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THE SYNTHESIS AND ISOTHERMAL AGING BEHAVIOR OF OXYGEN-FREE  
ACETYLENE TERMINATED QUINOXALINES

Polymer Branch  
Nonmetallic Materials Division

May 1981

Final Report for Period January 1979 to December 1980

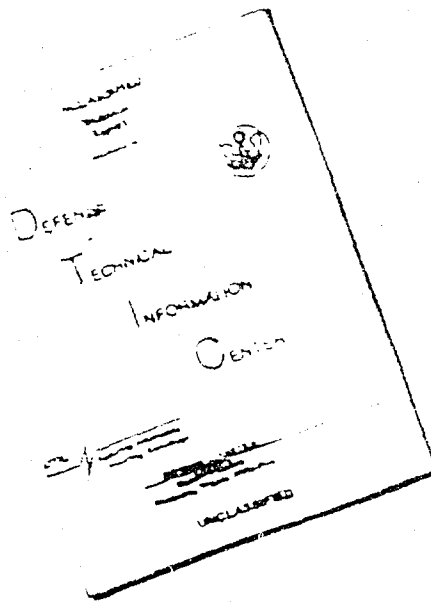
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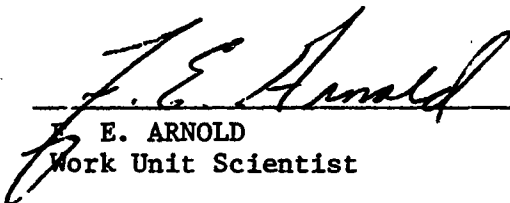
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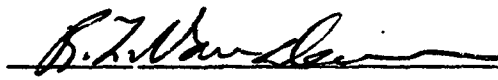
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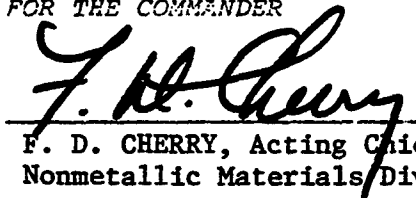
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E. ARNOLD  
Work Unit Scientist

  
R. L. VAN DEUSEN, CHIEF  
Polymer Branch  
Nonmetallic Materials Division

FOR THE COMMANDER

  
F. D. CHERRY, Acting Chief  
Nonmetallic Materials Division

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Acetylene-terminated resins prepared to date have contained phenyl ether groups, limiting their thermooxidative stability to 315°C, as determined by isothermal aging in air. In order to determine whether the thermooxidative stability of the acetylene cure site exceeds 315°C, a series of three acetylene-terminated quinoxaline isomer mixtures containing only aromatic and quinoxaline rings, known to have 371°C stability, were prepared and their isothermal aging behavior in air was studied at 315°C, 343°C, and 371°C. The thermooxidative stability of one system was comparable with that of an analogous acetylene		

terminated quinoxaline which contained phenyl ether linkages. The other two systems, which both contained ethynyl groups directly bonded to a quinoxaline ring, showed poorer thermooxidative stability than a phenyl ether containing system.

FOREWORD

This in-house report was prepared by the Polymer Branch, Nonmetallic Materials Division. This work was initiated under Project No. 2419, "Nonmetallic and Composite Materials", Task No. 241904, Work Unit Directive 24190415, "Structural Resins". It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFWAL/ML Work Unit Scientist. This report describes work conducted from January 1979 to December 1980.

The work described in this report was conducted in the Polymer Branch Laboratory by Dr. F. L. Hedberg and Dr. F. E. Arnold of the Materials Laboratory. The manuscript was released by the authors in June 1980 for publication as a Technical Report.

