ABSTRACT

Three new bis-Schiff base monomers were synthesized, completing the series of eleven monomers required for the polymer syntheses. Eleven Schiffbase polymers of the general structure,  $\{N-Z-N=HC \bigcirc CH\}_n$  were synthesized by both the bis-Schiff base exchange melt and the solution methods. In these polymers, -Z- represents the following structures:



representing polymers which contained conjugated, pseudoconjugated or nonconjugated backbone structure.

The thermal resistances in nitrogen and in air of the non-conjugated aliphatic polymers are much lower than those of the conjugated and pseudoconjugated polymers. Also, the thermal resistance in air and in nitrogen of the conjugated and pseudoconjugated polymers prepared in solution is much lower than the same polymers prepared by melt bis-Schiff base exchange procedures.

Both the conjugated and pseudoconjugated polymers prepared by bis-exchange reactions have very good thermal stabilities in nitrogen and in air; the highest values, however, are found in the conjugated polymers. When these polymers are condensed to a temperature of 400 °C (752 °F), the best conjugated polymer,  $\pm N - N = HC - CH = \frac{1}{n}$  shows a heat-resistance in nitrogen of 550 °C (1022 °F) compared to the two best pseudoconjugated polymers,  $\pm N - C - CH = \frac{1}{n}$  and  $\pm N - CH = \frac{1}{SO_2} - N = HC - CH = \frac{1}{n}$  which have a resistance in nitrogen of 525 °C (977 °F); while in air, the best conjugated polymer,

iii

 $\neq N$   $( ) N = HC ( ) - CH = 1_n$  shows a heat-resistance of 500°C (932°F) compared to the best pseudoconjugated polymers,  $\neq N$   $( ) - O - ( ) - N = HC - ( ) - CH = 1_n$  and  $\neq N - ( ) - CH = 1_n$ , both of which show a heat-resistance of 475°C  $SO_2$  (877°F) in air.

When the conjugated and pseudoconjugated polymers are condensed to higher temperature by postheating to 600°C, their thermal stabilities in nitrogen and in air are increased. The two conjugated polymers,  $f_N \leftarrow N = HC \leftarrow CH \neq_n$ and  $f_N \leftarrow N = HC \leftarrow CH \neq_n$ , which have been condensed to 600°C, show heat-resistances in nitrogen of 630°C (1066°F) and 645°C (1103°F) respectively, compared to a value of 550°C (1022°F) for the pseudoconjugated polymer,

$$\underbrace{ \{ N \in \mathcal{N}_{SO_2}^{n_2} \cap \mathbb{N} = HC \bigoplus CH \}_n }$$

When the conjugated and pseudoconjugated polymers are condensed to 1176°C by postheating, all the polymers so treated show a heat-resistance in nitrogen of about 1176°C (2025°F) with losses averaging about 3.0% of the polymers; with the conjugated polymer,  $\{N \land N=HC \land CH\}_n$  showing the highest thermal stability of 600°C (1112°F) in air.

Some secondary reaction appears to occur when the polymers are heated in nitrogen to temperatures above 600°C and the resulting polymers, even.. when heated to 1176°C, are not typical chars but retain their bright, shiny appearance.

The polymer prepared from dibenzylidene-m-phenylenediamine appears to have heat-resistance comparable to the p-phenylenediamine derivative, and because of lower cost of the meta compound, its future use is indicated.

Preliminary experiments indicate that the syntheses of the bis-Schiff bases can be circumvented by reacting all the reagents, namely, the aryldiamine, the terephthaldehyde, the aniline, and the benzaldehyde directly in a one-step melt process.

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I. Introduction.

Previous reports<sup>1,2</sup> on the syntheses of heat-resistant polymers describe the various reactions applicable to the syntheses of polymeric Schiff bases. Based on these investigations, three areas were selected for further studies.<sup>2</sup>

The first area, dealing with an exchange reaction between two difunctional Schiff bases which yield<sup>1,2</sup> black polymeric Schiff bases that pass through a fusible stage, is the subject of this report.

A second area, "The Synthesis and Evaluation of Polymeric Schiff Bases from Xylylidene Tetraalkyl Ethers", is the subject of a separate report.<sup>3</sup>

A third area of investigation, "Preliminary Studies on the Synthesis and Evaluation of Polymeric Azines", is also the subject of a separate report.<sup>4</sup>

This report concerns investigations on the synthesis of polymeric Schiff bases by bis-Schiff base exchange reactions and an evaluation of the heatresistant properties of the polymers so synthesized.

When two bis-Schiff bases react, one containing an aromatic dialdehyde moiety and the other an aromatic diamino moiety, the resulting product is a stable, non-volatile poly-Schiff base. This polymerization reaction is described by the following equation:

n C<sub>6</sub>H<sub>5</sub>CH=NArN=CHC<sub>6</sub>H<sub>5</sub> + n C<sub>6</sub>H<sub>5</sub>N=CHArCH=NC<sub>6</sub>H<sub>5</sub> 
$$\longrightarrow$$
  
 $\{$ NArN=CHArCH $\}_n$  + 2n C<sub>6</sub>H<sub>5</sub>N=C<sub>6</sub>H<sub>5</sub> (eq. 1)

in which Ar represents a divalent aromatic molety. Thus, the end groups of each of the two reacting monomeric bis-Schiff bases combine together to give rise to two equivalents of a more simple volatile Schiff base. The driving force of the reaction can be attributed to two factors; the formation of a very stable polymeric Schiff base and the removal of simple volatile Schiff base by distillation. A number of monomers, in which the terminal groups of the aromatic diamine Schiff base are C<sub>6</sub>H<sub>5</sub>CH= groups, and of the aromatic dialdehyde are C<sub>6</sub>H<sub>5</sub>N= groups, res-

pectively, are discussed in previous reports.<sup>1,2</sup>

Most of the earlier work<sup>1,2</sup> on the synthesis of the poly-Schiff bases by the bis-exchange reaction used reagents in which the Ar moiety was phenylene,  $-C_{6}H_{5}$ -, thus

n C<sub>6</sub>H<sub>5</sub>CH=NC<sub>6</sub>H<sub>4</sub>N=HCC<sub>6</sub>H<sub>5</sub> + C<sub>6</sub>H<sub>5</sub>N=HCC<sub>6</sub>H<sub>4</sub>CH=NC<sub>6</sub>H<sub>5</sub> 
$$\longrightarrow$$
  
 $=$  NC<sub>6</sub>H<sub>4</sub>N=HCC<sub>6</sub>H<sub>4</sub>CH $=$  n C<sub>6</sub>H<sub>5</sub>CH=NC<sub>6</sub>H<sub>5</sub> (eq. 2)

Further, both reactants, the dibenzalphenylene diamine,  $C_6H_5CH=N$  ( N=HCC<sub>6</sub>H<sub>5</sub>, and the xylylidenedianil,  $C_6H_5N=HC$  ( CH=C<sub>6</sub>H<sub>5</sub>, were para derivatives, to yield a para-para type polymer, thus:

n C<sub>6</sub>H<sub>5</sub>CH=N()-N=HCC<sub>6</sub>H<sub>5</sub> + n C<sub>6</sub>H<sub>5</sub>N=HC()-CH=NC<sub>6</sub>H<sub>5</sub> 
$$\longrightarrow$$
  
 $\neq$ N()-N=HC()-CH $\neq$ <sub>n</sub> + 2 C<sub>6</sub>H<sub>5</sub>CH=NC<sub>6</sub>H<sub>5</sub> (eq. 3)  
para-para polymer

The para derivatives were deliberately chosen on the expectation that the resulting polymer would possess the highest degree of linearity as a result of bond angles. It was expected that such a degree of linearity would contribute to maximum heat resistance.

It was indicated in a previous report<sup>2</sup> that, in the reaction with xylylidene tetramethyl ether, meta phenylenediamine and its dibenzylidene derivative appeared to be better reactants than their analogous para compounds because the meta compounds permitted a longer fusi ble stage during the polymer synthesis. As seen from the following equation, the conjugation in the resulting meta-para polymer would not be interrupted by the use of the meta diamine derivative:

$$n C_{6}H_{5}CH=N \underbrace{ }_{N=HCC_{6}H_{5}} + n C_{6}H_{5}N=HC} \underbrace{ }_{N=HC} \underbrace{ }_{N=HC} \underbrace{ }_{O}CH_{5} + 2n C_{6}H_{5}CH=NC_{6}H_{5} }_{meta-para polymer}$$
(eq. 4)

Accordingly, it was one purpose of this study to compare the dibenzylidene deri-

vatives of meta and para phenylenediamine in the polymerization reaction and to evaluate the differences, if any, in the thermal resistances of the resulting polymers. It will also be noted that present studies were limited to the para derivative for the dialdehyde moiety, namely, the p-xylylidenedianil aniline. This restriction exists for the present only, because the unavailability of the metaphthaldehyde. It is obvious that its use as a reagent with the meta and para diamines would produce meta-meta and para-meta type polymers respectively, which ultimately should be compared to the para-para and meta-para polymers. At the onset of the studies detailed in this report, it was not deemed advisable to dilute or divert the program to synthesize the meta-dialdehyde until evaluation of the meta-para type polymer have been completed. Then, if the meta-para type polymer were shown to have properties similar to the para-para polymers, future research would be devoted to the syntheses of meta-meta and para-meta Schiff base polymers.

An examination of equations 3 and 4 will show that the conjugation in the polymer is uninterrupted, that is, either a carbon-to-carbon double bond, C=C, or a carbon-to-nitrogen double bond, C=N, alternate with a carbon-to-carbon, C-C, single bond, or with a carbon-to-nitrogen single bond, C-N. Since the heat resistance<sup>1,2</sup> as well as their semi-conductor properties,<sup>2</sup> have been attributed to this uninterrupted conjugation, it was considered important to determine how the heat resistance of these polymers would be influenced by decreasing or interrupting the conjugation by inserting appropriate groups or structures in the backbone of the polymer. For the study of this specific phase, it was decided to maintain the dialdehyde moiety, =HC  $\bigcirc$  CH=, constant in the polymer structure and to introduce the changes in the conjugation in the diamine moeity, =N-Z-N=, to yield polymers of the general structure,  $\frac{1}{2}$  N-Z-N=HC  $\bigcirc$  CH=, wherein Z would represent the structure in which the changes in conjugation would be

introduced.

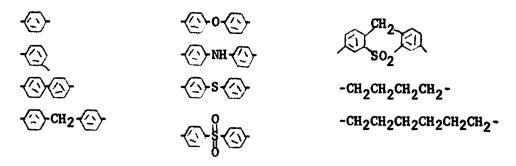
It was also a purpose of this study to evaluate the bis-exchange reaction in the syntheses of these polymers to determine the breadth of the applicability of the bis-Schiff base exchange polymerization reaction, thus

n C<sub>6</sub>H<sub>5</sub>CH=N-Z-N=HCC<sub>6</sub>H<sub>5</sub> + n C<sub>6</sub>H<sub>5</sub>N=HC 
$$\leftarrow$$
 CH=NC<sub>6</sub>H<sub>5</sub>  $\rightarrow$   
 $\neq$ N-Z-N=HC  $\leftarrow$  CH $\neq$ <sub>n</sub> + 2n C<sub>6</sub>H<sub>5</sub>CH=NC<sub>6</sub>H<sub>5</sub> (eq. 5)

Polymers in which Z is the phenylene group,  $-C_6H_4$ -, as given in equations 3 and 4, would thus become the reference point for the studies on the effects due to changes in the nature or the extent of conjugation. The conjugation can be effectively interrupted, completely by eliminating the arylene group as the Z structure between the nitrogen atoms and substituting therefore, an alkylene group,  $(CH_2)_n$ . Two such -2- structures,  $-(CH_2)_4$ - and  $-(CH_2)_6$ - were selected for evaluation as representing non-conjugated polymers of the general structure  $\frac{1}{2}N-(CH_2)_n-N=HC}{(S)}CH_n^{\frac{1}{2}}$ .

A relatively simple method of changing the character and extent of conjugation in aromatic compounds is to introduce changes in diphenyl,  $\langle \cdot \rangle \rangle$  by insertion of other atoms or groups of atoms, such as -O-, -S-, -SO<sub>2</sub>-, -CH<sub>2</sub>-, -NH-, etc. between the benzene rings so that they are bonded to the benzene rings by single bonds only, thus,  $\langle \cdot \rangle \cdot X - \langle \cdot \rangle$ , to give polymers of the general structure,  $\{ N-C_6H_4-X-C_6H_4-N=HC-C_6H_4-CH_{n} \}_n$ . Since a number of these X groups contain atoms with unshared pairs of electrons which can contribute to resonance structures, they cannot be considered as completely non-conjugated; rather, because of their character, they can be considered as "pseudoconjugated" and more closely related to  $\langle \cdot \rangle$  and to  $\langle \cdot \rangle \langle \cdot \rangle$  rather than to the aliphatic  $\langle CH_2 \rangle_4$  and  $\langle CH_2 \rangle_6$  structures.

Accordingly, for this study dealing with conjugation, polymers were prepared which contained the following 2 structures:



The syntheses of some of these polymers required the synthesis of some new polymers.

Another purpose of this research was to attempt to produce by the bis-Schiff base exchange reactions, black polymers which pass through a fusible stage, in those reactions which yield conjugated or pseudoconjugated structures and to compare their thermal properties with the corresponding polymers made directly from the dialdehyde and the diamine by solution polymerization. As shown in previous reports,<sup>1,2</sup> Schiff base polymers prepared by solution methods are of the infusible, insoluble, light colored, brick-dust type of lower molecular weight than the black polymers prepared by melt or exchange methods. In the specific case of  $\{N-C_6H_4-N=HC-C_6H_4-CH_n\}_n$ , the solution polymer is of yellow color, whereas the polymer prepared by a bis exchange reaction passes progressively from a yellow to an orange to a brown to a black polymer as the polycondensation proceeds. II. Synthesis of Monomers.

The synthesis of the following monomers used in this study was given in previous reports:<sup>1,2</sup>

Compound	Exper. No.	M.P. °C	Reference
p-C6H5N=HCC6H4CH=NC6H5	DA-24-42	78	1
P-C6H5CH=NC6H4N=HCC6H5	DA-24-43	140	1
m-C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> N=HCC <sub>6</sub> H <sub>5</sub>	DA-24-44	104-106	1
p-C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> N=HCC <sub>6</sub> H <sub>5</sub> -p	DA-29-176	130	2
$C_6H_5CH=N(CH_2)_4N=HCC_6H_5$	DA-29-178	26-27	2
C <sub>6</sub> H <sub>5</sub> -CH=N(CH <sub>2</sub> ) <sub>6</sub> N=HCC <sub>6</sub> H <sub>5</sub>	DA-29-181	25	2
p-C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> OC <sub>6</sub> H <sub>4</sub> N=HCC <sub>6</sub> H <sub>5</sub> -p	DA-29-184	182-183	2
p-C <sub>6</sub> H <sub>5</sub> CH=NC <sub>6</sub> H <sub>4</sub> NHC <sub>6</sub> H <sub>4</sub> N=HCC <sub>6</sub> H <sub>5</sub> -p	DA-29-188	183-186	2

Three new pseudoconjugated monomers for use in the current studies were also synthesized by the continuous azeotrope method used so successfully previously.<sup>1</sup> The diamine and benzaldehyde, in a molar ration of 1:2 respectively, were refluxed together in benzene in an apparatus to which was attached a Dean-Stark trap to collect the evolved water. When the theoretical amount of water had accumulated in the trap, the reaction mixture was allowed to cool, the product removed by filtration and recrystallized from benzene to a constant melting point. In all cases the yield of crude product was substantially theoretical. In some cases, difficulties encountered in recrystallization resulted in a low yield of recrystallized product. The data is summarized in Table 1.

#### Table 1

# Data on Some New Bis-Schiff Base Monomers

Monomer	Exper. No.	% Yield Product		Melting Point, °C		Ref.
		Crude	Recrys.	Found	Ref.	no.
C6H5-CH=N-()-S-()-N=CH-C6H5	DA-42-12	100	41.8	180	178	5
$C_{6}H_{5}$ -CH=N $()$ -SO <sub>2</sub> $()$ -N=CH-C <sub>6</sub> H <sub>5</sub>	DA-29-272	100	42.4	236	232	6
C6H5-CH=N (1) SO2 (1) N=CH-C6H5	DA-42-7	100	93.4	208	*	-
* Analysis: Theory: C, 74.50; H, 4.58; N, 6.44; S, 7.35.						

Found: C, 74.47; H, 4.65; N, 6.48; S, 7.44.

### III. Polymerization Reactions.

### A. Melt Polymerizations.

Three separate routes for the synthesis of Schiff base polymers by exchange reactions, namely, the amine exchange, the carbonyl exchange, and the bis-Schiff base exchange reactions were described in previous reports. 1,2 On the basis of these studies, the bis-Schiff base exchange reaction was selected as the most advantageous method for the preparation of the polymers. Though the amine exchange and the carbonyl exchange reactions proceed much more rapidly than the bis-exchange reaction, they are more difficult to control and in most cases produce a heterogeneous intermediate condensation product unless the reaction is performed in the presence of an active solvent such as benzalaniline. On the other hand, the bis-Schiff base exchange reaction proceeds very smoothly in the absence of benzalaniline, yielding homogeneous intermediate condensation products telomerized by the benzal and anilido moieties in a medium of by-product benzalaniline generated by the reaction. The bis-Schiff base exchange reaction is much slower than either the amine or the aldehyde exchange, but it can be accelerated by Lewis acids such as zinc chloride and toluene sulfonic acid. Since the purpose of this study was to compare the properties of a number of polymeric Schiff bases having substantially different backbone structures, it was considered necessary to select arbitrarily some of the reaction conditions for the polymerization which tend to equalize the diverse nature of the various dibenzylidene monomers. Because of the diverse natures of the dibenzylidenediamine monomers and the lack of knowledge of the interaction of such an active solvent as benzalaniline with these monomers, it was decided to perform the polymerization in the absence of benzalaniline. Also, it was considered that the uncatalyzed polymerizations would introduce less complications. Accordingly, it was decided to perform uncatalyzed, unsolvated polymerizations. With this decision it became

necessary to select time-temperature conditions under which all or most of the desired polymers would be synthesized.

Previous studies have shown<sup>1,2</sup> that polycondensation reaction involving exchange reactions is not completed at 325°C and the black polymers can undergo postcondensations in the solid state to tough polymers. Accordingly, a number of preliminary experiments in these studies showed, on the basis of preliminary thermogravimetric analyses, that the condensation is far from complete unless the temperature of condensation exceeds 400°C; in fact, it is not truly completed until the temperature of condensation approaches the 600°C region. This was evidenced by the continued elimination of benzalaniline when the polymeric Schiff bases synthesized by the bis-Schiff base exchange reactions, were heated to 1200°C in nitrogen in the thermogravimetric apparatus; these same preheated polymers, when reheated to 1200°C, showed minor heat losses.

On this basis, it was decided to prepare all the polymers under the identical temperature conditions of condensation up to 400°C under a standardized time and pressure schedule which would be maintained uniformly for all the polymerizations, whenever feasible. The polymers prepared up to a condensation temperature of 400°C would then be isolated and a portion would be postheated to 600°C. A temperature of 650-700°C would have been preferable to 600°C as the selected second higher temperature for postheating, but this was unfeasible because these temperatures are beyond the melting point of the aluminum block (623°C) used as the metal-heating apparatus and the operating conditions of the electric heating mantle surrounding the aluminum block.