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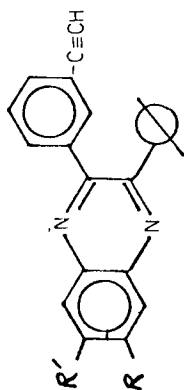


SECTION I  
INTRODUCTION

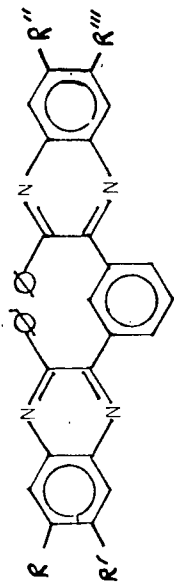
A variety of aromatic heterocyclic oligomers with terminal acetylene units has been reported in recent years (References 1 through 4). These systems have shown potential for thermoset curing to thermooxidatively stable composites and adhesives. The structure of the bonding obtained from the thermosetting reaction between acetylene groups has not yet been definitively ascertained, although this problem is being addressed (References 4, 5), and current evidence suggests a conjugated polyene. We were interested in determining the thermooxidative stability of this linkage, in order to learn the limiting use temperature of acetylene terminated thermosetting resins. Of particular interest was the possibility that appropriately designed resins might have 371°C utility. Most of the resin systems of this type prepared to date, such as the isomeric mixture of structures IIID - IIIE - IIIF, (Reference 1) have contained phenyl ether linkages, which have been found to be limited to 315°C by isothermal aging studies in air (Reference 6). Those polymer systems which showed very little weight loss after 160 hours of aging at 371°C, the polyphenylquinoxaline (PPQ) and polybenzimidazobenzophenanthroline (BBB) systems, exhibited greater than 80% weight loss after 160 hours at 371°C when a phenyl ether unit was contained in their backbone (Reference 6).

Our goal in this work was to prepare and cure acetylene-terminated quinoxalines containing only phenyl groups and quinoxaline units, and to determine the thermooxidative stability of the cured acetylene sites of these systems by isothermal aging measurements in air at 315°C, 343°C and 371°C. The three specific systems which were prepared and examined were the isomeric mixture of 6-ethynyl-2-(3-ethynylphenyl)-3-phenylquinoxaline (IA) and 6-ethynyl-3-(3-ethynylphenyl)-2-phenyl-quinoxaline (IB); the isomeric mixture of 2,2'-(1,3-phenylene) bis[6-ethynyl-3-phenylquinoxaline] (IIA), 2,2'-(1,3-phenylene)bis[7-ethynyl-3-phenylquinoxaline] (IIB) and 2,2'-(1,3-phenylene)-6,7'-diethynyl-bis[3-phenylquinoxaline] (IIC); and the

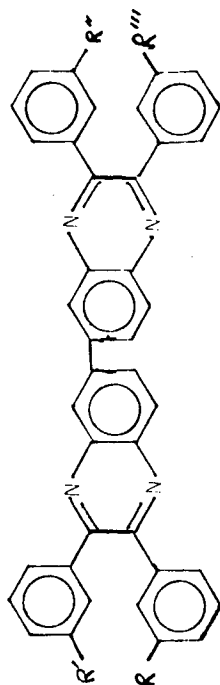
isomeric mixture of 2,2'-bis(3-ethynylphenyl)-3,3'-diphenyl-6,6'-biquinoxaline (IIIA), 3,3'-bis(3-ethynylphenyl)-2,2'-diphenyl-6,6'-biquinoxaline (IIIB), and 2,3'-bis(3-ethynylphenyl)-2',3'-diphenyl-6,6'-biquinoxaline (IIIC). For the purpose of comparison with an oxygen-containing quinoxaline, the previously reported (Reference 1) 2,2'-bis(4-[3-ethynylphenoxy]phenyl)-3,3'-diphenyl-6,6'-biquinoxaline (IIID), 3,3'-bis(4-[3-ethynylphenoxy]phenyl)-2,2'-diphenyl-6,6'-biquinoxaline (IIIE), and 2,3'-bis(4-[3-ethynylphenoxy]phenyl)-2',3'-diphenyl-6,6'-biquinoxaline (IIIF) isomer mixture was also run at 315°C and 343°C.