It was considered advisable also to complete the condensation further at some temperature in excess of 600°C and preferably to the region of 1000°C or higher. This required the development of a special procedure and it was accomplished by heating small samples of the order of 10 mg. of the polymer directly

in a thermogravimetric apparatus.

It was realized that in utilizing a standardized schedule of temperature, time, and pressure that the ultimate yields would not necessarily be the highest or the best attainable, since, if the polycondensation is not complete when the pressure over the condensation mass is reduced, reagents and oligomer may be lost by distillation or sublimation, reducing <u>ultimate</u> yields. However, in condensations which proceed by elimination of simple molecules by chain-end coupling, the ultimate polymer obtained, even at reduced yields, can be considered as sufficiently typical, if condensation reaction is continued far enough, for evaluation of thermal properties.

### 1. Standardization of Polymerization Procedure.

#### a. Experimental.

The reagents were placed in a reaction tube fitted with a side arm and heated by means of a metal heat sink which consisted of a cube of aluminum, three inches long on an edge. A hole, one inch in diameter, was drilled in the center of one face of the cube to house the reaction tube, and a probe hole was located within one-half inch of the inserted reaction tube. The metal cube was heated by a special Glas-Col square mantle, custom-made for the cube.

Temperatures up to 400 °C were maintained and controlled by a Model 1422-071 Temperature Controller from Cole-Parmer Instrument and Equipment Company. For heating above 400 °C, the temperature was controlled by a Variac and the temperature determined by a thermocouple. The maximum range of the apparatus equipped with guartz reaction tubes is 600 °C.

The reaction tube was equipped with a nitrogen bleeder supported by a Teflon adapter, a condenser, an adapter with side arm for evacuation, and a receiver which was submerged in a solid carbon dioxane-acetone trap. All joints were ground glass and standard taper.

A number of polymerizations, DA-29-244, DA-29-247, DA-29-262, DA-29-264 and DA-29-265 were performed in this apparatus in which the time, temperature and pressure cycles were varied over a wide range.

An evaluation of these polymerizations with respect to overall behavior such as ease of control, yield, etc., led to the selection of the standard conditions for all subsequent melt polymerization except those involving the aliphatic amine derivatives. The standardized conditions are shown in Table 2.

#### Table 2

Standardized Melt Polymerization Conditions Using Bis-Schiff Base Exchange Reactions

Time (hours)	Temperature (°C)	Pressure
2	200	atmospheric
2	260	atmospheric
10	320	atmospheric
20	380	1 mm
20	400	lmm

Under these standardized conditions, the polymerizations were found to proceed smoothly through the successive color changes from yellow to red to brown to black with the continuous evolution of benzalaniline. It is necessary to exercise care during the fourth stage of the polymerization when the pressure is reduced to avoid loss of reactants due to bumping of benzalaniline. It was found advisable to reduce the pressure slowly in successive stages over the course of about one-half an hour.

### 2. Standardized Polymerizations.

The polymers were prepared by the bis-Schiff base exchange reaction under melt conditions according to equation 5. The standardized condition was used in all cases except in the cases of the two polymers which contained aliphatic moieties in their backbone, namely:  $\{N-(CH_2)_4N=HC \land CH_n \}_n$  and  $\{N-(CH_2)_6-N=HC \land CH_n\}_n$ in which case decomposition was found to occur under these conditions.

However, it was found possible to synthesize these "aliphatic" Schiff bases under modified conditions which consisted primarily in lowering the temperature and decreasing the time of reaction. The modified conditions are shown in Table 3.

### Table 3

Conditions for Preparing "Aliphatic" Schiff Base Polymers

Time (hours)	Temperature (°C)	Pressure
2	150	atmospheric
10	200	atmospheric
10	250	1 mm
10	250	1 mm

The polymers prepared by the bis-Schiff base exchange reactions under melt conditions using standardized and modified standardized conditions, together with other pertinent information, is shown in Table 4. The general procedure consisted in mixing the reagents in the reaction vessel, evacuating the system, sweeping out the system with nitrogen and performing the polymerization under a nitrogen atmosphere under the selected conditions of temperature, pressure, and time. The polymerizations were carried out on a relatively small scale of 0.005 mole with respect to the monomers.

To determine whether or not changes in the standardized polymerization conditions would introduce changes in the heat resistance properties of the aromatic-type black, Schiff base polymers, Experiment DA-29-154 was performed to synthesize  $f(n) = HC (n) CH_n$  under non-standard, that is, modified conditions.

Experiment DA-29-154 corresponds to DA-43-13 in the reagents used but differs in the history of its polymerization conditions which are as follows:

Time (hours)	Temperature (°C)	Pressure
4	200	atmospheric
8	280	atmospheric
10	320	atmospheric
5	400	atmospheric
19	450	1.5 mm

The yield of black, shiny polymer was 127.7% of theory.

### Table 4

Polymers Prepared by Bis-Schiff Base Exchange Reactions

Polymer	Exper. No.	% Yield	Color	Polymerization Conditions
ŧn- <u>·</u> -n=HC- <u>·</u> -CH=	DA-42-13	109.7	black	standardized
	DA-42-14	105.0	black	standardized
ŧn ( , n=HC ( , ch+	DA-29-284	106.4	black	standardized
	DA-29-265	105.4	black	standardized
ŧN ()-0 () N <del>n I</del> IC () GH <del>J</del> n	DA-29-275	110.0	black	standardized
ŧn~~>nh~~>n=hc~~>ch=}n	DA-29-282	98.3	black	standardized
ŧn � s · n=hc · ch ł <sub>n</sub>	DA-42-16	100.0	black	standardized
₩ \$ 502 \$ N=HC \$ CH=]n	DA-29-285	89.6	black	standardized
ŧN € CH2 N=HC C CHJ <sub>n</sub>	DA-42-11	105.0	black	standardized
$=$ (CH <sub>2</sub> ) <sub>4</sub> -N=HC $\langle \cdot \rangle$ CH $=$ n	DA-29-286	79 <i>.</i> 8	orange	modified standardized
<b>ŧ</b> №- (CH <sub>2</sub> ) <sub>6</sub> -№=HC ⟨⟨⟩-CH <sup>‡</sup> <sub>n</sub>	DA-42-10	102.0	orange	modified standardized
₽N-CN=HC-Ch-Pn	DA-29-154	127.7	black	modified standardized

The bis-Schiff base exchange reaction was found to go well for all the monomers tried. For the conjugated and pseudoconjugated monomers, the poly-

merization was found generally to proceed through five stages:

1) the formation of a yellow melt;

2) changing to an orange melt;

3) the formation of a red-brown melt;

4) becoming dark brown; and

5) finally becoming a black, shiny, porous solid.

In contrast, the aliphatic, non-conjugated polymers were orange in color when the polymerizations were terminated.

In agreement with previous results,  $^{1,2}$  the yields of polymer were found generally to be in excess of 100% of the theoretically calculated value for a DP of  $\infty$  due to the difficulty of removing the by-product, benzananiline, from the polymer mass and to the incompleteness of the condensation at these temperatures.

Yields lower than 100% of theory can be attributed to loss of uncondensed reagents during the distillation stage under reduced pressure in the polymerization procedure. Later studies show that grinding these polymers and subjecting them to higher temperatures and lower pressures, the condensation reaction can be continued and more benzalaniline by-product obtained.

3. Miscellaneous Polymerizations.

A number of other polymerizations were performed to explore and extend the scope of the bis-exchange polymerization. Since the Schiff base exchange reactions were shown to be very facile reactions, it was believed that it would be unnecessary to prepare each of the monomers, p-xylylidenedianil and dibenzylidene-p-phenylenediamine separately for polymerization. It might be possible that these monomers could be prepared in situ from the constituent p-phenylenediamine, terephthaldehyde, benzaldehyde and aniline. Exchange would then take place between the various Schiff bases formed in the reaction mixture giving rise to the most stable end-product, the polymer.

To evaluate this concept, three polymerization reactions were performed. <u>a. Experimental</u>.

### i. (DA-29-252) Melt Polymerization of p-Phenylenediamine, Terephthaldehyde, Aniline, and Benzaldehyde.

Equimolar quantities (0.004 M) of each of the following compounds were weighed out and placed into the reaction tube in the following order: benzaldehyde, aniline, p-phenylenediamine, and terephthaldehyde. A yellow color immediately was formed and the reaction mixture solidified. The reaction tube was fitted with a condenser, a receiver and a nitrogen inlet and the reaction mixture subjected to a melt polymerization under the following conditions:

Time (hours	) Temperature (°C)	Pressure
2	220	atmospheric
8	320	atmospheric

During the eight-hour heating period, the polymer melt was observed to undergo a change in color from yellow to brown-black. When the reaction was discontinued, benzalaniline and water were found in the receiver and 0.824 g. (102% yield) of amorphous polymer was obtained.

ii. (DA-29-256) Repeat of DA-29-252 Using a Different Procedure.

The same quantities of reagents were used in this polymerization as in DA-29-252. The method of the addition of reagents, however, is different. The two amines, p-phenylenediamine and aniline were placed in a small mortar, then the mixture of benzaldehyde and terephthaldehyde was added with rapid stirring by means of a pestle. The mixing was accompanied by immediate formation of a yellow color in the pasty mass. After about five seconds the mixture solidified, was removed from the mortar, placed in a reaction tube and

Time (hours)	Temperature (°C)	Pressure
2	220	atmospheric
2	220-400	atmospheric
9	400	atmospheric
10	400	atmospheric
4	400	1.5 mm

melt polymerized under the following conditions:

After the completion of the reaction benzalaniline was found in the receiver and aniline and water in the dry ice-acetone trap. A black, dull, amorphous-appearing polymer was obtained in a 100% yield.

### <u>iii. (DA-29-260) Melt Polymerization Using m-Phenylenediamine,</u> Aniline, Benzaldehyde, and Terephthaldehyde.

Four-thousandths of a mole of each of the amines, m-phenylenediamine and aniline, were placed in a mortar and then a mixture of 0.004 mole of each of the aldehydes, benzaldehyde and terephthaldehyde, were added. Mixing by means of a pestle produced a yellow, very viscous, sticky oil which would not solidify at room temperature on standing. The reaction mixture was removed from the mortar as glassy chips by cooling the mortar in dry ice. The cold, glassy oligomer was transferred to a reaction tube and polymerized under the following conditions to yield a black, shiny polymer:

Time (hours)	Temperature (°C)	Pressure
12.5	260	atmospheric
1.0	370-390	atmospheric
7.0	414	atmospheric
9.0	360	1.5 mm

### b. Discussion.

The three experiments described above show that it is possible to obtain Schiff base polymers by a route which by-passes the initial synthesis of Schiff base monomers. The reactions involved in this synthesis are a mixture of three Schiff base exchange reactions as well as the simple condensation of an aldehyde and an amine.

Of the three experiments performed above, the polymerization involving m-phenylenediamine (DA-29-260) is the best. This result probably arises from the maintenance of homogeneity throughout the polymerization due to the nature of the geometry of a polymer with m-phenylene units. This synthesis is deserving of future studies.

### **B. Solution Polymerization.**

For purposes of this study, it was desired to compare the black Schiff base polymers prepared by the melt bis-Schiff base exchange reaction with the "yellow" infusible, brick-dust polymers prepared by another method. Since solution polymerization methods were shown<sup>1,2</sup> in the case of terephthaldehyde and phenylenediamine to yield such yellow polymers, the solution method was used to prepare these polymers. The solution method of Davidov and his coworkers<sup>7</sup> was modified to the continuous azeotropic method previously reported.<sup>1,2</sup> The amines used in these syntheses were purified before use either by crystallization or by distillation. The terephthaldehyde was recrystallized from water before use.

### 1. Experimental.

To a three-necked round-bottomed flask equipped with a condenser and a Dean-Stark trap is added 150 ml. of benzene and 0.005 mole of the appropriate diamine and the mixture heated to reflux temperature. Then terephthaldehyde (0.005 M) in 150 ml. of benzene was added to the amine solution by means of a dropping funnel while the mixture was vigorously stirred. The mixture was then refluxed for twenty hours; the azeotroped water collected in the Dean-Stark trap. The polymer appeared as a precipitate and at the end of the

reaction it was removed by filtration, washed with benzene, and dried in a vacuum oven.

A modification of this procedure was used in the preparation of the solution polymer from 4,4'-diaminodiphenylamine since this monomer was obtained in the form of its sulfate salt. There was first dissolved in 250 ml. of water 0.02 mole of 4,4'-diaminodiphenylamine sulfate, which then was neutralized with an equivalent amount of sodium carbonate. Next, 0.02 mole of recrystallized terephthaldehyde was added and the entire mixture was refluxed for twenty hours. The orange polymer which precipitated during the reaction was recovered by filtration and washed with water. After drying 3.49 g. of polymer were obtained, representing a 58.7% yield.

Table 5 lists the polymers prepared by the solution method and gives yields and the color of the polymer.

Tał	le	5

<sup>°</sup> Polymer	Exper. No.	% Yield	Color
ŧN-〈()-N=HC-()-CH=n	DA-29-94	98.4	yellow 🛛
	DA-29-276	82.6	yellow
ŧN-(_)-CH <sup>+</sup> n	DA-29-277	55.2	yellow
$+N-(-)-CH_2-(-)-CH_n$	DA-29-266	92.3	yellow
f = N - (1) - O - (1) - N = HC - CH = n	DA-29-278	32.6	yellow
ŧN () NH () N=HC ()CH łn	DA-29-281	58.7	orange
I = I = I = I = I = I = I = I = I = I =	DA-42-15	91.4	yellow
$=$ $N < SO_2 < N = HC < CH_n$	DA-29-270	95.9	yellow
$\underbrace{ + N - \underbrace{ (1 - CH_2) - 1 - N - HC}_{SO_2} - N - HC - 1 - CH = n $	DA-42-6	95.8	light green
$f_{N-(CH_2)_4-N=HC}$ $(CH_2)_4-N=HC$	DA-29-269	86.8	white
$\neq$ N-(CH <sub>2</sub> ) <sub>6</sub> -N=HC $\bigcirc$ -CH $\downarrow$ <sub>n</sub>	DA-29 <b>-268</b>	81.0	white

Polymers Prepared by Solution Method

#### 2. Discussion.

Solution polymerization yielded a number of polymers with varying backbone structures. The color varies in these polymers depending on the amount of conjugation and upon the degree of polymerization. None of the solution polymers is black, indicating their low molecular weight and oligomeric character Most of the conjugated and pseudoconjugated oligomers are yellow, or near yellow such as orange or light green, while the oligomers containing alighatic moieties in their backbones are white.

### IV. Postheating of Polymers.

The polymers prepared under standardized polymerization conditions were condensed to a maximum temperature of 400 °C. The black polymer,

 ${}^{+}N \underbrace{ \bigcirc } N=HC \underbrace{ \bigcirc } CH_{n}^{+}$ , DA-42-13 is one of these typical polymers. Preliminary thermogravimetric analyses in nitrogen of polymer DA-42-13 indicated that the polycondensation is not complete at this temperature and that a weight loss begins at about 600°C and levels off at about 800°C. When the same polymer,  ${}^{+}N \underbrace{ \bigcirc } N=HC \underbrace{ \bigcirc } CH_{n}^{+}$ , DA-29-154 was prepared under modified conditions and condensed to a temperature of 450°C, the thermogravimetric analysis in nitrogen also showed that a weight loss began at about 600°C and levelled off at about 800°C, but that the weight loss was much less than the polymer condensed to 400°C. It was also observed that there was no substantial difference in the infrared spectra of the polymers condensed to temperatures of 400°C and 600°C.

These observations suggested that an evaluation should be made of polymers condensed to a temperature in the region of 600°C as well as to some temperature in the region of 1000°C or higher.

It would have been more desirable to have reacted the original reagents in a melt and condensed them directly to a temperature of 600°C or higher. The available polymerization apparatus permitted a maximum temperature of about

600 °C. For heating to temperatures in excess of 600 °C other means would have to be devised.

Since polymers which had been condensed to a temperature of 400°C were on hand, it was believed that the objectives of the study would be met in good measure by postheating the available 400°C polymers to 600°C and to some higher temperatures.

### A. Postheating to 600°C.

The procedure for postheating the polymers prepared at 400°C consisted in grinding the polymers to a fine powder with a mortar and pestle, then placing in a quartz reaction tube similar in design and dimensions to the reaction tube used in the melt polymerization apparatus. This quartz reaction tube was equipped with the same accessories used for the melt polymerizations. After the samples were weighed into the quartz tubes, the nitrogen bleeder supported by a Teflon adapter and the other glassware was attached, then nitrogen was introduced into the system and the reaction tube inserted into the aluminum block which had already reached the desired temperature. The system was then placed under reduced pressure, and the polymers postheated at 600°C for twenty minutes at 1 mm Hg. Table 6 lists the polymers which were postheated to 600°C. The designation H600 is placed at the end of the number of the polymer to indicate that it has been postheated to 600°C.

#### Table 6

Polymers Postheated to 600°C at 1.0 mm Hg for Twenty Minutes

Exper. No.	Polymer
DA-42-13-H600	
DA-42-14-H600	
DA-42-42-H600	$\underbrace{ + N - \underbrace{CH_2}_{SO_2} \longrightarrow N = HC - CH_n^2 $

### B. Postheating to Temperatures Above 600 °C.

It is desirable to evaluate the thermal and other properties of polymers which have been heated to temperatures above 600°C, preferably to temperatures in the vicinity of 1000°C, and means for achieving this heat treatment had to be devised. The apparatus used in heat-treating the polymers to 400°C and 600°C is not suitable for this purpose since the temperature limitation on the heating mantle is set at about 610°C. Accordingly, the du Pont 950 Thermogravimetric Analyzer was adapted for this purpose in the following manner. The sample was placed in the TGA cell of the 950 Analyzer and heated, under nitrogen, to a recorded 1200°C, which is corrected for the non-linearity of the chromel-alumel thermocouples to 1176°C. Then the furnace and the sample was allowed to cool to room temperature in nitrogen. These samples, after heating to 1176°C, are designated by the addition of R to the polymer number and are designated as recycles. Table 7 lists the specific polymers which were postheated to 1176°C.

### V. Thermogravimetric Analyses.

It was predicted<sup>1</sup> at the beginning of this research that conjugated Schiff base polymers should show a high degree of thermal stability. This assumption was based both on theoretical considerations and upon the actual thermal stabilities of some conjugated polymers.<sup>1</sup>

Polymer Used	Exper. No.	Designation After Heating
<b>₽</b> N (2) N=HC (2) CH = n	DA-42-13	DA-42-13-R
₽N () N=HC () CH = n	DA-42-13-H600	DA-42-13-H600-R
	DA-42-14	DA-42-14-R
	DA-42-14-H600	DA-42-14-H600-R
ŧN ↔ N=HC ↔ CH= n	DA-29-284	DA-29-284-R
<b>₩</b> ()-CH <sub>2</sub> ()-N=HC ()-CH= <sub>n</sub>	DA-29-265	DA-29-265-R
<b>ŧ</b> Ν (2)-0-(1) N=HC (1)-CH <b>↓</b> <sub>n</sub>	DA-29-275	DA-29-275-R
ŧn � hh   h=hC   h=hC	DA-29-282	DA-29-282-R
ŧN ()-S ()-N=HC ()-CH=In	DA-42-16	DA-42-16-R
<b>ŧ</b> Ν ⟨ <b>1</b> ⟩ SO <sub>2</sub> ⟨ <b>1</b> ⟩ - N=HC ⟨ <b>1</b> ⟩ - CH <b>‡</b> <sub>Π</sub>	DA-29-285	DA-29-285-R
$\texttt{HN} \underbrace{\overset{CH2}{\overset{CH2}{\overset{C}}{\overset{C}{\overset{C}{\overset{C}{\overset{C}{\overset{C}}{\overset{C}{\overset{C}{\overset{C}{\overset{C}}}}}}}}}$	DA-42-11	DA-42-11-R
ŧN CH2 CH2 CH−N=HC C→CH <sup>↓</sup> n	DA-42-11-H600	DA-42-11-H600-R
	DA-42-154	DA-42-154-R

# Table 7 Polymers Postheated to 1176°C in Nitrogen

Topchiev and his coworkers report<sup>9</sup> a decomposition temperature for the low molecular weight yellow polymer obtained from the solution polymerization of terephthaldehyde and p-phenylenediamine to have a decomposition temperature of 350 °C. Stivala, Sacco and Reich report<sup>10</sup> that the yellow polymer obtained from solution polymerization of m-phenylenediamine and terephthaldehyde in dimethyl-formamide and subsequently heated to 250 °C in nitrogen is stable up to about 400 °C.

In our studies, the thermal stability of the polymers was evaluated by thermogravimetric techniques. The du Pont 950 Thermogravimetric Analyzer in conjunction with a 900 Differential Thermal Analyzer was used to determine the thermal properties of the polymers at a heating rate of 15°C per minute. A number of thermogravimetric measurements were made in nitrogen and in air at gas flow rates of one (1) standard liter per minute. A sample weight of 10 mg was used in most determinations. A temperature correction has been made in the measurements for the non-linearity of the chromel-alumel thermocouples.

These studies consisted in performing thermoanalyses in a sufficient number of polymers to be able to correlate their thermal stabilities in nitrogen and in air to various experimental parameters such as

- the degree of polymerization as reflected in color of the black polymers in contrast to the "yellow" or light-colored polymer,
- 2) the nature and extent of conjugation,

3) the final temperature of condensation used in the polymerization. Accordingly, the studies were divided into the classification: a) melt and solution polymers; b) 600°C postheated polymers; c) 1176°C postheated polymers.

### A. Melt and Solution Polymers.

The polymer prepared under melt polymerization conditions, namely, the black conjugated-type polymers condensed to 400°C and the aliphatic, non-conjugated polymers condensed to 250°C were thermoanalysed in nitrogen and in air and compared to their corresponding lighter-colored polymers prepared in solution. Table 8 summarizes and contrasts the thermal behavior of the melt (400°C) and solution polymers which were thermoanalyzed in nitrogen. The thermograms obtained for the respective polymers are given under the appendix number. Table 8 also gives the percentage of weight loss beginning at 200°C in increments of 100°C to the recorded limit of the apparatus of 1200°C, which has been corrected to 1176°C for the non-linearity of the chromel-alumel thermocouple. Table 9 summarizes and contrasts the thermal behavior of the melt (400°C) and solution polymers which were thermoanalyzed in air; the thermograms of the polymers thermoanalyzed in air are given under the appendix number .

Table 8

Curve No. -----Appen. No. 23 26 13 16 18 - **1** 11 30 28 ~ 32 33 29.4 28.6 ୦ 34.4 35.4 35.0 1 1 1 1111 1111 1 1 1 1170 1100 26.6 25.6 31.6 32.0 32.4 1 + 1111 1111 111 1 1 24.4 72.0\* 1000 37.6\* 71.6\* 30.0 61.0<del>4</del> 51.6\* 21.6 55.0 28.6 28.8 1 1 1 111 23.4 70.6 20.4 50.6 900 54.4 36.6 70.6 27.4 27.0 28.4 59.6 | E | | | | | 111 22.0 66.8 18.6 53.0 25.6 26.4 58.0 800 49.4 0.06 35.2 68.4 25.4 1 1 1 1 ပ္ပ Weight Loss at 18.4 66.8 14.8 50.6 89.2 32.0 67.6 47.6 700 24.0 23.0 69.4 22.2 54.8 1 10.0 600 9.2 42.6 24.6 64.6 15.4 73.0 44.8 88.0 16.4 63.0 12.6 48.0 24.4 0.6 33.6 2.0 65.0 500 7.0 2.4 6.9 41.0 3.2 45.8 2.4 9.0 1.2 0.6 4.4 0.4 68.0 4.2 0.4 0.5 400 0.6 1.2 8.0 300 0.0 5.4 0.0 3.0 0.0 54.0 0.0 0.2 4.6 0.8 6.4 0.0 0.6 0.6 200 2.4 0.0 0.0 0.0 1 0.0 0.0 1 1 1 ŧN ⟨♪ CH<sub>2</sub> ⟨♪ N=HC ⟨♪ CH<sup>J</sup><sub>h</sub> black DA-29-265  $\operatorname{fu}\left( \xrightarrow{} \operatorname{he}\left( \xrightarrow{} \operatorname{he}\left( \xrightarrow{} \operatorname{he}\right) \operatorname{he}\left( \xrightarrow{} \operatorname{he}\right) \operatorname{he}\left( \xrightarrow{} \operatorname{he}\right) \operatorname{he}\left( \xrightarrow{} \operatorname{he}\left( \operatorname{he}\left( \xrightarrow{} \operatorname{he}\right) \operatorname{he}\left( \operatorname{he}\left( \operatorname{he}\left( \operatorname{he}\left( \operatorname{he}\right) \operatorname{he}\left( \operatorname{he}\left($  $f_{\rm N}$  () - 0 () N=HC ()  $CH_{\rm n}$ black DA-29-275 FN S S N=HC CH<sup>1</sup>n black DA-42-16 ○ N=HC () CH<sup>1</sup>/<sub>h</sub> DA-29-284 far CH<sup>J</sup>n=HC CHJn b1ack n. . DA-29-282 DA-29-281 DA-29-276 DA-29-266 DA-29-277 DA-29-271 €N ← N=HC ← Ch-B black DA-42-13 DA-29-94 DA-42-15 Experiment No. Polymer and yellow yellow yellow fn () yellow yellow yellow yellow black

Per Cent Weight Loss of Melt and Solution Polymers at Various Temperatures While Being Heated in Nitrogen

Table 8

Curve No. -Appen. No. 39 41 45 49 47 51 ŝ 1176 20.4 1 111 111 111 111 111 1100 16.4 1 5 5 5 1111 111 111 1 111 111111 1 24.6**\*** 69.6**\*** 28.6<del>\*</del> 52.4\* 14.4 1000 1111 1 1 1 111 13.6 22.6 67.2 900 22.4 52.0 73.0 1 1 1 1 1 t 1 1 72.6 21.2 66.4 19.2 50.0 85.4 61.2 12.0 800 ပ္ပ Weight Loss at 17.6 8.0 65.0 15.0 44.4 84.0 59.6 71.0 700 11.6 61.0 13.5 37.0 600 71.0 56.6 68.4 72.8 3.6 2.2 25.0 500 1.4 17.2 60.0 49.0 51.6 62.0 0.8 0.8 6.0 16.0 20.4 0.2 9.0 18.0 31.0 400 0.2 300 0.0 0.6 2.0 2.0 2.4 8.0 0.0 19.0 200 0.0 0.0 0.6 0.6 0.8 0.0 CCH2 CD-N=HC C-CH4 ŧN (\_\_\_) SO<sub>2</sub> (\_\_\_) N=HC (\_\_\_) CH J<sub>h</sub> b1ack DA-29-285 **€N-** (CH<sub>2</sub>)<sub>4</sub>-N=HC (<u>)</u>-CH<sup>3</sup>n orange DA-29-286 white DA-29-269  $(H_2)_6 - N = HC (-) CH_h$ DA-29-270 DA-29-285 DA-29-268 DA-42-11 DA-42-6 DA-42-10 Experiment No. Polymer and orange white yellow yellow black , A A

Per Cent Weight Loss of Melt and Solution Polymers at Various Temperatures While Being Heated in Nitrogen

\* When the measurement was made on a scale of 100°C per inch, the maximum temperature recorded was 1000°C.

Polymer and Experiment Number		Per C	°C	Appendix			
	200	300	400	500	600	700	Number
$ \begin{array}{c} \downarrow \mathbb{N} &  \mathbb{N} = \mathbb{HC} &  \mathbb{CH} \\ \mathbb{DA} - 42 - 14 \\ \mathbb{DA} - 42 - 14 \\ \mathbb{DA} - 29 - 94 \end{array} $	1.6	0.0	0.0	3.2 75.6	69.0 100.0	100.0	2 6
$ \begin{array}{c} \begin{array}{c} \begin{array}{c} \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \begin{array}{c} \\ \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ \end{array} \\ \end{array} \\ \end{array} \\ \begin{array}{c} \\ \end{array} \\ $	 0.6	1.8	0.0 3.6	3.2 51.4	64.6 98.0	100.0 100.0	8 12
$ \begin{array}{c} f \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ $	1.6	0.0 58.4	0.6 59.0	16.6 95.0	96.8 100.0	100.0	14 17
$ \begin{array}{c} \downarrow N & \frown CH_2 & \frown N = HC & \frown CH_1 \\ \text{black} & DA - 29 - 265 \\ \text{yellow} & DA - 29 - 266 \end{array} $			0.0 28.4	12.6 82.0	94.0 99.0	100.0 100.0	19 22
$ \begin{array}{c}                                   $	0.0	0.6	0.0 60.0	5.0 97.0	70.0 100.0	100.0	24 27
$ \begin{array}{c} \neq N & \textcircled{()} & NH & \textcircled{()} & N=HC & \textcircled{()} & CH \\ black & DA-29-282 \\ yellow & DA-29-281 \end{array} $	1.4 2.8	1.8 7.0	2.6 32.0	54.0 69.0	100.0 91.0	100.0	29 31
$ \begin{array}{c} = N & -S & -N = HC & -CH \\ \text{black} & DA - 42 - 16 \\ \text{yellow} & DA - 42 - 15 \end{array} $	0.6	1.0	0.0 1.6	6.0 31.0	83.0 88.8	100.0 100.0	33 35
$ \begin{array}{c} = \mathbb{N} &  \\ & \searrow \\ & \text{black} \\ & \text{DA-29-285} \\ & \text{yellow} \\ & \text{DA-29-270} \\ \end{array} $	1.2	0.0 3.6	6.4 10.0	90.4 77.2	100.0 97.6	100.0	37 40
$= N \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ \left\{ \left\{ \begin{array}{c} CH_2 \\ SO_2 \end{array} \right\} = N = HC \left\{ $							
black DA-42-11 yellow green DA-42-6	1.2 0.0	1.2	0.8 2.0	4.6 18.0	87.0 90.0	100.0 100.0	42 46
<b>€N-(CH<sub>2</sub>)<sub>4</sub>-N=HC</b> (C)-CH orange DA-29-286 white DA-29-269	2.0	16.6 4.0	22.0 16.4	34.0 31.0	92.6 94.0	100.0 100.0	48 50
$fN-(CH_2)_6-N=HC$ $(\Delta)-CH=_n$ orange DA-42-10 white DA-29-268	0.4 1.2	1.6 9.0	10.0 18.8	62.6 50.0	89.6 98.6	100.0 100.0	52 54
$ \frac{1}{2} N - N = HC - CH = \frac{1}{2}$ black DA-29-154		0.0		5.2	29.2	72.4	56

# Per Cent Weight Loss of Melt and Solution Polymers at Various Temperatures while Being Heated in Air

Table 9

Table 10 summarizes the temperatures at which the 20, 30, 40, and 100 per cent weight losses occur in nitrogen and in air, as well as the point of inflection of the thermogravimetric curve which corresponds to the onset of thermal degradation.

#### Table 10

Temperatures of Weight Losses and Points of Inflection for Melt (400°C) and Solution Polymers While Being Heated in Air or in Nitrogen

Polymer and		Atm	Tempe	rature	°C at	: Which	Point of	Appendix
Experiment	Number	ACM	<u>weign</u> 20	t Loss 30	<u>0ccu</u> 40	100	Infl. °C	Number
			20	30	40	100		
₽N-C-								
	42-13	N <sub>2</sub>	730	*			540	1
	42-13	Air	470	476	480	701	480	2
	29-94	N <sub>2</sub>	500	504	511		450	5 6
	29-94	Air	407	410	413	598	420	6
+N-() N=HC-	Ŋ-сн <sub>₽</sub>							
	42-14	N <sub>2</sub>	846	*			530	7
black DA-	42-14	Air	563	524	580	*	500	8
yellow DA-	29-276	N <sub>2</sub>	460	487	550	*	425	11
yellow DA-	29-276	Air	437	494	498	635	403	12
<b>ŧ</b> Ν-⟨ <u>∩</u> ⟩ N=H	С {СН]						· · · · · · · · · · · · · · · · · · ·	
black DA-	29-284	N <sub>2</sub>	535	545	560	*	530	13
black DA-	29-284	Air	510	543	532	615	440	14
yellow DA-	29-277	N <sub>2</sub>	264	275	285	*	245	16
yellow DA-	29-277	Air	248	258	266	518	232	17
€N ( ) CH2 ( )	≻N=HC ()-CH = n							
black DA-	29-265	N2	600	640	*		503	18
black DA-	29-265	Air	513	522	530	645	450	19
•	29-266	N <sub>2</sub>	475	481	488	*	460	21
yellow DA-	29-266	Air	326	419	447	605	318	22
€N-{\_}O-{\_}N	=HC - (1)-CH = n							
black DA-	29-275	N <sub>2</sub>	625	1050	*	1	525	23
	29-275	Air	546	558	566	660	475	24
yellow DA-	29-271	N <sub>2</sub>	242	286	343		400	26
yellow DA-	29-271	Air	378	386	410	550	375	27
€N-{\> NH-{\>	N=HC (()-CH=]							
black DA-	29-282 "	N <sub>2</sub>	654	*	1		520	28
black DA-	29-282	Air	478	487	492	598	430	29
yellow DA-	29-281	N <sub>2</sub>	470	478	488	*	460	30
yellow DA-	29-281	Air	285	387	485	620	375	31
-								31

### Table 10 (cont.)

# Temperatures of Weight Losses and Points of Inflection for Melt (400°C) and Solution Polymers While Being Heated in Air or in Nitrogen

1

La Weight Loss Occure	endix
$\frac{1}{1} \frac{20}{100} \frac{30}{40} \frac{40}{100} \frac{100}{100} $	mber
black DA-42-16 Air 453 458 466 682 475 yellow DA-42-15 N2 515 522 541 * 490 yellow DA-42-15 Air 440 490 525 687 428 $\frac{1}{2} N (2) SO2 (2) N = HC (2) CH \frac{1}{2} N2 745 * 528 538 546 645 475 75 7516 7516 7516 7516 7516 7516 7516$	moer
black DA-42-16 Air 453 458 466 682 475 yellow DA-42-15 N2 515 522 541 * 490 yellow DA-42-15 Air 440 490 525 687 428 $\frac{1}{2} N (2) SO2 (2) N = HC (2) CH \frac{1}{2} N2 745 * 528 538 546 645 475 75 7516 7516 7516 7516 7516 7516 7516$	
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	32
yellow yellowDA-42-15 DA-42-15N2 Air515 440522 490541 \$525* 687490 428 $\#N (\Delta) SO_2 (\Delta) N=HC (\Delta) CH = I_n$ blackDA-29=285 DA-29=285N2 Air745 528* 538546 545645 645475 300 $\#N (\Delta) SO_2 (\Delta) N=HC (\Delta) CH = I_n$ blackDA-29=285 DA-29=270N2 	33
yellowDA-42-15Air440490525667428 $\ddagger N ( ) SO_2 ( ) N=HC ( ) CH = h_n$ blackDA-29=285N2 Air745* 528538546645475blackDA-29=285Air V2528538546645475yellowDA-29=270N2 V2495507516* 300300yellowDA-29=270Air403407410635280 $= N \cdot So_2 \cdot N = HC \cdot CH = h_n$ N2 So_2 \cdot N = HC \cdot CH = h_nN2 So_2 \cdot N = HC \cdot CH = h_n792 So_2 \cdot N = HC \cdot CH = h_nSo So545550682 So490blackDA-42-11Air So So513554630614 So400yellow greenDA-42-6Air So So518522673400 $\ddagger N \cdot (CH_2) 4^{-N=HC} \cdot C \cdot CH = h_norangeN2DA-29-286415AirSo2415So428So452So*So\ddagger N - (CH_2) 4^{-N=HC} \cdot C \cdot CH = h_norangeN2DA-29-269AirSo302So390So462So*So235\ddagger N - (CH_2) 6^{-N=HC} \cdot C \cdot CH = h_norangeN2DA-29-269410Air444So474673300$	34
black DA-29-285 Air 528 538 546 645 475 pellow DA-29-270 N2 495 507 516 * 300 yellow DA-29-270 Air 403 407 410 635 280 $\frac{1}{10000000000000000000000000000000000$	35
black DA-29-285 Air 528 538 546 645 475 black DA-29-270 N2 495 507 516 * 300 yellow DA-29-270 Air 403 407 410 635 280 $\oint N - (CH_2)_6 - N = HC - CH_{\pi}^2 N2 + 500 + 100 +$	
black DA-29-285 yellow DA-29-270 yellow DA-29-270 Air 403 407 410 635 280 $\frac{1}{100}$ $\frac{1}{100}$	36
yellowDA-29-270N2 Air495 403507 407516 410* 635300 280 $fN - CH_2$ So2N=HC - CH $\frac{1}{2}$ N=HC - CH $\frac{1}{2}$ N=HC - CH $\frac{1}{2}$ N - CH 2 - N=HC - CH $\frac{1}{2}$ N - CH 2 - N=HC - CH $\frac{1}{2}$ N - CH 2 - N=HC - CH $\frac{1}{2}$ N - CH N - CH 2 - N - HC - CH $\frac{1}{2}$ N - CH N - CH 2 - N - HC - CH $\frac{1}{2}$ N - CH N - CH 2 - N - HC - CH $\frac{1}{2}$ N - CH N - CH N - CH N - CH - CH - CH N - CH - CH N - CH - CH - CH - CH 	37
yellowDA-29-270Air403407410635280 $\pounds N \leftarrow CH_2$ N=HC < CH=	39
$\frac{1}{2}N - \frac{1}{2}N $	40
black DA-42-11 Air 540 545 550 682 490 yellow green DA-42-6 $N_2$ 513 554 630 614 400 yellow green DA-42-6 Air 508 518 522 673 400 $\frac{1}{N} - (CH_2)_4 - N = HC CH_{+n}$ orange DA-29-286 $N_2$ 415 428 452 * 320 orange DA-29-286 Air 362 370 523 645 250 white DA-29-269 $N_2$ 302 390 462 * 235 white DA-29-269 Air 352 417 520 635 225 $\frac{1}{N} - (CH_2)_6 - N = HC $	
black DA-42-11 Air 540 545 550 682 490 yellow green DA-42-6 $N_2$ 513 554 630 614 400 yellow green DA-42-6 Air 508 518 522 673 400 $\frac{1}{N} - (CH_2)_4 - N = HC \sqrt{-}CH_{n}^{+}$ $N_2$ 415 428 452 * 320 orange DA-29-286 Air 362 370 523 645 250 white DA-29-269 $N_2$ 302 390 462 * 235 white DA-29-269 Air 352 417 520 635 225 $\frac{1}{N} - (CH_2)_6 - N = HC \sqrt{-}CH_{n}^{+}$ $N_2$ 410 444 474 673 300	41
yellow green DA-42-6Air508518522673400 $$=N-(CH_2)_4-N=HC}$ $$=N_2$ $$=15$ $$=22$ $$=673$ $$=400$ orangeDA-29-286 $N_2$ $$=415$ $$=28$ $$=52$ $$=320$ orangeDA-29-286Air $$=362$ $$=70$ $$=250$ whiteDA-29-269 $N_2$ $$=302$ $$=390$ $$=462$ $$=235$ whiteDA-29-269Air $$=352$ $$=417$ $$=20$ $$=352$ $$=N-(CH_2)_6-N=HC}$ $$=N-42-10^n$ $N_2$ $$=410$ $$=444$ $$=474$ $$=673$ $$=300$	42
yellow green DA-42-6Air508518522673400 $$= N-(CH_2)_4-N=HC}$ $$= CH_2^+ n$ $$= N_2$ 415428452 $*$ 320orangeDA-29-286N2415428452 $*$ 320orangeDA-29-286Air362370523645250whiteDA-29-269N2302390462 $*$ 235whiteDA-29-269Air352417520635225 $$= N-(CH_2)_6-N=HC}$ $$= CH_2^+ n^{-1}$ $N_2$ 410444474673300	45
orangeDA-29-286N2415428452*320orangeDA-29-286Air362370523645250whiteDA-29-269N2302390462*235whiteDA-29-269Air352417520635225 $\frac{1}{N}$ -(CH2)6-N=HC ( $\frac{1}{N}$ -CH $\frac{1}{N}$ N2410444474673300	46
orangeDA-29-286N2415428452*320orangeDA-29-286Air362370523645250whiteDA-29-269N2302390462*235whiteDA-29-269Air352417520635225 $\frac{1}{N}$ -(CH2)6-N=HC ( $\frac{1}{N}$ -CH $\frac{1}{N}$ N2410444474673300	
orangeDA-29-286Air362370523645250whiteDA-29-269N2302390462*235whiteDA-29-269Air352417520635225 ${=}N-(CH_2)_6-N=HC-(-)-CH=)/0rangeDA-42-10^nN2410444474673300$	47
whiteDA-29-269Air352417520635225 $\frac{1}{4}N-(CH_2)_6-N=HC-(1)-CH_2^2)_6-N=HC-(1)-CH_2^2-$	48
whiteDA-29-269Air352417520635225 $\frac{1}{4}N-(CH_2)_6-N=HC-(1)-CH_2^2)_6-N=HC-(1)-CH_2^2-$	49
orange DA-42-10" N <sub>2</sub> 410 444 474 673 300	50
orange DA-42-10" N <sub>2</sub> 410 444 474 673 300	
	51
	52
white DA-29-268 N <sub>2</sub> 400 436 460 * 275	53
white DA-29-268 Air 408 436 460 635 240	54
<b>ŧ</b> Ν √(Σ)- N=HC √(Σ)- CH <sup>1</sup> / <sub>2</sub>	
black DA-29-154 No 1165 * 550	55
black DA-29-154 Air 410 534 590 783 480	56