- IA. R = C≡CH, R' = H  
 IB. R = H, R' = C ≡ CH



- IIA. R = R'' = C ≡ CH, R' = R''' = H  
 IIB. R = R'' = H, R' = R''' = C ≡ CH  
 IIC. R = R''' = C ≡ CH, R' = R'' = H



- IIIA. R = R''' = C ≡ CH, R' = R'' = H  
 IIIB. R = R''' = H, R' = R'' = C ≡ CH  
 IIIC. R = R'' = C≡CH, R' = R''' = H  
 IIID. R = R''' = 0--C≡CH, R' = R'' = H  
 IIIE. R = R''' = H, R' = R'' = 0--C ≡ CH  
 IIIF. R = R'' = 0--C ≡ CH, R' = R''' = H

SECTION II  
EXPERIMENTAL

In the preparative procedures, care was taken to avoid any purification steps involving precipitation or crystallization. Although precipitation has been routinely utilized for purification of larger oligomers of acetylene terminated quinoxalines, we have found that in the case of IA-IB, there is a marked difference in solubility behavior of the two isomers (Reference 7).

The general synthetic procedure utilized for each isomeric mixture IA-IB, IIA-IIB-IIC and IIIA-IIIB-IIIC derived from a one-hour acetic-acid-catalyzed, reflux in tetrahydrofuran of stoichiometric amounts, respectively, of 4-iodo-o-phenylenediamine (Reference 8) and 3-bromobenzil (Reference 6); 4-iodo-o-phenylenediamine (Reference 8) and 1,3-bis(phenylglyoxaloyl)benzene (Reference 9); and 3-bromobenzil (Reference 6) and 3,3'-diaminobenzidine. The crude isomeric mixtures of halogenated quinoxalines obtained after removal of solvent were converted in two steps, following the procedure developed by Sabourin (Reference 10), to the acetylene-terminated quinoxalines which were purified by chromatography on silica gel. Overall yields, T<sub>g</sub> values, onset and maximum of cure exotherm (T<sub>onset</sub> and T<sub>max</sub>) determined by DSC at 10°C/min under nitrogen, elemental analyses, H<sup>1</sup> NMR and C<sup>13</sup> NMR are as follows:

IA-IB, 55%; T<sub>g</sub> = 20°C (after cycling through an initial T<sub>m</sub> at 129°C); T<sub>onset</sub> = 120°C; T<sub>max</sub> = 231°C; anal. calcd, for C<sub>24</sub>H<sub>14</sub>N<sub>2</sub>: C, 87.27; H, 4.24; N, 8.48. found: C, 87.43, 87.27; H, 3.84, 3.98; N, 8.41, 8.50; H<sup>1</sup> NMR spectrum (in CDCl<sub>3</sub>, δ in ppm from TMS): 3.05 (singlet), 3.28 (singlet), 7.1-7.6 (multiplet), 7.7-7.9 (multiplet), 8.0-8.2 (doublet), 8.3 (singlet); C<sup>13</sup> NMR Spectrum (in CDCl<sub>3</sub>, δ in ppm from TMS): 153.844, 153.546, 152.897, 152.603, 140.946, 140.798, 140.698, 140.500, 138.863, 138.180, 133.250, 132.944, 132.811, 132.414, 130.083, 129.636, 129.136, 129.041, 128.248, 127.950, 123.882, 122.390, 77.663, 79.196, 82.943, 82.710.

IIA-IIB-IIC, 54%,  $T_g = 96^\circ\text{C}$ ;  $T_{\text{onset}} = 120^\circ\text{C}$ ;  $T_{\text{max}} = 120^\circ\text{C}$ ; anal. calcd. for  $\text{C}_{38}\text{H}_{22}\text{N}_4$ : C, 85.39; H, 4.12; N, 10.49; found: C, 85.43, 85.64; H, 4.10, 3.95; N, 10.57;  $^1\text{H}$  NMR Spectrum (in  $\text{CDCl}_3$ ,  $\delta$  in ppm from TMS): 3.3 (singlet), 7.1-7.6 (multiplet), 7.8 (multiplet), 7.9 (multiplet), 8.1 (multiplet), 8.3 (multiplet);  $^{13}\text{C}$  NMR Spectrum (in  $\text{CDCl}_3$ ,  $\delta$  in ppm from TMS): 153.915, 153.588, 153.266, 152.976, 141.137, 140.847, 139.256, 138.958, 133.174, 132.684, 131.666, 130.281, 129.930, 129.285, 128.926, 128.148, 127.690, 123.978, 123.878, 83.046, 79.552.