 \* The maximum loss occurred at some value below the per cent indicated by the asterisk.
 For values consult the specific thermograms and Tables 8 and 9.

### B. Polymers Postheated to 600°C.

Tables 11, 12 and 13 summarize the data obtained from the thermoanalyses of the three selected polymers which were postheated to 600°C. The thermograms obtained for the polymers evaluated are given under the appendix number in the tables. The thermal behavior of the H600 polymer when heated in nitrogen is given in Table 11 and in air in Table 12. Table 13 summarizes the temperatures at which the 20, 30, 40, and 100 per cent weight losses occur in nitrogen and in air, as well as the point of inflection of the thermogravimetric curve which corresponds to the onset of degradation.

Table 11

Per Cent Weight Losses of H600 Polymers While Being Heated in Nitrogen

Polymer and	Per Cent Weight Loss at °C									Curve No.1		
Experiment Number	200	300	400	500	600	700	800	900	1000	1100	1176	Appen. No.
<b>ŧ</b> Ν-⟨♪ N=HC ⟨♪ CH <b>↓</b> <sub>n</sub> DA-42-13-H600	0.6	1.0	1.6	1.8	2.0	4.0	7.2	8.8	10.0	12.0	14.4	3
$ = \frac{1}{2} \frac$			0.4	0.6	1.0	3.2	7.0.	8.8	10.2	12.6	15.0	. 9
$ \underbrace{ + \mathbb{N} - \underbrace{ \mathbb{C} \mathbb{H}_2}_{SO_2} \underbrace{ \mathbb{C} \mathbb{H}_2 - \mathbb{N} = \mathbb{H} \mathbb{C} \underbrace{ \mathbb{C} \mathbb{H}_n}_{n} } $												
DA-42-11-H600	1.8	2.0	2.0	2.4	2.8	4.8	9.4	12.2	13.8	14.6	18.0	43

#### Table 12

Per Cent Weight Losses of H600 Polymers While Being Heated in Air

Polymer and	T	Appendix					
Experiment Number	200	300	400	500	600	700	Number
<b>ŧ</b> Ν ( ) - N=HC ( ) - CH <b>↓</b> <sub>n</sub> DA-42-13-H600			0.0	1.6	70.5	98.0	4
<b>₩</b> () N=HC () -CH = n DA-42-14-H600			0.0	0.8	58.0	100.0	10
$\underbrace{ \{ N \in \mathcal{C} \\ SO_2 \\ SO_2 \\ SO_2 \\ CH = HC \\ C \\ CH = HC \\ C \\ CH = HC \\ C $							
DA-42-11-H600	3.6	4.0	4.0	6.0	68.0	100.0	44

Polymer and Experiment Number	Atm			at Wi oss Od 40	nich % ccurs 100	Point of Infl: °C	Appendix Number
<b>€N € N</b> =HC <b>€ C H</b> = <b>H</b> C <b>1 C H</b> = <b>H</b> C <b>1 1 C H</b> = <b>H</b> C <b>1 1 1 H</b> = <b>H</b> C <b>1 1 1 1 1 1 1 1 1 1</b>	N2 Air	*	* 577	* 582	* 654	630 535	3 4
<b>€N</b> (N=HC ()-CH=] <sub>n</sub> DA-42-14-H600 DA-42-14-H600	N2 Air	* 5 <b>7</b> 1	* 580	<b>*</b> 588	* 701	645 550	9 10
$\frac{1}{4} N \left( 1 \right) \left( \frac{CH_2}{SO_2} \right) - N = HC \left( \frac{CH_2}{C} - CH \right) = HC$							
DA-42-11-H600 DA-42-11-H600	N <sub>2</sub> Air	* 563	* 579	* 586	* 659	600 525	43 44

### Temperatures of % Weight Losses and Points of Inflection for H600 Polymers in Nitrogen and in Air

Table 13

 \* In all cases the maximum loss was less than 20% even at 1176°C. For specific values consult Table 11 and the specific thermogram.

### C. Polymers Postheated to 1176°C.

#### 1. In Nitrogen.

Postheating of the polymers to temperatures much higher than 600°C was accomplished by use of the thermogravimetric analyzer. The finely divided 10 mg. sample was inserted in the apparatus and the sample heated at the rate of 15°C per minute in a nitrogen atmosphere at a flow rate of one (1) standard liter per minute. The heating was continued to the limit of the apparatus, recorded as 1200°C which, corrected for the non-linearity of the thermocouple, is 1176°C.

2. Recycled in Nitrogen.

The selected polymers which were heated in nitrogen to 1176°C were considered for the purposes of these studies, as fully condensed. Accordingly, the samples after this first heating to 1176°C were thermoanalyzed in nitrogen by the simple expedient of allowing the sample and the equipment to cool to room temperature, and recycling the polymer in the equipment under the standard flow of nitrogen. The polymers so treated are designated by the appendix R added to the experiment number. Thus, Experiment DA-42-13-R describes the thermal behavior in nitrogen of polymer DA-42-13, which has been postheated once to 1176°C, and DA-42-13-H600-R that of DA-42-13-H600, which has been postheated once to 1176°C.

#### 3. Recycle in Air.

To contrast the thermal behavior in air of polymers heat-treated to 1176°C with those prepared at 400°C and 600°C the polymer samples which had been subjected to 1176°C in nitrogen in the thermogravimetric analyzer were recycled in the apparatus in the presence of air. Preliminary experiments showed that there was no substantial difference in thermal behavior in air between those samples which had been processed once to 1176°C and those which had been recycled under nitrogen. In the interest of economy of time, the thermoanalyses in air of samples heated to 1176°C, were performed on samples which were allowed to remain in the thermogravimetric analyzer after the recycle, that is, the second cycle in nitrogen to 1176°C.

These polymers are designated by appending the letter <u>a</u> to the experiment number of the polymer which has been recycled in nitrogen. Thus, DA-42-13-R-a describes the thermal behavior in air of polymer DA-42-13-R which has been heated twice in nitrogen to  $1176^{\circ}$ C.

Table 14 lists the appendix number of the thermograms of the polymers which were postheated to 1176°C. In these thermograms, curve 1 plots the data obtained when the polymer was heated to 1176°C, curve 2 describes the thermal behavior of the polymer of curve 1 recycled in nitrogen to 1176°C, and curve 3 plots the data obtained when the polymer of curve 2 was recycled in air.

Table 15 lists the per cent weight loss at 1176°C of the polymers when recycled in nitrogen to a temperature of 1176°C. All polymers showed final

#### Table 14

Polymers Thermoanalyzed in Nitrogen to 1176°C, Recycled in Nitrogen to 1176°C, Followed by Recycle in Air

Thermogram Appendix No.	Run in Nitrogen Curve No. 1	Recycled in Nitrogen Curve No. 2	Recycled in Air Curve No. 3
1	DA-42-13	DA-42-13-R	DA-42-13-R-a
3	DA-42-13-H600	DA-42-13-H600-R	DA-42-13-H600-R-a
7	DA-42-14	DA-42-14-R	DA-42-14-R-a
9	DA-42-14-H600	DA-42-14-H600-R	DA-42-14-H600-R-a
15	DA-29-284	DA-29-284-R	DA-29-284-R-a
20	DA-29-265	DA-29-265-R	DA-29-265-R-a
25	DA-29-275	DA-29-275-R	DA-29-275-R-a
28	DA-29-282	DA-29-282-R	DA-29-282-R-a
32	DA-42-16	DA-42-16-R	DA-42-16-R-a
38	DA-29-285	DA-29-285-R	DA-29-285-R-a
41	DA-42-11	DA-42-11-R	DA-42-11-R-a
43	DA-42-11-H600	DA-42-11-H600-R	DA-42-11-H600-R-a
55	DA-29-154	DA-29-154-R	DA-29-154-R-a

weight losses of less than 5%, most of which occurred after the polymers had reached temperatures of the order of about 1000°C. The slope of these weight loss curves is very small and none of the curves shows a marked inflection point.

Table 16 summarizes the behavior of the recycled polymers when heated in air, giving the temperature at which weight loss begins, the inflection temperature, the temperature at which a 20% weight loss occurs, and the temperature at which the polymer has completely disappeared as a result of oxidation.

Table 1	.5
---------	----

Per	cent	Weight	Loss	at	1176°	C of	Polymer	Recycled	in Nitrogen	
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Polymer	% Loss 1176°C	Experiment No.	Appen. No.	Curve No.
ŧn-⟨♪}n=HC-⟨⊥⟩-CH=Ìn	4.2	DA-42-13-R	1	2
ŧn <u>{`</u> }-n=HC -{`}-CH=J <sub>n</sub>	2.4	DA-42-13-H600-R	3	2
	2.6	DA-42-14-R	7	2
₽N-C - CH= n	4.0	DA-42-14-H600-R	9	2
ŧN < N=HC < CH <sup>1</sup> n	2.6	DA-29-284-R	15	2
<b>₩</b> () CH <sub>2</sub> () N=HC () CH <sup>1</sup> <sub>n</sub>	2.4	DA-29-265-R	20	2
<b>₩</b> () 0 () N=HC () CH <sup>1</sup> / <sub>n</sub>	3.0	DA-29-275-R	25	2
<b>₩</b> () NH () N=HC () CH <b>→</b> <sub>n</sub>	2.8	DA-29-282-R	28	2
fn  S  N HC  C HL	4.0	DA-42-16-R	32	2
<b>€N-{</b> SO <sub>2</sub> -{ N=HC-{ C} CH} <sub>n</sub>	4.4	DA-29-285-R	38	2
€N CH2 CH2 N=HC CH3n	2.8	DA-42-11 -R	41	2
₩ CH2 CH2 N=HC CH3n	2.8	DA-42-11-H600-R	43	2
ŧn ⟨Ţ⟩ n=HC ⟨Ţ⟩ CH∃ <sub>n</sub>	2.8	DA-29-154-R	55	2

## Table 16

Polymer	Experiment Number	Sample Begins to Lose Wt. at °C	20% Wt. Loss at °C	Sample disap- pears at °C	Infl. Point
ŧn-(1)-n=HC-(1)-CH=In	DA-42-13-R-a	510	565	800	550
ŧn < > n=HC < > CH łn	DA-42-13-H600-R-a	600	<b>6</b> 60	1000	600
ŧN-⟨□]_N=HC-⟨□)-CH <sup>↓</sup> n	DA-42-14-R-a	430	560	700	450
ŧN-⟨¯) <sub>N=HC</sub> -⟨¯)-CH=J <sub>n</sub>	DA-42-14-H600-R-a	550	620	830	565
	DA-29-284-R-a	<b>52</b> 0	650	800	550
<b>₩</b> () CH <sub>2</sub> () N=HC () - CH <del>]</del> <sub>n</sub>	DA-29-265-R-a	450	590	660	480
₩~2>0~2>N=HC-~2>CH <sup>1</sup> / <sub>n</sub>	DA-29-275-R-a	<b>52</b> 0	620	860	550
ŧn- NH- NH- Ch- CH+n	DA-29-282-R-a	550	660	900	578
$\texttt{+N}  S  N \texttt{=} \texttt{HC}  C \texttt{H} \texttt{+}_n$	DA-42-16-R-a	420	530	740	490
$\texttt{IN} \textcircled{SO}_2 \textcircled{SO}_2 \textcircled{SO}_2 \textcircled{C} \texttt{N=HC} \textcircled{C} \texttt{CH}_n$	DA-29-285-R-a	480	620	900	560
$\underbrace{ = \mathbb{N} \underbrace{ \mathbb{C} \mathbb{H}_2 }_{SO_2} \mathbb{N} = \mathbb{H} \mathbb{C} \underbrace{ \mathbb{C} \mathbb{C} \mathbb{H}_n}_{n}$	DA-42-11-R-a	475	620	720	525
$ = \frac{1}{10000000000000000000000000000000000$	DA-42-11-H600-R-a	500	630	860	580
ŧn ⟨Ţ⟩-n=HC -⟨Ţ⟩-CH Ĵ <sub>n</sub>	DA-29-154-R-a	480	580	660	545

## Temperatures at Which Weight Loss Begins, Has Occurred to 20%, is Complete When Polymers are Heated in Air After Being Heated to 1176°C in Nitrogen

## D. General Discussion.

The data of the thermograms show that

- 1. The polycondensations performed to a temperature of 400°C are not complete. This is indicated by the losses in weight in nitrogen of these polymers compared to the much lower losses found in polymers condensed to higher temperatures, such as to 600°C and to 1176°C. This observation confirms earlier data,<sup>1,2</sup> as well as the results of recent studies<sup>3</sup> involving the acetal exchange syntheses of the polymers.
- 2. The thermal stabilities in nitrogen and in air of the black conjugated and pseudoconjugated polymers prepared by the melt bis-exchange reaction are much higher than the stabilities of the corresponding yellow-type brick-dust polymers prepared in solution.
- 3. The thermal stabilities in nitrogen and in air of the aliphatic-type non-conjugated Schiff-base polymer prepared either by the melt bisexchange reaction in solution are much lower than the conjugated and pseudoconjugated polymeric Schiff bases.
- 4. The differences in the thermal stabilities of the aliphatic-type Schiff base polymers prepared by melt Schiff base exchange and by solution methods are small. This contrasts with the data on the conjugated and pseudoconjugated Schiff base polymers and is attributed to the fact that the polymerization condensation of the aliphatic-type polymers is homogeneous in both melt and solution systems, whereas, in the aromatic type the condensation is homogeneous in the melt bisexchange system and heterogeneous in the solution system.
- 5. The thermal stabilities of the aliphatic-type Schiff bases studied,  $\pm N-(CH_2)_4-N=HC-C_6H_4-CH_n$  and  $\pm N-(CH_2)_6-N=HC-C_6H_4-CH_n$  are surprisingly

good; of the order of 250°C in nitrogen and in air. They undergo decomposition in nitrogen and in air in the region of 300°C to 350°C.

6. The thermal stabilities can be compared generally in a number of ways such as from 1) the weight losses at specific temperatures, 2) the temperatures at which specific weight losses occur, or 3) their decomposition temperature as indicated by points of inflection in the weight-temperature thermogravimetric plots. On this basis, a number of observations can be made concerning the thermal stability of the conjugated and pseudoconjugated polymers condensed to 400°C.

a. Thermal Stability in Nitrogen of Polymers Condensed to 400°C.

- i. The thermal stabilities of all the polymers in nitrogen below the inflection point is very good and within the range of 500-550°C.
- ii. The completely conjugated polymers show the best general overall thermal stability in nitrogen as judged from the inflection point and total weight loss at 1000°C and 1176°C.

Polymer	Exper. No.	Appen. No.	Infl. Point		Loss at 1176°C
ŧN√N=HC -{}-CH ₽n	DA-42-13	1	540	24.4	29.4
<b>ŧ</b> N-⟨``) N=HC-⟨`}CH <b>↓</b> <sub>n</sub>	DA-29-154	55	550	14.4	20.4
<sup>€N</sup> € N=HC € CH	DA-42-14	7	540	21.6	28.6
	DA-29-284	13	530	55.0	58.0

At high temperatures, the polymer containing the diphenyl moiety, DA-29-284, shows less stability than would be expected. The anomaly cannot be explained at this time.

iii. There is no substantial difference in the thermal stability in nitrogen of the polymers prepared from the dibenzylidene derivatives of para-phenylenediamine and meta-phenylenediamine. Since the cost of meta-phenylenediamine is lower than the para compounds, its use is preferred and recommended.

iv. The effect of thermal stability in nitrogen of the polymers resulting from changes in conjugation of the polymers is not as great as would be expected in the case of those polymers which are pseudoconjugated, that is, polymers of the structure, fN-Ar-X-Ar-N=HC-Ar-CH<sup>1</sup>/<sub>n</sub>, in which the conjugation is not completely inhibited by a X bridge between the aromatic rings.

The pseudoconjugated polymers in which the bridges are  $-CH_2$ -, -0-, -NH-, -S-,  $-SO_2$ -, and  $\begin{array}{c} -CH_2 \\ SO_2 \end{array}$  have inflection points of the order of 25-50°C lower in temperature than those of the conjugated polymers; and their weight losses in the range of 600°C to 1000°C are about 0-50% higher than those of the conjugated polymers. The greatest loss at 1000°C is shown by the polymer containing the -CH<sub>2</sub>- bridge. The weight losses in nitrogen of the pseudoconjugated polymer in increasing order of stability at 1000°C for the various X bridges are:  $-CH_2$ -, 37.6%; -S-, 30.0%; -NH-, 28.8%;  $\begin{array}{c} -CH_2 \\ SO_2 \end{array}$ , 28.6%;  $-SO_2$ -, 24.6%.

v. The thermogravimetric analytical data obtained on the pseudoconjugated polymers which were prepared under arbitrarily selected polymerization conditions indicate a good possibility that the thermal properties of these polymers for use in a nitrogen or other inert atmosphere can be developed to approximate those of the conjugated polymers.

## b. Thermal Stability in Air of Polymers Condensed to 400°C.

i. When the conjugated and pseudoconjugated polymers are condensed to a temperature of 400°C, the heat-resistance of the polymers in air lies in the range of 430-500°C. The best heat-resistance is shown by conjugated polymers,  $\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$ , DA-42-13, DA-42-14, and DA-29-154 with the meta diamine polymer,  $\{N-C_{1}, C_{1}, C_{1}\}_n$  having the highest value of 500°C. Of the pseudoconjugated polymers, the oxygen polymer,  $\{N-C_6H_4-0-C_6H_4-N=HC-C_6H_4-CH\}_n$ , DA-29-275, shows the highest resistance in air with a temperature of inflection of 475°C. In fact, its weight loss in air at 600°C of 70% compares favorably with the values of 69% and 64% for the conjugated polymers, DA-42-13 and DA-42-14, respectively.

The indication that the polymerization is not completed at 400°C is found in the difference of the thermoanalyses of the polymers  $\{N-C_6H_4-N=NC-C_6H_4-CH_{n}\}_n$ , DA-42-13 and DA-29-154, in which the former was condensed to 400°C and the latter to 450°C. At 600°C in air, the per cent weight loss of DA-42-13 is 69% and of DA-29-154 is 39.2%. These data indicate the possibility of achieving greater thermal stability in the Schiff base polymers is continuing the condensation to temperatures higher than 400°C and under condition of time, temperature and pressure determined independently for the specific polymer to be synthesized.

- ii. The thermal stability of the aliphatic-type non-conjugated Schiff bases in air is relatively poor and of the order of 250°C, losing about 20% of their weight by 400°C.
- 7. When the condensation of the polymers is performed to a temperature of 600°C a number of effects due to the heating to this temperature are noted. It can be concluded from the nature of the weight-

temperature curves of the polymers thermoanalyzed in nitrogen, that twenty minutes heating time at 600°C is insufficient to cause complete condensation in the polymers. The thermograms indicate that polycondensation, and possibly other types of condensations continue to 1176°C.

## a. Thermal Stability in Nitrogen of Polymers Condensed to 600°C.

- i. The thermograms of the polymers, DA-42-13-H600, DA-42-14-H600 and DA-42-11-H600, condensed to a temperature of 600°C, clearly show that their stabilities in nitrogen are greatly increased over the same polymers condensed to 400°C. All the H600 polymers show losses of less than 20% of their weight at 1176°C. The two phenylenediamine polymers, DA-42-13-H600 and DA-42-14-H600 lose only about 15% of their weight at 1176°C, about 10% at 1000°C, and about 5% at 750°C. Based on inflection points, the thermal stability in nitrogen of these three polymers are DA-42-13-H600, 630°C; DA-42-14-H600, 645°C; and DA-42-11-H600, 550°C.
- ii. In the thermograms of these three H600 polymers (appendix numbers 3, 9, and 43), it will be observed in the weighttemperature plots, that little or no loss in weight is found as the samples are heated to a higher temperature until some definite temperature is reached; there a first distinct negative slope occurs until it reaches a second higher temperature where it tends to level out as a second but smaller negative slope becomes evident which continues to the temperature limit of the apparatus, namely, 1176°C.

The first negative slope can be attributed to losses of by-

products due to continued condensation polymerization and the temperature at which it originates depends, as would be expected, on the previous thermal history of the sample. For example, in those polymers which had been polymerized to a temperature of 400°C, the first negative slope is found approximately in the 500-600°C region; in those postheated to 600°C it is found in the region of 700°C.

The second negative slope may be interpreted from the nature of the plots as originating <u>before</u> the factors responsible for the first negative slope are completed and it may be approximated that generally it takes origin in the 800-850°C range. Though the losses in this region may be attributed in part to continued condensation which would be expected to be minor, they also may be due to condensations between polymer chains to yield fused ring structures by loss of hydrogen or other by-products.

An insight into the nature of these reactions can be better obtained by analyzing the gasses or products collected during the thermogravimetric run, and by differential thermal analysis by reference to the infrared spectra, if interpretable, of the polymers resulting from such treatment. Such studies are contemplated in future research. In any case, the thermograms performed in nitrogen indicate that condensation polymerization should be continued for a sufficient time to some temperature above 600°C, probably to a temperature in the region of 760-800°C. This will require metal heating blocks capable of withstanding these temperatures; for this purpose, copper, M.P.  $\rangle$ 

1000°C, may be satisfactory. It would also require a new design or structure in the means of heating the block and of maintaining the desired temperature thermostatically.

It is interesting to note the appearance of the polymers after heating to 1176°C in nitrogen; the finely powdered samples have the appearance of relatively shiny, very black particles of the original shape, and not of a dusty, powdery product characteristic usually of carbonized polymers. The yellow brick-dust polymers, when heated in nitrogen to 1176°C, also became black but they retained a brick-dust character.

### b. Thermal Stability in Air of Polymers Condensed to 600°C.

The thermal stabilities in air of the polymers condensed to 600°C are higher than the values found for the same polymers condensed to 400°C. For example, the thermal stability, as based on inflection points, in air for the polymer DA-42-13-H600 is 535°C compared to 480°C for DA-42-13; for DA-42-14-H600 it is 550°C compared to 500°C for DA-42-14; and for DA-42-11-H600 it is 525°C compared to 490°C for DA-42-11.

## 8. Thermal Stabilities of Polymers Condensed to 1176°C.

a. In Nitrogen.

When any or all of the polymers which have been heated to 1176°C in nitrogen in the thermogravimetric apparatus are recycled under nitrogen there is no evidence of further condensations as indicated by the substantially horizontal linear plots of weight versus temperature in each curve 2 of the thermograms of appendix numbers 1, 3, 7, 9, 15, 20, 25, 28, 32, 38, 41, 43, and 55. The weight losses vary from 2.4 to 4.4% in the thirteen polymers studied.

This means that by pretreating the polymers in an inert atmosphere at temperatures in excess of 800°C, for example, in the region of 1000°C, a polymer is obtained which shows heat stability in nitrogen or inert atmosphere to 1176°C. At the present time, it is not known whether or not the nitrogen reacts with the polymers at these temperatures. Accordingly, it is intended in future research to evaluate high purity helium as the inert atmosphere relative to nitrogen, and to perform some of the thermograms at reduced pressures.

b. In Air.

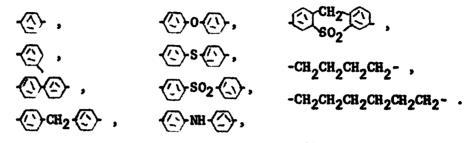
When any or all of the polymers which have been heated to 1176°C in nitrogen in the thermogravimetric apparatus are recycled in air as shown in each curve 3 of the thermograms of appendix numbers 1, 3, 7, 9, 15, 20, 25, 28, 32, 41, 43, and 45, all showed heat stabilities in air in excess of 480°C with a spread in temperature range of 480-600°C. Polymer DA-42-13-H600-R (Appendix No. 31) showed stability to 600°C (1112°F) in air.

9. When the polymers are meant for use in air, condensation to a temperature of about 600°C, or to some slightly higher temperature to be chosen after more studies, appears to be satisfactory. Whereas, if the polymers are intended for use in an inert atmosphere to temperatures in excess of 600°C, the polycondensation should be performed to temperatures of the order of 1000°C or higher.

#### VI. Summary and Conclusions.

 Three new bis-Schiff base monomers have been synthesized completing the series of eleven (11) monomers containing representative conjugated, pseudoconjugated and non-conjugated structures. The con-

tinuous azeotrope method<sup>1,2</sup> was successfully applied in these syntheses.
2. Eleven polymers containing conjugated, pseudoconjugated and non-conjugated moieties in their backbone structures were prepared. They can be represented by the general formula, fN-Z-N=HC-(1)-CH<sup>1</sup>/<sub>2</sub>, wherein -Z-represents



In these polymers the dialdehyde moiety, =HC-(2)-CH= was maintained constant.

- 3. The eleven polymers were synthesized in duplicate by two methods:<sup>1,2</sup>

  a) the bis-Schiff base exchange melt process, and b) the solution method. By the solution method, the conjugated and pseudoconjugated polymers were obtained as yellow-type brick-dust polymers. The same polymer prepared by the melt bis-Schiff exchange process were black, glossy polymers in all cases which, during synthesis, passed through a fusible, viscous, fabricable stage changing in color progressively from yellow to orange to brown to black, confirming the broad applicability of this reaction and process. As was expected, the non- conjugated polymers containing the aliphatic bridges, (CH<sub>2</sub>)<sub>4</sub> and (CH<sub>2</sub>)<sub>6</sub> were very light in color, when prepared by either the melt bis-exchange or the solution process, giving evidence of substantial inhibition of the conjugation in their linear structures.
- 4. The melt bis-exchange conjugated and pseudoconjugated polymers were prepared under identical conditions selected on the basis of limited preliminary experiments. These conditions are referred to as

"standardized conditions" in which the condensation is performed to a maximum temperature of 400°C. These conditions were found to be too severe for the synthesis of the non-conjugated aliphatic-type Schiff base polymers, for which 250°C was the maximum temperature used in the polycondensation; at this temperature, some decomposition, as evidenced by change in color of the polymer from white to orange, is noted.

- 5. Three exploratory polymerizations were performed with the intention of by-passing the syntheses of the bis-Schiff base monomers. These polymerizations involved the direct use of the two amines, and the two aldehydes, which constitute the monomers. A black polymer, which passed through the fusible stage, was obtained by the direct melt polymerization of m-phenylenediamine, aniline, terephthaldehyde and benzaldehyde. This reaction warrants further study.
- 6. Thermovravimetric analyses performed on the polymers clearly show that the polymers prepared by the bis-exchange reaction have greater thermal resistance than the polymers prepared by solution methods. This difference, however, is lowest in the non-conjugated aliphatictype Schiff base polymers.
- 7. The non-conjugated aliphatic-type have much lower heat-resistance than the conjugated and pseudoconjugated Schiff base polymers.
- 8. Analyses of the thermograms of the conjugated and pseudoconjugated polymers show that the polymers prepared by the melt bis-exchange reaction have very good thermal stabilities.
- 9. The conjugated and pseudoconjugated polymers condensed to a temperature of 400°C show a heat-resistance in nitrogen of 500-550°C. The conjugated polymers,  $\pm N-C_6H_4-N=HC-C_6H_4-CH=_n$ , have the highest values of 540°C and 550°C; the slightly lower values in the range of 500-525°C

for the pseudoconjugated polymers is surprisingly high.

- 10. The conjugated and pseudoconjugated polymers condensed to 400°C show a heat-resistance in air of 430-500°C. The conjugated polymers,  $\pm N-C_6H_4-N=HC-C_6H_4-CH=_n$ , have the highest values with a value for the meta-diamine polymer,  $\pm N-C_6H_4-N=HC-C_6H_4-CH=_n$  of 500°C. The pseudoconjugated polymer,  $\pm N-C_6H_4-N=HC-C_6H_4-CH=_n$ , shows a heatresistance in air of 475°C.
- 11. The conjugated polymer,  $\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$  prepared from dibenzylidene-m-phenylenediamine has heat-resistance at least as good as that prepared from the p-phenylenediamine derivative.
- 12. The non-conjugated aliphatic Schiff-base type polymers show a heatresistance of about 250°C and decompose in the range of 300-350°C in both nitrogen and in air.
- 13. The data on the thermograms indicate that the polycondensation is not completed at 400°C and should be continued to at least 600°C.
- 14. The two conjugated and one pseudoconjugated polymers which were condensed further by postheating the polymers in nitrogen to 600°C show a marked improvement in their stability in nitrogen. The conjugated polymers, {N-C<sub>6</sub>H<sub>4</sub>-N=HC-C<sub>6</sub>H<sub>4</sub>-CH<sup>1</sup>/<sub>n</sub>, showed the highest resistance with values of 630°C for DA-42-13-H600, and 645°C for DA-42-14-H600. The pseudoconjugated polymer, {N-C<sub>1</sub>-CH<sub>2</sub>-N=HC-C<sub>1</sub>-CH<sup>1</sup>/<sub>n</sub>, DA-42-11-H600 has a heat-resistant value of 550°C.
- 15. The thermal stability in air is also increased in those polymers which were condensed further by postheating to 600°C. The two conjugated polymers,  $\{N-C_6H_4-N=HC-C_6H_4-CH\}_n$ , DA-42-13-H600 and DA-42-14-H600 showed heat-resistance in air of 535°C and 550°C respectively, while the pseudoconjugated polymer, DA-42-11-H600,

showed a heat-resistance in air of 525°C.

- 16. The thermogravimetric analyzer apparatus was used as an instrument to postheat the conjugated and pseudoconjugated polymers in nitrogen to 1176°C to complete the polycondensation. These polymers were considered as fully condensed and their thermal stabilities in nitrogen and in air were evaluated. Judging from the nature of the thermogram curves, the polycondensation appears to continue to the 800-1000°C region. Some other type of condensation may be occurring also in the 800-1176°C region.
- 17. Polymers condensed to 1176°C (2026°F) show a heat-resistance in nitrogen of about 1176°C (2026°F). The data in the thermograms show only small total losses of the order of two to five per cent. Most or all of these losses occur after about 1000°C as is evident by a slight inflection in the curves. This loss at temperatures above 1000°C may be due to loss of hydrogen resulting from coupling of aromatic rings.
- 18. Polymers condensed to 1176°C show a heat-resistance in air in the range of 480-600°C. The fully conjugated polymer, DA-42-13-H600-R showed a stability in air of 600°C (1112°F). This appears to be the temperature region in which the combustion of the polymer occurs.
- 19. When the polymers are meant for use in air a condensation temperature of about 600°C appears to be satisfactory, but if the polymers are intended for use in an inert atmosphere to temperatures in excess of 600°C, the polycondensation should be performed to temperatures of the order of 1000°C or higher.
- 20. The experimental work detailed in this report points to the need for further study in a number of areas.

#### VII. Future Research.

- Establish the best overall conditions for the condensation polymerization of p-xylylidenedianil with dibenzylidene-m-phenylenediamine and dibenzylidene-p-phenylenediamine respectively, within the following reaction parameters.
  - a. without and with catalysis
  - b. establish temperature range of reaction
  - c. establish time limits of reaction.
- 2. Explore the synthesis of polymers directly in a one-stage melt process from m-phenylenediamine, terephthaldehyde, aniline and benzaldehyde with the following reaction parameters:
  - a. with and without catalysis
  - b. establish temperature range of reaction
  - c. establish time limits of reaction.
- 3. Establish methods for the determination of the kinetics of the bis-Schiff base exchange polymerization reaction. To date, an unambiguous method for this study has not been established.
- 4. Synthesize the meta-phthaldehyde,  $m-C_6H_4-(CHO)_2$ , and evaluate it in the syntheses of para-meta and para-para type polymers by
  - a. bis-Schiff exchange reactions and
  - b. direct synthesis using the phenylenediamines, the meta-phthaldehyde, aniline, and benzaldehyde.
- 5. Perform differential thermal analyses (DTA) on representative polymers in this report and the polymers prepared under items 1 to 4 inclusive.
- 6. Study the postheating to the region of 800-1000°C of polymers prepared to temperatures of about 600°C to determine what changes occur in the polymers, by

a. changes in the IR spectra of the polymers

b. mass-spectra analyses of by-products of reactions.

- 7. Determine best point in the polymerization at which the fusible polymer should be isolated for conversion to infusible condition:
  - a. evaluate the use of Lewis acids in the process of conversion to infusibility.
- Compare nitrogen and helium as the gaseous media in the postheating of polymers to 1176°C and in TGA measurements.
- 9. Undertake appropriate physical studies involving the following solid state properties of selected polymers and to correlate these properties by
  - a. semi-conductor measurements as a function of temperature and conformance to Ohm's law,
  - b. EPR measurements as a function of temperature and relationship to the number of "free" electrons to conductivity,
  - c. heat capacity measurements as a function of temperature for correlation to conductivity and EPR.
- 10. Evaluate conjugated perfluoro polymeric Schiff bases in which the hydrogen atoms in the benzene rings have been replaced by fluorine atoms with the expectation of improving the thermal stability of the polymers, especially in air. This study shoud, for comparative purpose, be performed in three stages to produce polymers of the general structure

a) 
$$f_{N} \xrightarrow{F_{4}} N = HC \xrightarrow{F_{4}} CH_{n}$$
  
b)  $f_{N} \xrightarrow{F_{4}} N = HC \xrightarrow{F_{4}} CH_{n}$   
c)  $f_{N} \xrightarrow{F_{4}} N = HC \xrightarrow{F_{4}} CH_{n}$   
 $F_{4} = F_{4}$ 

- 11. Attempt to determine molecular weight of polymers by end-group analysis using perfluoro compounds such as  $F_5C_6CHO$  and  $F_5C_6NH_2$  as end groups in the bis-Schiff bases,  $F_5C_6CH=N-C_6H_4N=HC-C_6F_5$ , and  $F_5C_6N=HC-C_6H_4-CH=N-C_6F_5$  from which the polymers are prepared.
- 12. Attempt to determine molecular weight of the polymers by reacting the polymers with various quantities of benzalaniline to reduce the molecular weights to points where colligative properties can be measured. Then apply statistical analysis and computor programming to attempt to solve this problem.
- 13. Initiate study to evaluate the photoconductivity of the polymers as a function of
  - a. wavelength of the incident light,
  - b. temperature.

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	OPERATOR JVC HEATING RATE 15 °C ATM. (1) N2, (2) N2, min.	TIME CONSTANT 2 C.							CITCA 950TGA
Y-AXIS	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION 0 mg.			7				
X-AXIS	TEMP. SCALE 200 °C inch SHIFT 0 inch	TIME SCALE (ALT.) 0							3
SAMPLE: DA-42-13	$f^{\rm n}$ -c <sub>6</sub> H <sub>4</sub> -N=IIC-c <sub>6</sub> H <sub>4</sub> -CH <sup>+</sup> <sub>n</sub>	SIZEng.							