IIIA-IIIB-IIIC, 57%;  $T_g = 111^\circ\text{C}$  (after cycling through an initial  $T_m$  at  $219^\circ\text{C}$ );  $T_{\text{onset}} = 200^\circ\text{C}$ ;  $T_{\text{max}} = 250^\circ\text{C}$ ; anal. calcd. for  $\text{C}_{44}\text{H}_{26}\text{N}_4$ : C, 86.56; H, 4.26; N, 9.18; found: C, 86.39, 86.59; H, 4.12, 4.17; N, 9.09, 9.19;  $^1\text{H}$  NMR Spectrum (in  $\text{CDCl}_3$ ,  $\delta$  in ppm from TMS): 3.1 (singlet), 7.2-7.6 (multiplet), 7.8 (multiplet), 8.3 (singlet), 8.6 (singlet);  $^{13}\text{C}$  NMR spectrum (in  $\text{CDCl}_3$ ,  $\delta$  in ppm from TMS): 153.7, 153.3, 152.76, 152.35, 141.3, 141.1, 141.0, 140.8, 140.6, 139.0, 138.3, 133.2, 132.3, 130.6, 130.1, 129.6, 128.9, 128.2, 127.9, 127.2, 122.3, 82.98, 77.63.

A sample of IIID-IIIE-IIID was prepared as previously reported (Reference 1).

For isothermal aging studies, the samples were cured for six hours at  $280^\circ\text{C}$  under nitrogen, in preparation for the  $315^\circ\text{C}$  runs, and cured for an additional two hours at either  $343^\circ\text{C}$  for the  $343^\circ\text{C}$  run or at  $371^\circ\text{C}$  in preparation for the  $371^\circ\text{C}$  runs. None of the cured samples showed any  $T_g$  upon DSC analysis. Isothermal weight loss measurements were carried out under an air flow rate of 40cc/min with a SRL 633-1 instrument.

### SECTION III

#### RESULTS AND DISCUSSION

The synthesis of the three new acetylene terminated quinoxalines IA-IB, IIA-IIB-IIC and IIIA-IIIB-IIIC was straightforward. The T<sub>g</sub> value obtained for IA-IB, however, was surprisingly low for such a rigid, symmetrical system. A thorough thermoanalytical examination of this system and its two individual isomers has been carried out and reported elsewhere (Reference 7).

For the isothermal aging run at 371°C, the composite results are shown in Figure 1. An interesting criterion of comparison of the samples is the time required to reach 90% weight loss. This choice was made because the rate of weight loss in all three samples diminished substantially shortly after this point, possibly due to formation of a semistable graphitic char. When the reciprocal of this time is correlated with the percentage of terminal acetylene component in the respective quinoxaline structures, the following results are obtained:

IA-IB:	$3.3 \times 10^{-2} \text{hrs}^{-1}$	, 15.2%
IIA-IIB-IIC:	$2.0 \times 10^{-2} \text{hrs}^{-1}$	, 9.4%
IIIA-IIIB-IIIC:	$1.2 \times 10^{-2} \text{hrs}^{-1}$	, 8.2%

From these results, it would appear the rate of weight loss is directly related to the percentage of acetylene component.

For the isothermal aging runs at 343°C and 315°C, the composite results are shown in Figures 2 and 3. In both cases, a sample of IIID-IIIE-IIIF was included to determine the effect of a phenyl ether moiety. It is apparent that the thermooxidative stabilities of IIID-IIIE-IIIF and IIIA-IIIB-IIIC are very similar to one another at both of these temperatures. It is also apparent, however, that the thermooxidative stability of IA-IB is significantly poorer at both temperatures, and

that the poorest thermooxidative stability at both temperatures is shown by IIA-IIB-IIC.