SCALE 2 mg. SCALE 2 mg. (SCALE SETTING X 2) SUPPRESSION 0 mg. TIME CONSTANT 2 sec.
950TGA
950TGA

15-65	(3) air	sec.											OTGA
DATE 9-15-65	JVC 15 N2, (	7											OTCA
-	5	TIME CONSTANT									· · · ·		•
RUN NO.	OPERATOR HEATING RATE ATM. (1) N <sub>2</sub> , (	CON		•				 					
RUN	OPE HEA ATM	1											
		-ng.											
5		0								۰.			
Y-AXIS	mg incl IG X 2)	NOI		7	2		2 - -						
	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION						• • • •					
	SCAI (scal	SUPI					-					3	
	°C inch	0	<u>-</u> 										· · · ·
	-5												
X-AXIS								 					
	TEMP. SCALE SHIFT0	TIME SCALE (AI											
	TEMP. SHIFT_	TIME											
3-H600	-cH <sub>J</sub> n					на, страна (1997) 1970 г. – Страна (1997) 1970 г. – Страна (1997)			- - -		· · · · · ·		
SAMPLE: DA-42-13-H600	€N-C <sub>6</sub> H <sub>4</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -CH <sup>}_</sup> n	-mg.											
LE: D	H=N-₽	10								· · · · · · · · · · · · · · · · · · ·			
SAMP	€N-C6]	SIZE		· · · ·									

# WEIGHT, mg.

## Appendix No. 3

· APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

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1

TEMPERATURE\*, °C

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en de la companya de La companya de la comp	ſ						-		3		RUMENT PR	ODUCTS DI		-,	• <u>5</u>	
SAMPLE: DA-42-13-H600	00		×	X-AXIS					Y-AXIS			RUN	RUN NO.		DATE 9-14-65	14-65
ŧn-c <sub>6</sub> H₄n=Hc-c <sub>6</sub> H₄CB <sup>∔</sup> n		TEMF	Š	1	o inch	· ·	SCALE 2 mg. inch	E 2	inch	.  _		OPE	OPERATOR HEATING RATE		<u>JVC</u> 15	°.
1 		SHIFT	0	inch			(SCALE	SETTIN	G X 2)		·	ATM.			air	min.
SIZE <u>9.2</u> mg.		TIME	TIME SCALE (ALT.)	(ALT.)	0		SUPP	<b>SUPPRESSION</b> .	NOI	0	-mg.		TIME CONSTANT	TANT	2	- sec.
										-				•		
•	· ·															
				, 												
									-							
											-					
										$\square$						
											1				OTGA	OTGA
					TEMPERATURE*	ERATU		ပိ	•.	APPLY COR	RECTION FO	R NON-LINEA	• APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES	MEL-ALUMEL	THERMOCOL	IPLES

INSTRUMENT PRODUCTS DIVISION

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·	DATE 7-9-65	JVC 25 °C min.	- 2 sec.							OTCA	EL THERMOCOUPLES
TS DIVISION	RUN NO.	OPERATOR JVC HEATING RATE 25 ATM. nitrogen	TIME CONSTANT_								• APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
QULUND HATRAGENT PRODUCTS DIVISION	R		00								PPLY CORRECTION FOR NON
TTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTTT	Y-AXIS	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION		•			/			° C
O		°C SCA inch (sca	<u> </u>	 				: :	· · · · · · · · · · · · · · · · · · ·		TEMPERATURE*
	X-AXIS	CALE 100 0 inch	TIME SCALE (ALT.)							•	TE
		TEMP. SCALE SHIFT 0	TIME SC	 							
•	-29-94	c <sub>6</sub> H4.℃H <b>}</b> n ymer	-mg.	 	/				 	<u>.</u>	
	SAMPLE: DA-29-94	€N-C <sub>6</sub> H <sub>4</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -CH <mark>}</mark> n yellow polymer	SIZE_10						 		

	20-65	°C Min.	sec.									OTGA	PLES
	DATE 7-20-65	JVC 15 air	2									etter 950TGA	• APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
•		0	TIME CONSTANT					 			 		SOMEL-ALUMEI
VIGION	RUN NO.	OPERATOR HEATING RATE ATM.	E CON							 			URITY OF CHI
CULURD THERNART PRODUCTS DIVISION	RUN	OPER HEAT ATM.						 					R NON-LINE
RUMENT PE			mg.	-									RECTION FO
	S	He	a										APPLY COL
3	Y-AXIS	mg. inch VG X 2)	SION									)	
-		SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION										°.
		SCALE.	SUP										rure *
		•C inch											TEMPERATURE*
		-	0 (.		г						-		TEM
	X-AXIS		TIME SCALE (ALT.)										
		sc	SCAL										
		TEMP. SHIFT_	TIME										
۰.	4	cH}n r											
	A-29-9	-C <sub>6</sub> H4- polyme	-mg.					 					
	SAMPLE: DA-29-94	H <sub>4</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -Ci yellow polymer	10										
	SAMP	ŧN-C <sub>6</sub> H4-N=HC-C <sub>6</sub> H4-CH}n yellow polymer	SIZE			L	· · · · · · · · · · · · · · · · · · ·	 					

Appendix No. 6

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· · ·	RUN NO. DATE 9-29-65	OPERATORJVCHEATING RATE15ATM.(1) N2, (2) N2, (3) air	TIME CONSTANT 2 sec.							CITCA 950TGA	• APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
	Y-AXIS	SCALE 2 mg. inch (scale setting X 2)	SUPPRESSION 0 mg.			7					°c
	X-AXIS	TEMP. SCALE 200 °C inch SHIFT 0 inch	TIME SCALE (ALT.) 0								TEMPERATURE*
- *	SAMPLE: DA-42-14	m €N-C <sub>6</sub> H <sub>4</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -CH <sup>‡</sup> n	SIZE 10 mg.								

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UUPUAD INSTRUMENT PRODUCTS DIVISIO

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Appendix No. 7

ZH Z	TEMP. SCALE 100 SHIFT 0 inch TIME SCALE (ALT.)	SCALE 2 mg. (scale setting x 2) SUPPRESSION	Y-AXIS TTING X 2) TTING X 2)	ν <del>ο τ</del>	Ö E	RUN NO. D OPERATOR JW HEATING RATE ATM. air TIME CONSTANT	DATE DATE JS air 15 air 2 TANT 2	8-27-65 % C min. sec
								000GA

•.		· · ·	
SAMPLE: DA-42-14-H600	X-AXIS	Y-AXIS	RUN NO. DATE 8-30-65
$\sharp^{n}c_{6H_4}-^{n=1;\mathbb{C}}\cdotc_{6H_4}-^{c_{1}}d_{\mathbf{n}}$	TEMP. SCALE 200 °C inch SHIFT 0 inch	SCALE 2 mg. inch (SCALE SETTING X 2)	OPERATOR       JVC         HEATING RATE       15       °C         ATM.(1) N2, (2) N2, (3) air
SIZE 10 mg.	E SCALE (ALT.) 0	SUPPRESSION 0 mg.	
		7	
		-	
	°		OFFIN 950TGA
	TEMPERATURE*	°c	APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

-

	X-AXIS	Y-AXIS	<b></b>
$\lim_{\substack{f}N^{-}C_{G}H_{4}^{-}N^{-}HC^{-}C_{G}^{-}\mathfrak{g}_{q}^{-}CH^{2}_{H}^{-}H^{-}G^{-}H^{-}G^{-}H^{-}H^{-}G^{-}H^{-}G^{-}H^{-}G^{-}H^{-}G^{-}H^{-}G^{-}H^{-}H^{-}H^{-}H^{-}G^{-}H^{-$	TEMP. SCALE 100 °C inch SHIFT 0 inch	SCALE 2 mg. inch (SCALE SETTING X 2)	OPERATOR JVC HEATING R.TE 15 °C ATM. air min.
	TIME SCALE (ALT.) 0	SUPPRESSION 0	mg. TIME CONSTANT 2 .
		1	
			CIGA 950TGA

· · ·	. DATE 7-9-65	OR JVC 3 RATE 15 °C nitrogen min.	TIME CONSTANT 2 sec.			 				950TGA	<ul> <li>APPLY CORRECTION FOR NON-INEARITY OF CHROMEL-ALUMEL THERMOCOUPLES</li> </ul>
	RUN NC.	OPERATOR HEATING RATE ATM. nitrog	mg. TIME CC					•			CTION FOR NON-LINEARITY OF
	Y-AXIS	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION 0								ن ە
	X-AXIS	TEMP. SCALE 100 °C inch SHIFT 0 inch	TIME SCALE (ALT.) 0								TEMPERATURE*
	SAMPLE: DA-29-276	i o	SIZE10mg.								

OUND INSTRUMENT PRODUCTS DIVISION

•	RUN NO. DATE 7-2-65	OPERATORJVCHEATING RATE15ATM.air							COTCA	The second set of the sec
•	Y-AXIS	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION 0 mg.						<b>J</b>	°c .
•	X-AXIS	TEMP. SCALE 100 °C inch SHIFT 0 inch	TIME SCALE (ALT.) 0							
	SAMPLE: DA-29-276	m ∉N-C <sub>6</sub> H4-N=HC-C <sub>6</sub> H4-CH}n yellow polymer	SIZE 10 mg.							

CUUND INSTRUMENT PRODUCTS DIVISION

Appendix No. 12

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7-16-65	°C min.	sec.							COLOR 950TGA
ш	DR JVC RATE 15 nitrogen	TANT 2							
RUN NO.	OPERATOR HEATING RATE ATM. nitrog	TIME CONSTANT						 	
<u>æ</u>	O H A	mg.		1					
S	یز <u>د</u>	0				1			
Y-AXIS	SCALE 2 mg. inch (SCALE SETTING X 2)	SION							. :
	ALE	SUPPRESSION							
	SC (SC	SU			 				
	°C inch	0							
XIS	100 inch	ALT.)							
X-AXIS	SCALE 0	CALE (/				 			
	TEMP. SCALE SHIFT 0	TIME SCALE (ALT.)							
							 •		
284	с <sub>6</sub> н <sub>4</sub> -сн				<u> </u>				
<b>SAMPLE:</b> DA-29-284	ŧn-c <sub>6</sub> H <sub>4</sub> -c <sub>6</sub> H <sub>4</sub> -n=Hc-c <sub>6</sub> H <sub>4</sub> -cH <sup>}</sup> <sub>h</sub>	-mg.							
PLE:	<sup>н</sup> 4-С6 <sup>н</sup> 4	10							
SAM	€N-C <sup>6</sup> 1	SIZE							

· APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE<sup>\*</sup>, °C

Appendix No. 13

•	RUN NO. DATE 7-21-65	OPERATOR JVC HEATING RATE 15 °C ATM. air <sup>min.</sup>	TIME CONSTANT 2 sec.							COTCA	APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
	RUI	OPER HEAT ATM.	mg. TIM								ON FOR NON-LINI
	Y-AXIS	mg. inch 2)	0								<ul> <li>APPLY CORRECTION</li> </ul>
•	<i>1-</i> λ	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION_								RE*, °C
•		inch S	0							-	TEMPERATURE*
	X-AXIS	100 inch									TEN
	~	TEMP. SCALE SHIFT 0	TIME SCALE (ALT.)				<u> </u>				
			Ŧ		-						-
••	29-284	$f^{\mathrm{H}-\mathrm{C}_{\mathrm{H}_{\mathrm{C}_{\mathrm{C}}}}}$ , $^{\mathrm{C}_{\mathrm{G}}}$ , $^{\mathrm{H}_{\mathrm{d}}}$ , $^{\mathrm{N}=\mathrm{H}\mathrm{C}-\mathrm{C}_{\mathrm{G}}}$ , $^{\mathrm{H}_{\mathrm{d}}}$ , $^{\mathrm{C}_{\mathrm{H}_{\mathrm{d}}}}$	ň	 					 		
•	<b>SAMPLE:</b> DA-29-284	и <sub><i< sub=""> -с<sub>6</sub>н<sub>4</sub>-1</i<></sub>	10 mg.								
	SAMP	€N-C	SIZE								

ULTUIL TRAINGERN PRODUCTS DIVISION

· ....

RUN NO. DATE 8-28-65	OPERATOR JVC · · · · · · · · · · · · · · · · · · ·	TIME CONSTANT 2 sec.						COTGA 250TGA
- Y-AXIS RUI	SCALE 2 mg. SCALE 2 mg. (scale setting x 2) ATN	0 mg.					· ·	
X-AXIS	TEMP. SCALE 200 °C SCA inch (scA	TIME SCALE (ALT.) 0 SUP						6
SAMPLE: DA-29-284	H4-CH <sup>J</sup> n	SIZE 10 mg.						

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UUUUD INSTRUMENT PRODUCTS DIVISION

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·			
S/MPEE: DA-29-277	X-AXIS	Y-AXIS	RUN NO. DATE 7-22-65
$\mathbb{C}^{\mathbb{N}^{n}}C_{6}\mathbb{N}_{4}^{*}^{*}C_{6}\mathbb{N}_{6}^{*}^{*}^{*}\mathbb{M}^{*}^{*}\mathbb{M}^{*}^{*}C^{*}C_{6}\mathbb{N}_{6}^{*}^{*}^{*}^{*}^{*}^{*}^{*}^{*}^{*}^{*$	TELAP. SCALE 100 °C inch SHIFT 0 inch	SCALE 2 mg. inch (SCALE SETTING X 2)	OPERATOR JVC HEATING RATE 15 °C ATM. ¢ ir min.
SIZE_10n.	TIME SCALE (ALT.)0	SUPPRESSION 0. mg.	TIME CONST/
			如刑刑 950TGA
	TEMPER	TEMPERATURE*, °C • APPLY CORRECTION FOI	<ul> <li>APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES</li> </ul>

DATE 7-16-65	min.	sec.							
	DR JVC RATE 15 nitrogen	STANT 2				 			
RUN NO.	OPERATOR HEATING RATE. ATM. nitro	TIME CONSTANT				 	•		
		-mg.							 
Y-AXIS	, mg. , inch NG X 2)	SION0_							 
	SCALE 2 mg. · inch (SCALE SETTING X 2)	SUPPRESSION							
	°C inch	0							
X-AXIS	NLE 100	E (ALT.)							
	$ \frac{1}{6} n - c_0 n_4 - c m_2 - c_0 n_6 - c_0 n_4 - c m_3 TEMP. SCALE - c_0 n_4 - c m_3 TEMP. SCALE - c_0 n_4 - c m_3 TEMP. CALE - $	TIME SCALE (ALT.)	 - Andrew Constant (1997) (1997)						
	-c <sub>6</sub> 11 <sub>4</sub> -cn	3 3 3 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4 4							
D/-29-265	ce <sup>r</sup> e no	mg.							
SAMPLE:	-c <sub>6</sub> n <sub>4</sub> -cn <sub>2</sub> -	1 1						•	

· APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE\*, °C

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-	RUN NO. DATE 7-21-65	OPERATOR JVC	air air	TIME CONSTANT 2 sec.							で の し の て の て の て の て の て の し の の し の の し の の し の の の の の の の の の の の の の	APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
	RU	Ч О Ц	ATM.	mg. TIN								ECTION FOR NON-LI
	Y-AXIS	mg.	inch ( 2)	Ν								APPLY CORRE
* *	۲-۱	SCALE 2	inch (SCALE SETTING X 2)	SUPPRESSION		· · · · ·						E*, °C
				รา								TEMPERATUŖE*
	X-AXIS	100	inch inch	ALT.) 0	 /							TEMF
	/-X	<u></u> {N-С <sub>6</sub> Н <sub>4</sub> -СН <sub>2</sub> -С <sub>6</sub> Н <sub>4</sub> -N=HC-С <sub>6</sub> Н <sub>4</sub> -СН <sup>+</sup> ]ТЕМР. SCALE_	FT 0	TIME SCALE (ALT.)								
		A-CH	SHIFT	TIM				 				
÷	-265	-N=HC-C <sub>6</sub> H	>									
-	SAMPLE: DA-29-265	-сн <sub>2</sub> -с <sub>6</sub> н <sub>4</sub>	F > 4	<u>10</u> mg.			 					
	SAMPI	€N-C <sub>6</sub> H <sub>4</sub>		SIZE						•		

UUPUAU ING FOURENT PRODUCTS DIVISION

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•	26-65	°C min.	- sec.									OTGA	IPLES
	DATE 8-26-65.	OPERATOR JVC HEATING RATE 15 °C ATM.(1) N <sub>2</sub> , (2) N <sub>2</sub> , (3) air	7									DIM 950TGA	APPLY CORRECTION FOR NON-LUNEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
•		ATE	TIME CONSTANT									A	IJWITT-TIWO
NOISI	RUN NO.	OPERATOR HEATING RATE ATM.(1)_N <sub>2</sub> ,(2)	CONS										RITY OF CHR
ODUCTS DIV	RUN	OPE HEA ATM			,					•			R NON-LINEA
RUMENT PR			.gm										RECTION FO
OUPUID INSTRUMENT PRODUCTS DIVISION	S	, He	0	1									APPLY COL
<b>j</b>	Y-AXIS	SCALE <sup>2</sup> mg. inch (SCALE SETTING X 2)	NOIS					7					
-		LE 2 E SETTIN	SUPPRESSION										°.
Ċ		SCALE.	SUP								· · · ·		TURE <sup>4</sup>
Ċ.		°C inch	0										TEMPERATURE*
	S	200 inch											TEN
	X-AXIS		TIME SCALE (ALT.)		-	 	/					۳ س	
		IP. SC	E SCAI										
		I∯ TEMP. SHIFT_	TIM										
		с <sub>6</sub> н4-сі											
~	-265	- N=HC -(								, <u>, , , , , , , , , , , , , , , , , , </u>			
~ •	DA-29-265	2-C <sub>6</sub> H4	mg.	 						*			
	SAMPLE:	$f_{\rm N}-c_{6}H_{4}-cH_{2}-c_{6}H_{4}-N=HC-c_{6}H_{4}-cH_{1}$	10										
	SAM	ŧn-c,	SIZE										

	DATE 9-11-65	JVC	2 sec									-	COTGA
• • •		ATE nitro	TIME CONSTANT	· · · · · · · · · · · · · · · · · · ·									<u>-</u>
	RUN NO.	OPERATOR HEATING RATE ATM. niti											
WE WITH WE WING ON M. DECANANT			.gm	1			-						
	Y-AXIS	mg. inch X 2)	0 NC	- 		· · · · ·			•				
	×	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION										
		SCALE (scale se	SUP										
		o C inch	0										
	X-AXIS	E 100	(ALT.)										
	×	IP. SCAL	TIME SCALE (ALT.)										
		CH TEMP.	TIM								•		
	92	IC-С <sub>6</sub> Н4-( : <b>r</b>								•			
۰.	DA-29-266	Here and the second sec	-mg.										
nanta 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	SAMPLE	6H4-CH2- yello	10										
	SAN	-c' €N-C	SIZE		•								

WEIGHT, mg.

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Appendix No. 21

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•	DATE 7-22-65.		min.	sec.									● BOTGA	DUMES
() :	DATE 7		e <u>15</u> air	NT 2										A Service State and and a state of the service o
	VO.	ATOR	HEALING RALE ATM.	TIME CONSTANT										isnuant at a
T PRODUCTS DIVISION	RUN NO.	DFERATOR	HEALI ATM.							•		i Angria Internet		
				mg.										
	S		÷	0	1					• •				
<b>3</b>	Y-AXIS	Ĕ	inch (SCALE SETTING X 2)	SION_										-
·		SCALE 2	LE SETTI	SUPPRESSION										ບ •
$\odot$		SC A	(SCA	- suf										TEMPERATURE <sup>4</sup>
Ŭ		ပ	inch	0	- 1 -	•								NPERA
	ร	100	_ inch	.T.)										1 1 1
	X-AXIS	ALE	0	TIME SCALE (ALT.)				 			· · · ·			
		AP. SC	FT	E SCA		$\int$		 		• • •				
	<u></u>	TEN TEN	SHIFT	TIM	·			,						
		, н, -сн					   							
•_	9-266	- NHHC - C			-		 							
	DA-29	-C <sub>6</sub> H <sub>4</sub> .	c c t olymer	mg.			 							
	<b>SAMPLE:</b> DA-29-266	ĘN-C <sub>ζ</sub> H, -CH, -C <sub>ζ</sub> H, -N=HC-C <sub>ζ</sub> H, -CH <sup>‡</sup> TEMP. SCALE	vellow Dolvmer	SIZE 10			· · · · · · · · · · · · · · · · · · ·	 						
	SAI	, _N-C	- 47	SIZ					:	•				

WEIGHT, mg.

## Appendix No. 22

1008

7-15-65	min.	sec.									OTGA
mi	JVC 15 n	2									altituto 950TGA
	8	TIME CONSTANT						8 1			
NO.	ATO ING	CON							· · · · · · · · · · · · · · · · · · ·		
RUN NO.	OPER HEATI ATM		· ·								
		-mg.									
		0			1						
Y-AXIS	mg. inch G X 2)	NOI	 •								
-	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION				· .					
	SCALE_	SUPF									
	°C inch						1 2 4 , 1 , , ,				· · · · ·
	00 • inch	0 (.			* * * - 1						
X-AXIS		: (ALT				· ·					
	TEMP. SCALE SHIFT0	TIME SCALE (ALT		· · · · · · · · · · · · · · · · · · ·							
	TEMP. Shift.	TIME								- L <sup>-</sup> - J	
	-cH≩n	10 mm/r							· · · · ·		 · · ·
:75	ŧn-с <sub>6</sub> н4-0-с <sub>6</sub> н4-ищс-с <sub>6</sub> н4-сн <sup>}</sup> п										
DA-29-275	- N=HC	-mg.							· · · · ·		
	-0-C <sup>6</sup> B	10									
SAMPLE:	N-C6H4	SIZE	]	-		 					

WEIGHT, mg.

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## Appendix No. 23

DATE 7-16-65	°C min.	sec									950TGA
DATE	JVC TE 15 air	ANT 2	· ·		 					- - 	
RUN NO.	OPERATOR HEATING RATE ATM	TIME CONSTANT									
RUN	OPER HEAT ATM							:			1
		-Bm									
5	d.e	0									
Y-AXIS	2 mg. inch NG X 2)	NOI					-				
	L	SUPPRESSION									
	SCALE (SCALE	SUP	r								
	o C inch	0	,								
10	100 6 - inch	<b>(</b> )				,					
X-AXIS		E (ALT									
	TEMP. SCALE. SHIFT_0	TIME SCALE (ALT.)									
		TIME						×		• • •	
	-cH∄										
275	<sup>7</sup> H <sup>9</sup> 2-21										
<b>SAMPLE:</b> DA-29-275	ŧn-с <sub>6</sub> н <sub>4</sub> -о-с <sub>6</sub> н <sub>4</sub> -м=нс-с <sub>6</sub> н <sub>4</sub> -сн <sub>}</sub> п	-mg.									
PLE: I	1 <sub>4</sub> -0-c <sub>f</sub>	10									
SAM	ŧn-c <sub>6</sub> i	SIZE	·	1							

Appendix No. 24

	3-65	°C .	air sec.									TGA	2
Ċ	DATE 9-13-65	1 1	(2)			-						950TGA	APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
,	D	ATE	ATM. <u>(1) N<sub>2</sub>, (2) N<sub>2</sub>,</u> TIME CONSTANT 2							• • • •			OMEL-ALUMEL
VISION	RUN NO.	OPERATOR HEATING RATE	ATM. <u>(1) N<sub>2</sub>, (2)</u> TIME CONSTANT						• • •				RITY OF CHR
ST CO (MC)	RUN								•				R NON-LINEA
INSTRUCTION CONTRACT FOODUCTS DIVISION		1977	mg.										RECTION FO
	ω υ		0										APPLY COR
8	Y-AXIS	mg incl incl	NOI		~	4							
		SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION										°°,
÷		SCALE (SCALE ST	SUP								· · ·		rure*
Ų		°C inch		,									TEMPERATURE*
	10		_ Incn .T.) 0									Ĩ	TEM
	X-AXIS		(AL										
		sci	SCAL										
		TEMP.	TIME										
		-cH <sup>‡</sup> n							······································				
۰.	275	с-с <sub>6</sub> н4.											
	DA-29-	14-N-41	-mg.	•									1
	SAMPLE: DA-29-275	ём-с <sub>6</sub> н <sub>4</sub> -о-с <sub>6</sub> н <sub>4</sub> -м=нс-с <sub>6</sub> н <sub>4</sub> -сн <sub>∃</sub> п	10										1
	SAM	<sup>=</sup> N−C6H4	SIZE						· · · · ·				

2

DATE 9-13-65		2 sec					 		pendix	950TGA
	JVC ATE 15 nitrogen	TANT								
RUN NO.	ATOR ING R	TIME CONSTANT								
RUN	OPER HEAT ATM									· · · ·
		mg.								
S		0						I j − − J − C		
Y-AXIS	inc vg X 2)	NOI	 		,					
	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION		• •						
	SCA (scal	SUP								
	°C inch	0								
.0	100 1 i inch	<u>.</u>								
X-AXIS		E (AL								
	TEMP. SCALE SHIFT 0	TIME SCALE (ALT.)				· · · · ·			- 2 · · · · · · · · · · · · · · · · · ·	
		TIME							•	
	4-CH}n									
271	HC-C <sub>6</sub> H									
SAMPLE: DA-29-271	ŧN-C <sub>6</sub> H4-O-C <sub>6</sub> H4-N≓HC-C <sub>6</sub> H4-CH}n yellow polymer	Bæ								
2LE: 1	14-0-C <sub>(</sub> rellow	10								
SAMF	⊧N-C6 <sup>E</sup> y	SIZE								

#### Appendix No. 26

22-65	ain.	sec										OTGA
DATE 7-22-65	JVC 15 r	7										OTGA
	ATEa1	TIME CONSTANT		а. 					н н 			
RUN NO.	©DERATOR HEATING RATE ATMa	E CON										
RUN	OPER HEAT ATM.											
	<i>*<sup>137 -</sup></i>	mg.						· · · · · · · · · · · · · · · · · · ·				3
S	عاد	0										
Y-AXIS	SCALE 2 mg. inch (scale setting x 2)	NOI										
	E 2 E SETTIN	SUPPRESSION										
	SCALE_	SUPI			-	:		• • •	• 4 •			
	°C inch	0	х •									<ul> <li>A set of the set of</li></ul>
	100 ° - inch											
X-AXIS		TIME SCALE (ALT.)		(								
	TEMP. SCALE	SCALI										
	TEMP. Shift_	TIME					· · · · · ·				• • •	
	-cHJn									: : : 		
71	c-c <sub>6</sub> H <sub>4</sub> er									· · ·		
A-29-2	I4-N≓H polym	-mg.			·		 					
ТЕ: D	l4-0-C <sub>6</sub> H4-N=HC- yellow polymer	10								<u> </u>		
SAMPLE: DA-29-271	ŧN-C <sub>6</sub> H4-O-C <sub>6</sub> H4-N=HC-C <sub>6</sub> H4-CH <sup>}</sup> n yellow polymer	SIZE			•							

WEIGHT, mg.

# Appendix No. 27

INSTRUMENT PRODUCTS DIVISION

THE RELATENCE DIVISION	X-AXIS Y-AXIS RUN NO. DATE 9-13-65	MP. SCALE200 °CSCALE2mg.OPERATORJVCinchinchinchHEATING RATE15°CIFT0inch(SCALE SETTING X 2)ATM.(1) N2, (2) N2, (3) air	0 SUPPRESSION 0 mg.						
	X-AXIS	TEMP. SCALE 200 °C inch SHIFT 0 inch						· ·	
••	SAMPLE: DA-29-282	$f^{N-C_6H_4-NH-C_6H_4-N=NC-C_6H_4-CH_h}$	SIZE 10 mg.		· · ·				

MEIGHT, mg.

Appendix No. 28

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• APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

.

TEMPERATURE<sup>\*</sup>, °C

	D/	OPERATOR JVC HEAT RATE 15 °C ATM. afr inin.	THE CONSTA						COTGA	<ul> <li>APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES</li> </ul>
ALL TANKER REALIZED REALIZED REALIZED RELEASED REALIZED RELEASED REALIZED	Y-AXIS RI	SCALE 2 mg. 0 inch HI (scALE serTING X 2) A1	, mg.							
	X-AXIS	1.00 °C inch inch	TIME SCALE (ALT.) 0							TEMPERATURE*,°C
	SAMPLE: DA-29-282	EN-C6D4-NH-C6H4-N-IIC+C6H4-CH3 TEMP. SCALE	SIZE 10 mg.							

and the second s

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-13-65	. U C C	۰ . در .					 		· · · · · · · · · · · · · · · · · · ·	 	OTCA 950TGA
DATE7-13-65	JVC 15	2					 				
RUN NO.	OFERATOR HEATING F ATH.	TIN CONST. 2		· · · · · · · · · · · · · · · · · · ·	·						
£		mg.									
c.		0									
Υ-Α	2			-				/			
	CCALE 2 mg. inch (SCALE SCITING X 2)	SUL	s 				 -				
	• C inch		•		$\langle$	 					
515	100 inch	LT.)									
SIXA-X	CM.L.	THE SCALE (ALT.)				 					
	fN-C <sub>6</sub> II <sub>4</sub> -NE+C <sub>6</sub> , R=II0+C <sub>6</sub> H <sub>4</sub> -CII} nE: crange polyner										
281	ale of										
0A-29-2	4~Wive <sub>6</sub> 0., malle erange_polymer	-mg.		a a cura a cu							
SAMPLE: DA-29-281	4-NL-C orange	SIZE 10 mg.									
SAMI	{n-c <sub>6</sub> n	SIZE		•							

<u> </u>		•	[]	<u></u>	1				·····	 	[		
DATE 7-27-65	°C min.	sec.											
ATE 7-	JVC 15 air	7		-									
D		<b>LANT</b>											
0.	ATOR NG RA	CONST											
RUN NO.	OPERATOR HEATING RATE ATM.	TIME CONSTANT								•			
		Bu											
		0							-				
Y-AXIS	mg. 2)												$\mathbf{J}$
-γ	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION					 						
	SCALE_	UPPRI							-				
	 ເ ເ	<u>.</u>											
	°C inch	0										•••	
	100 inch												ан ал 1917 - Ал
X-AXIS		E (ALT											
×	. SCAI	SCALE								· · · · · · · · ·			:
	TEMP. SCALE SHIFT 0	TIME SCALE (ALT.)											
1				1						 			
31	-c <sub>6</sub> H4 <b>-</b>												
DA-29-281	ëN-C <sub>6</sub> H <sub>4</sub> -NH-C <sub>6</sub> H <sub>4</sub> -N≓HC-C <sub>6</sub> H <sub>4</sub> -CH <sup>‡</sup> n orange polymer	mg.								 			
	-C <sub>6</sub> H <sub>4</sub> nge p	E							 	 			
SAMPLE:	I4-NH ora						 						
SAM	м-с <sub>6</sub> і	SIZE											.

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Appendix No. 31

· APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE\*, °C

	DATE 9-12-65	OPERATOR JVC HEATING RATE 15 °C ATM. (1) N <sub>2</sub> , (2) N <sub>2</sub> , (3) air	TANT 2 sec.							COTGA	IEL-ALUMEL THERMOCOUPLES
DUCTS DIVISION	RUN NO.	OPERATOR HEATING RATE ATM.(1) N <sub>2</sub> , (2					-				NON-LINEARITY OF CHROM
THE AND ALL AN	Y-AXIS	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION 0 mg.			 2					°C • APPLY CORRECTION FOR
	X-AXIS	TEMP. SCALE 200 °C inch SHIFT 0 inch	TIME SCALE (ALT.) 0 3								TEMPERATURE
•	SAMPLE: DA-42-16	ŧ <sup>n-c</sup> 6 <sup>H</sup> 4-s-c <sub>6</sub> H4- <sup>N=HC-c</sup> 6 <sup>H</sup> 4-cH <sup>4</sup>	SIZE <u>10</u> mg.							•	

WEIGHT, mg.

Appendix No. 32

	-12-65	°C min.	sec.		-							SOTGA
	DATE 9-12-65	JVC 15 air	T2					 				(1) 050TGA
			TIME CONSTANT		-			 		 		
TS DIVISION	RUN NO.	OPERATOR HEATING RATE ATM.	IME CO			 			•			
OUNT INTROMENT FRODUCTS DIVISION	<u>ь</u> с.		mg.		(							1
OLD INSTRU			0									
5	Y-AXIS	SCALE 2 mg. inch (scale setting x 2)	SION									ŕ
•		SCALE (SCALE SETTI	SUPPRESSION									
2 )		SC.	SU		-/	 					-	
		• C inch	0					 	 			
	X-AXIS	. 100 inch	(ALT.)									
	'-X	TEMP. SCALE_	TIME SCALE (ALT.)					 				
		TEMP. SHIFT_	TIME S	·						- 		
		-cH}n									•	
•	-16	н <sup>9</sup> о-он										
<b>* '</b>	SAMPLE: DA-42-16	ŧ́N-с <sub>6</sub> H <sub>4</sub> -S-с <sub>6</sub> H <sub>4</sub> -N <del>=</del> HC-с <sub>6</sub> H <sub>4</sub> -сн <sub>∃</sub> n	mg.									
	MPLE:	6H4-S-1	2E 10			 		 				
	SA	€N-C	SIZE		4							

-

	DATE 9-14-65	JVC JVC ( ATE 15 °C ) nitrogen min.	TANT_2sec						ATTAC STCA
	RUN NO.	OPERATOR JVC HEATING RATE 15 ATM. nitroge	TIME CONSTANT						
ULTUIL THE REPART A PLANT	Y-AXIS	mg. inch 2)	N 0 mg.						
•	<i>4-</i> λ	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION						
· · ·	X-AXIS	TEMP. SCALE 100 °C inch SHIFT 0 inch	TIME SCALE (ALT.) 0						
		<u> </u>	TIME						
•••	SAMPLE: DA-42-15	⊧N-C <sub>6</sub> H <sub>4</sub> -S-C <sub>6</sub> H <sub>4</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -CH <sup>]</sup> <sub>n</sub> yellow polymer	SIZE 10 mg.						

1

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	-14-65	°C min.	sec.									SOTGA	UPLES
and the second sec	DATE 9-14-65	JVC 15 air	5									COLOR DE COLOR	APPLY CORRECTION FOR NON-LUNEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
•		0	TIME CONSTANT						 				HROMEL-ALUMI
NOISIVI	RUN NO.	OPERATOR HEATING RATE ATM.	E CON										EARITY OF CI
RODUCTS	RUI	OPER HEAT ATM.					 						OR NON-LIN
RUNENT PREMI			mg.	 -								1	RECTION F
OUNT NETRUMENT PRODUCTS DIVISION	0	÷E	0										APPLY CO
3	Y-AXIS	mg. inch IG X 2)	NOI										•
		SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION										°.
•		SCALE_	SUPI										URE*
<u>.</u>		°C inch									- 		TEMPERATURE*
		100 ° inch	.) 0	$\square$									TEM
	X-AXIS		TIME SCALE (ALT.)									. 1	
		sc/	SCALI										
		TEMP. SHIFT_	TIME										
		cu <del>]</del> n											
	5	-c <sub>6</sub> H4-											
- •	A-42-1	4-N=HC polym	-mg.										
	<u>а</u> 	+-S-C <sub>6</sub> H4-N=HC-C yellow polymcr	9.5										
	SAMPLE: DA-42-15	EN-C <sub>6</sub> H <sub>4</sub> -S-C <sub>6</sub> H <sub>4</sub> -N≕HC-C <sub>6</sub> H <sub>4</sub> -CH <sup>‡</sup> n yellow polymer	SIZE			· · · ·							

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•	RUN NO. DATE 7-19-65	OPERATOR JVC HEATING RATE 15 °C ATM	TIME CONSTANT 2 sec.							COTGA	• APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
	RL		AI mg.		· · /						RRECTION FOR NON-
	Y-AXIS	mg. inch X 2)	0 N	 +							• APPLY CO
•	Υ-	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION	 	/					· · · ·	°°°
		SCALE (SCALE S	SUI				 				TEMPERATURE*
		100 °C inch	0 (								TEMPE
	X-AXIS		LE (ALT								
		JTEMP. SC SHIFT	TIME SCALE (ALT.)								-
			) <del> -</del>								
~	DA-29-285	-N=HC-C	_								
		$f^{N-C_6H_4}-SO_2-C_{6H_4}-N=HC-C_{6H_4}-CH=\frac{1}{n}TEMP. SCALE$	9.8 mg.				 				
	SAMPLE:	€N-C <sub>6</sub> H4.	SIZE								

UNUTION INSTRUMENT PRODUCTS DIVISION

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XO	D	OPERATOR JVC HEATING RATE 15 °C ATM. air min.	TIME CONSTANT 2 sec.						(1) 950TGA	<ul> <li>APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES</li> </ul>
RODUCTS DIVISI	RUN NO.	OPERATOR HEATING R/ ATM.								TIREAULTINE DO
CULUIND HISTRUMENT PRODUCTS DIVISION			0 mg.							APPLY CORECTION F
CULUD.	Y-AXIS	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION						/ 	
•		SCALE_	SUPPRI	 /		 				TURE <sup>*</sup> .°C
<u>.</u> .		• C inch	0							TEMPERATURE*
	X-AXIS	ALE 100	-E (ALT.)							•
		ŧn-c <sub>6</sub> н₄-so <sub>2</sub> -c <sub>6</sub> н₄-n=hc-c <sub>6</sub> н₄-ch= <mark>∔</mark> ТЕМР. SCALE SHIFT0	TIME SCALE (ALT.)				 			
		с <sub>6</sub> Н4-СН=	•							
•	-29-285	6H4 - N=HC - 1	Bu		 					
	<b>SAMPLE: DA-29-285</b>	5 <sup>H</sup> 4-S02-C,	10							
	SAN	ŧn-c	SIZE							