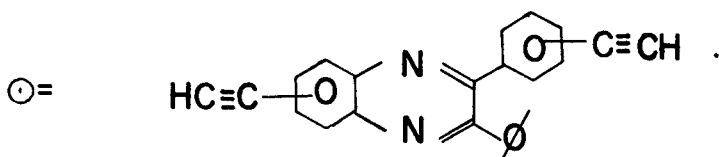
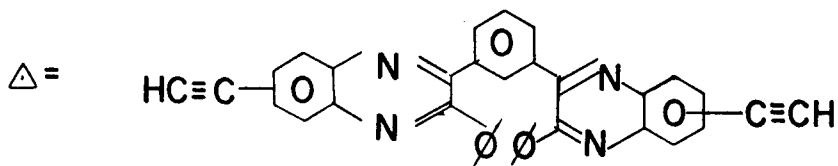
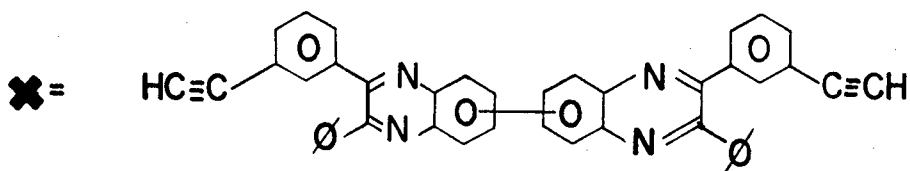
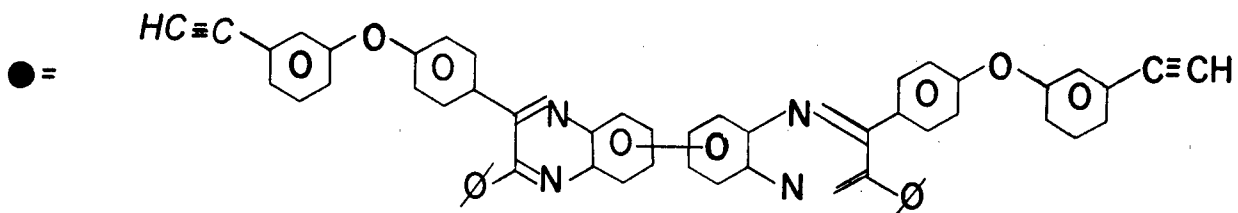
On the basis of the above results, it can be concluded that the cured acetylene site obtained from phenylethynyl groups is of approximately the same order of thermooxidative stability as a phenyl ether site, and is suitable for short-term usage at 600°F. The stability of an acetylene cure site, however, is dependent upon the nature of the substituent to which the acetylene group is bonded. In the case of IA-IB-IC, one of the acetylene groups is bonded directly to a quinoxaline ring system, and in the case of IIA-IIB-IIC, both acetylene groups are bonded directly to a quinoxaline ring. For these compounds, the acetylene cure site exhibits less stability than a phenyl ether site. Two possibilities can be considered to explain the direct correlation of decreasing thermooxidative stability with increasing ethynylquinoxaline content: either the cure site itself is destabilized toward oxidative attack by electronic interaction with the quinoxaline ring, or the mechanism of cure is different than that obtained from a phenylethynyl group. The greater stability of IIA-IIB-IIC versus IA-IB at 371°C can be explained in either case by a change in relative rates of degradation for the cure site at that temperature.

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9. A sample of this material was provided by Dr. C. S. Marvel of the University of Arizona, to whom we acknowledge our gratitude.
10. E. J. Sabourin, ACS Petroleum Chem. Prep., 24 (1), 233 (1979).