INTERNATION DE VENOURS ECO (MC) INSTRUMENT PRODUCTS DIVISION

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Appendix No. 38

	.65	O U U U U					·		1			/			KO. 5.
•	7-10-		sec.								 				150TG
	DATE 7-10-65	JVC 15 nítrogen	5												OTGA
	D	TE	ANT												
		OPERATOR HEATING RATE ATM.	TIME CONSTANT		·····										
	RUN NO.	OPERATOR HEATING R/ ATM.													
	RU	OPER HEAT ATM.													
			ъ					,				•			
												• •			
	XIS	mg. 2)	0												
	Y-AXIS	2 ING X 2	SION								/				
		E SETT	PRES												
		SCALE 2 mg. inch (scale setting X 2)	<b>SUPPRESSION</b> .									•			
	<del></del>					-7									
		° C inch	0			ļ <i></i>				· · · · · · · · · · · · · · · · · · ·					
	S	00 inch													
	X-AXIS	E 1(	TIME SCALE (ALT		)										
	×	SCAI 0	CALE												· · ·
		JTEMP. SHIFT_	ME S		-{										
		St St	F												
		H4-CI		•											
	c	HC-C6			1										
	0-27	I4-N≓ ymer			<del>\</del>										
-	SAMPLE: DA-29-270	fN-C <sub>6</sub> H <sub>4</sub> -SO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -CH=H yellow polymer SHIFT 0	•    ,		<b>!</b>					 					
-	PLE.	14-SO	10		}										
	SAM	N-C6I	SIZE_		\$										
Į						1	L	L	1	L		L	L	L	Ll

TIPLE C DU POUT DE MEMOURS & CO TAC) INSTRUMENT PRODUCTS DIVISION

Appendix No. 39

	7-22-65	0	min.	- sec.										TGA
	DATE 7-	JVC 15	air	2										050TGA
•		ATE		TIME CONSTANT									 	
MOISIVI	RUN NO.	OPERATOR	<u>и</u> .	E CON									 	
RODUCTS	RUI	OP1 HF	ATM.		 						-			
OUND METRUMENT PRODUCTS DIVISION				mg.										
	10		<b>-</b>	0										
3	Y-AXIS	Bu	Inci IG X 2)	-NOI										ŧ
		E 2	Inch (SCALE SETTING X 2)	SUPPRESSION					-				$\square$	
•		SCALE	(SCALI	SUPI		-								
N.,		ပ •	ucu								1			
			- inch	0 (		_	•				J			
	X-AXIS	E 100		ALT		/								
	×	. scal	0	SCALE										
		TEMP	SHIFT_	TIME SCALE (ALT.)										
		<sup>1</sup> 4-СН <del>]</del>												
	0	arc-c <sub>6</sub> 1	អូ											
`	DA-29-270	6 <sup>H</sup> 4 −N=	polyme	- mg.								- 		
		<b>€</b> N-с <sub>6</sub> H <sub>4</sub> -so <sub>2</sub> -с <sub>6</sub> H <sub>4</sub> -N=Hс-с <sub>6</sub> H <sub>4</sub> -сн <mark>∄</mark> ТЕМР. SCALE	yellow polymer	0									 	
	SAMPLE:	4-C6H4	Š	SIZE 10	 									
	U)			S		1		1		l				

· APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE<sup>\*</sup>, °C

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Appendix No. 40

	RUN NO. DATE 8-21-65	OPERATOR JVC HEATING RATE 15 °C	TIME CONSTANT 2						· · · · · · · · · · · · · · · · · · ·	COLCA
OUDIND INSTRUMENT PRODUCTS DIVISION	Y-AXIS	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION 0mg.		5 1					
	X-AXIS	TEMP. SCALE200°C inchinch	CALE (A							
	SAMPLE: DA-42-11	-N So2 N=HC-C <sub>6</sub> H <sub>4</sub> -CH <sub>n</sub>	SIZE 10 mg.							

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Appendix No. 41

TEMPERATURE<sup>\*</sup>, °C

20-65	°C min.	sec.								OTGA
DATE 8-20-65	JVC 15 air	2								950TGA
	ATE	TANT								<del>Q</del>
NO.	OPERATOR HEATING RATE ATM.	TIME CONSTANT								
RUN NO.	OPER. HEATI ATM									1
		Bu						-		
		0								
Y-AXIS	mg inch G X 2)	NOI								
	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION				 	 			
	SCALE. (SCALE S	SUPF		- /						
	°C inch			7						
	<u>م</u> ا	0 (.								
X-AXIS	LE 100 inc	TIME SCALE (ALT.)								
	TEMP. SCALE SHIFT 0	SCALI	-						 	
	TEMP. : SHIFT	TIME								
			•		 				 <u>-</u>	
11										
DA-42-11	$\begin{bmatrix} CH_2 \\ SO_2 \end{bmatrix}_{N=HC-C_6H_4} - CH_{-n}$	-mg.								
	H2 102	10								
SAMPLE:		SIZE 10		]	•	 				1

INSTRUMENT PRODUCTS DIVISION

.

APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE<sup>\*</sup>, °C

WEIGHT, mg.

	OPERATORJVCHEATING RATE15ATM. (1)N2, (2)N3, (3)air	mg. TIME CONSTANT 2 sec.							• APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
Y-AXIS RUN NO	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION 0 mg		 2				e	°C
X-AXIS	TEMP. SCALE 200 °C inch SHIFT 0 inch	TIME SCALE (ALT.) 0							TEMPERATURE*
SAMPLE: DA-42-11-H600	The solution of the second sec	SIZE 10 mg.							

INSTRUMENT PRODUCTS DIVISION

Appendix No. 43

	DATE 8-21-65	°C min.	sec.				 				CITIN 950TGA
Ċ	DATE 8		alf NT 2								
-	0.	OPERATOR HEATING RATE	TIME CONSTANT		 						
OUDIN MATAULAN PRODUCTS DIVISION	RUN NO.	OPERATOR HEATING R/							•		
GETRUMENT PR			-mg.						 	 ]	
AIDIN	Y-AXIS	mg. inch	0								
	<i>t-</i> λ	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION					 			
		SCALE.	SUPPI					·			
(.		• C inch	0		 						
	XIS	100 it						 	 		
	X-AXIS	TEMP. SCALE 100	TIME SCALE (ALT.)								
		TEMP. S	TIME S								
	00										
•	42-11-H6	:-с <sub>6</sub> н <sub>4</sub> -с	D							 	
	SAMPLE: DA-42-11-H600	N So2 N=HC-C <sub>6</sub> H <sub>4</sub> -CH	9.9 mg.		 				 	 	
	SAMPL	- CH	SIZE 9.9								

· APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE<sup>\*</sup>, °C

Appendix No. 44

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DDUCT& DIVISION	DA	OPERATOR JVC HEATING RATE 15 °C ATM. nitrogen min.	TIME CONSTANT 2 sec.						如何ND 950TGA	APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES
ULUND INSTRUMENT PRODUCTS DIVISION	Y-AXIS	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION 0 mg.							°c
÷	X-AXIS	TEMP. SCALE 100 °C inch SHIFT 0 inch	TIME SCALE (ALT.) 0							TEMPERATURE*
•	SAMPLE: DA-42-6	CH2 N SO2 N=HC-C <sub>6</sub> H <sub>4</sub> -CH green polymer	SIZE 10 mg.							

INSTRUMENT PRODUCTS DIVISION

	DATE 8-17-65	°C min.	sec.	 						OTGA 950TGA	COUPLES
	DATE	JVC TE <u>15</u> air	ANT 2								EL-ALUMEL THERMO
co (wc)	RUN NO.	OPERATOR HEATING RATE ATM.	TIME CONSTANT_								<ul> <li>APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES</li> </ul>
TINN CLARTER PRODUCTS DIVISION			0 mg.							<u> </u>	PPLY CORRECTION FOR
	Y-AXIS	SCALE 2 mg. inch (SCALE SETTING X 2)	SSION								
÷		SCALE (SCALE SET	SUPPRESSION								rure*, °c
Ċ;		°C inch	0								TEMPERATURE*
	X-AXIS	NLE 100	E (ALT.)								
		TEMP. SCALE SHIFT0	TIME SCALE (ALT.)_								
	· · · ·										
· · ·	DA-42-6	SO2^N=llC-C_6ll_4-CHn	mg.								
-	SAMPLE: 1	So2 <sup>CH2</sup> So2 <sup>D</sup> 1	SIZE 10	<b>.</b>			1				
	SAN		sızı								

0-65	o uiu viu	sec.									pendix	
DATE7-20-65	JVC E 15 nitrogen	IT 2										
RUN NO.	ATOR	CONSTH										
RUI	OPER HEATI ATM											
		mg.										
S	ch.	0										
Y-AXIS	m in NG X 2)	SION		ļ			 					
	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION							/			
	SCA (scal	SUP										
	°C inch											
	ch l	.) 0										
X-AXIS	щ	TIME SCALE (ALT.)	/									
	TEMP. SCAI SHIFT0	SCALI										
	TEMP SHIF1	TIME			-	<u></u>						
86	-cn}n		1 ¥									
DA-29-286	3-C6H4 Lyner	mg.		1			<u> </u>					
	$f_{\rm N}=({\rm CH}_2)_4$ -N=HC-C $_6$ H $_4$ -CH $_{\rm I}$	10										
SAMPLE:	=(CH <sub>2</sub> )	SIZE										<u> </u>

WEIGHT, mg.

APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE\*, °C

65	min.	sec.			1						[	¥5
DATE 7-20-65	0 5	Se				 			 			950TGA
DATE	JVC E 15 air	2	 			 						
	ATE	LAN										
0.	ATOR ING R	CONS								· · ·		
RUN NO.	OPERATOR HEATING RATE ATM.	TIME CONSTANT										
		- mg.										
		0						· .				
IS	mg. 2)					 						)
Y-AXIS	2 n in NG X 2)	SION										
	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION										
	SCALE_	SUPF										1
	Le				7					1		
	o °C inch	0	 									
X-AXIS	100 inch	TIME SCALE (ALT.)	 	$\left  \right $		 						
X-A	TEMP. SCALE_ SHIFT0	ALE (I	 	/								
	IP. S(	E SC/										
	TEMP.	TIM										
286	-cн}n	1										
DA-29-286	-c <sub>6</sub> H <sub>4</sub>	-mg.	 					· · ·				
	<b>€</b> N-(CH <sub>2</sub> )4-N=HC-C <sub>6</sub> H4-CH <sup>‡</sup> n orange polymer					 						
SAMPLE:	CH2)4 oran	SIZE 10	 			 						
SAN	•u+ (	SIZI										

-13-65	min <sup>o</sup> C	sec.					- 		·	
DATE 7-13-65	JVC TE 15 nftrogen	ANT 2						 		OF OT CA
RUN NO.	OPERATOR HEATING RATE ATM	CONST	 							
		- Bu								
S	n <del>-</del>	0	 							
Y-AXIS	MG X 2)	SION								
	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION		-						
	SC /	SUF					 /			,
	•C inch	0								
IS	100 inch	.T.)	 					 		
X-AXIS	ALE 0	TIME SCALE (ALT.)				/ 	 	 		
	TEMP. SCALE SHIFT 0	IE SCA	 						 	
	TEN	TIM	4							
	n≢n									
DA-29-269	c <sub>6</sub> H4-C er									
	<b>€</b> N-(CH <sub>2</sub> )4-N=HC-C <sub>6</sub> H4-CH <sup>}/</sup> <sub>h</sub> white polymer	. mg.					 	 		
SAMPLE:	(CH <sub>2</sub> )4 white	SIZE 10								
SAI	fn-	SIZ			1. S. 1.					

· APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE<sup>\*</sup>, °C

IPUN INSTRUMENT PRODUCTS DIVISION

*	0. DATE 7-26-65	OPERATOR JVC JVC HEATING RATE 15 °C min.	TIME CONSTANT 2 sec.							OTCA	• APPLY CORRECTION FOR \$20-UNEARITY OF CHROMEL-ALUMEL THEMOCOUPLES
ODUCTS DIVISI	RUN NO.	OPERATOR HEATING R/						•			R 400-LINEARITY
C	Y-AXIS	SCALE 2 mg. inch (scale setting x 2)	SUPPRESSION 0 mg.							<u>}</u>	ູ ວຸ
	X-AXIS	TEMP. SCALE 100 °C inch SHIFT 0 inch	CALE (A								TEMPERATURE*
۰.	SAMPLE: DA-29-269	=N- C	SIZE 10 mg.								

WEIGHT, mg.

Appendix No. 50

	-19-65		min.	sec.									SOTGA
C	DATE 8-19-65	JVC	E 15 nitrogen	Т 2								 	0100 950TGA
•		DR	RATE nit	NSTAN				 					
IS DIVISION	RUN NO.	DPERATOR	HEATING RATE ATM. ni	TIME CONSTANT							1	 	
QUPUND INSTRUMENT PRODUCTS DIVISION	~		A. T	TI TI	4				•	 •			
			1	0									
	Y-AXIS	mg.	inch (SCALE <b>S</b> ETTING X 2)	NOI			· · · · · · · · · · · · · · · · · · ·						
-		LE 2	LE SETTIN	SUPPRESSION									
		SCA	(SCA	SUF								 	
		°C	inch	0						 		 	
	X-AXIS	100		ALT.)			$\square$	 				 	
	A-X	TEMP. SCALE	0	TIME SCALE (ALT.)		$\left  \right $		 					
		TEMP.	SHIFT 0	TIME S						 		 	
			c.					 		······			· · · · · · · · · · · · · · · · · · ·
•	-10	.нсн <del>4</del>	ymer										
₽-	DA-42.	N=HC-C	orange polymer	-mg.									
	SAMPLE: DA-42-10	<b>fn- (сн. ) , -</b> n=нс-с ,н, -сн <del>1</del>	ora	SIZE 10									
	SA	-n∔		SIZ									

· APPLY CORRECTION FOR NON-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE<sup>\*</sup>, °C

MEIGHT; mg.

-65	ပ	min.	sec.		2									GA
DATE 8-19-65	JVC 15		2 5	1										OTCA
DA			TANT	· · · · · ·								: •		
NO.	OPERATOR		TIME CONSTANT											
RUN NO.	OPEI	ATM.		• • • •					1					
			-mg.							i i	•••			
	   . ,	_	0						на с се на на с с се на на с		1 2 		$\mathcal{I}$	
Y-AXIS	2 2 2 2	(SCALE SETTING X 2)	ION				· · ·						:	
	Ц Ш	E SETTIN	SUPPRESSION				: . : .							
	SCALE	(SCALI	SUPI											
		5					:				-	:	 	
	יי 100	- inch	0 (.						•	-	· ·			
X-AXIS	1 1		E (ALT.)						: : *					
	TEMP. SCALE	0	TIME SCALE (AI						-					
	TEMI	SHIFT_	TIME	1				1						
	đ	1											· .	n a g
0	B₄-CB∔	ушег				· · · · · · · · · · · · · · · · · · ·								
DA-42-;	رم #10-0	orange polymer	-mg.									•		
SAMPLE: DA-42-10	ŧn- (ch₂) 6-n=HC-C <sub>6</sub> H4-CH <sup>}_</sup> n	oranį	1			E of								
SAM	€n- (ci		SIZE											

WEIGHT, mg.

Appendix No. 52

										Apj	pendix	No. 5
DATE 7-13-65	air.	sec.							 			950TGA
ATE_7	TE 15	08eii						 				6
		CONSTANT	iu									
NO.	OPERATOR HEATING RATE	CONS					• . • .					
RUN NO.	OPER HEAT											
		ug.										
	ł	0										
Y-AXIS	2 mg. inch 6 X 2)	NO										
	SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION							1			
	SCAL (scale	SUPP				·						
	100 °C inch	0 (			•							
X-AXIS		TIME SCALE (ALT.)										
×	TEMP. SCALE SHIFT 0	SCALE			7							
	TEMP. Shift	TIME		1								
1							<u> </u>					
68	-cH <b>∮</b> n						· · · ·					
DA-29-268	C-C <sub>6</sub> H <sub>4</sub> ymer	Bu	-								· · · · · · · · · · · · · · · · · · ·	
	ŧN-(CH <sub>2</sub> ) <sub>6</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -CH}n white polymer	10						<u> </u>		· · · · · · · · · · · · · · · · · · ·		
SAMPLE:	N- (CH <sub>2</sub> wh f	SIZE										

.

WEIGHT, mg.

1:

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Appendix No. 53

26-65		°.	un.	_ sec						a A.		OTGA	
DATE 7-26-65	JVC	15	air	3								950TGA	
		ATE	đ	TIME CONSTANT		1						<b>Y</b>	
NO.	<b>OPERATOR</b>	HEATING RATE		CONS									
RUN NO.	OPEI	HEAT	ATM.							1		•	
				mg.							• • • •		
		-		0									
Y-AXIS		inch.	(SCALE SETTING X 2)	NO								7	
		Ы	SETTIN	SUPPRESSION			<u> </u>						
	1	SCALE	(SCALE	SUPP									
		inch <sup>o</sup>		-			/						
			_ inch	.) 0									
X-AXIS				TIME SCALE (ALT.)									
		TEMP. SCALE		SCALI									
		TEMP	SHIFT_	TIME									
-268		[4-CH <sup>]</sup> 1	юГ										
DA-29-268		HC-C6H	white polymer	-mg.									
		2)6 <sup>-N=</sup>	white	10				<u> </u>					
SAMPLE:	I	$\frac{1}{6}$ N-(CH <sub>2</sub> ) <sub>6</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -CH <sup>3</sup> <sub>n</sub>		SIZE									

.

	21-65		sec.	-	:								OTGA
$\bigcirc$	DATE 7-21	JVC 15 N <sub>2</sub> , (3)	2			`)		:			1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 - 1 -		Determine of the second
-		ATE J	TANT							4			A
NOIS	NO.	OPERATOR HEATING RATE ATM. (1) N <sub>2</sub> , (2)	TIME CONSTANT										
LE REMOURT E LU CAE J RENT PROBACTS DIVI 1. OLLIMAT	RUN NO.	OPEI HEAT ATM.											
			mg.						•				
	0	d.e	0			 . : .							
9	Y-AXIS	mg incl VG X 2)	NOI			0							
		SCALE 2 mg. inch (SCALE SETTING X 2)	SUPPRESSION										
$(\cdot)$		SCA	SUP										
		°C inch											
	10	200 2 - inch	r.) 0					1					
	X-AXIS		TIME SCALE (ALT.)	-			n an						
		TEMP. SCALE. SHIFT 0	: SCAL										
		TEMP.	TIME										
					1								
3	-154	-ca <sub>1</sub>											
	DA-29-154	IC-C <sub>6</sub> H	6 1 1										
	SAMPLE:	<b>ŧn-c<sub>6</sub>n</b> 4-n <del>-n</del> c-c <sub>6</sub> n4-cn <sup>‡</sup> n	10										
	SAM	- - - - - - - - - - - - - - - - - - -	SIZE										

.

WEIGHT, mg.

Appendix No. 55

· APPLY CORRECTION FOR MOM-LIMEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE\*.°C

	SAMPLE: DA-29-154 ŧN-C <sub>6</sub> H <sub>4</sub> -N=HC-C <sub>6</sub> H <sub>4</sub> -CH <sup>‡</sup> n SIZE <u>9.8</u> g.	X-AXIS TEMP. SCALE 100 °C inch SHIFT 0 inch TIME SCALE (ALT.) 0	Y-AXIS SCALE 2 mg. inch (scale setting x 2) SUPPRESSION 0 mg.	RUN NO. DATE 7-14-65 OPERATOR JVC OPERATOR JVC OPERATOR JVC OPERATOR ATM air min. ATM. air min.
	-			
950TGA				
1				entrine 950TGA

· APPLY CORRECTION FOR ADM-LINEARITY OF CHROMEL-ALUMEL THERMOCOUPLES

TEMPERATURE\*, °C