KEY TO FIGURES 1, 2 AND 3



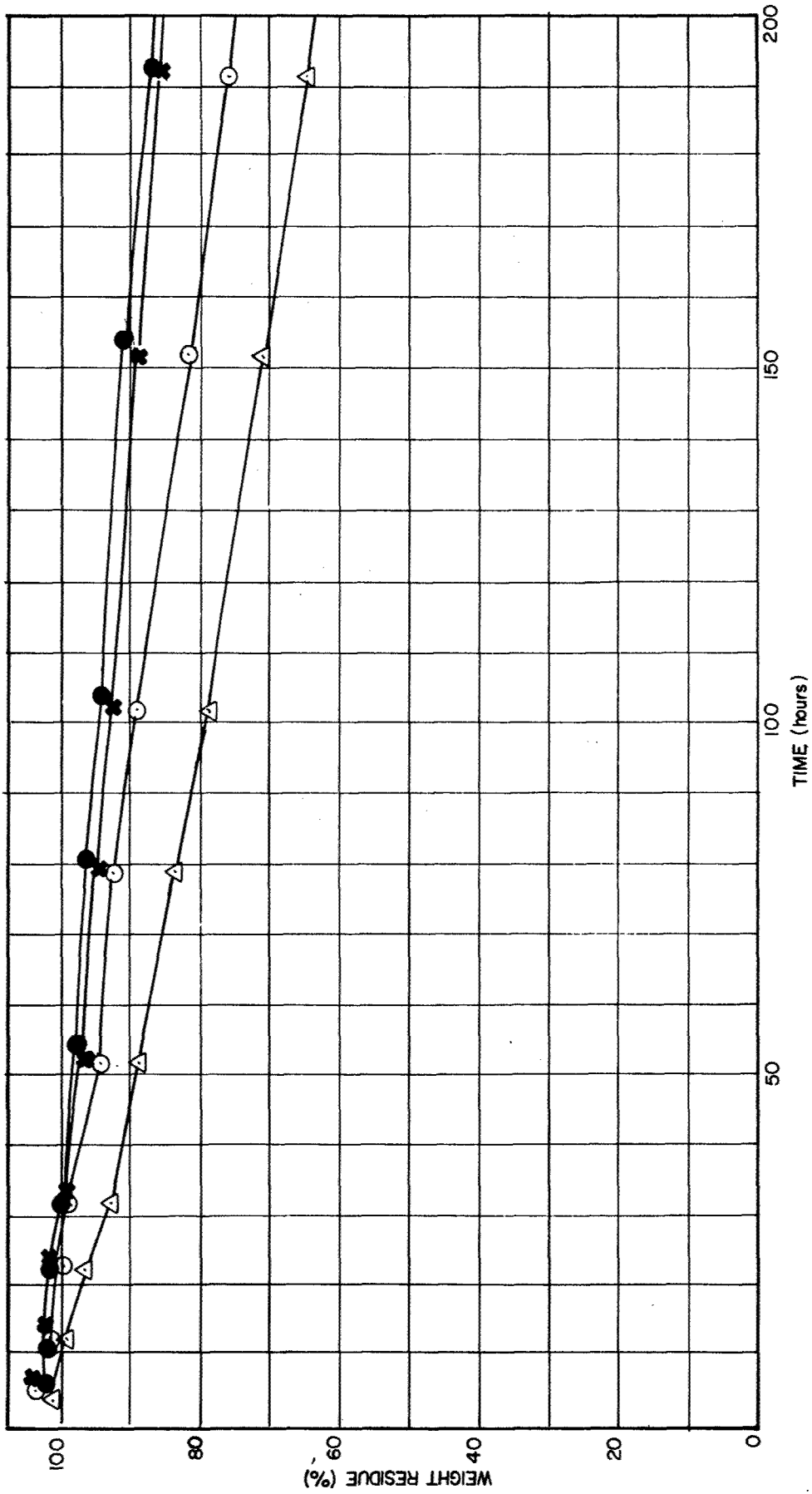


Figure 1. Composite Plot from 315°C Isothermal Aging Runs

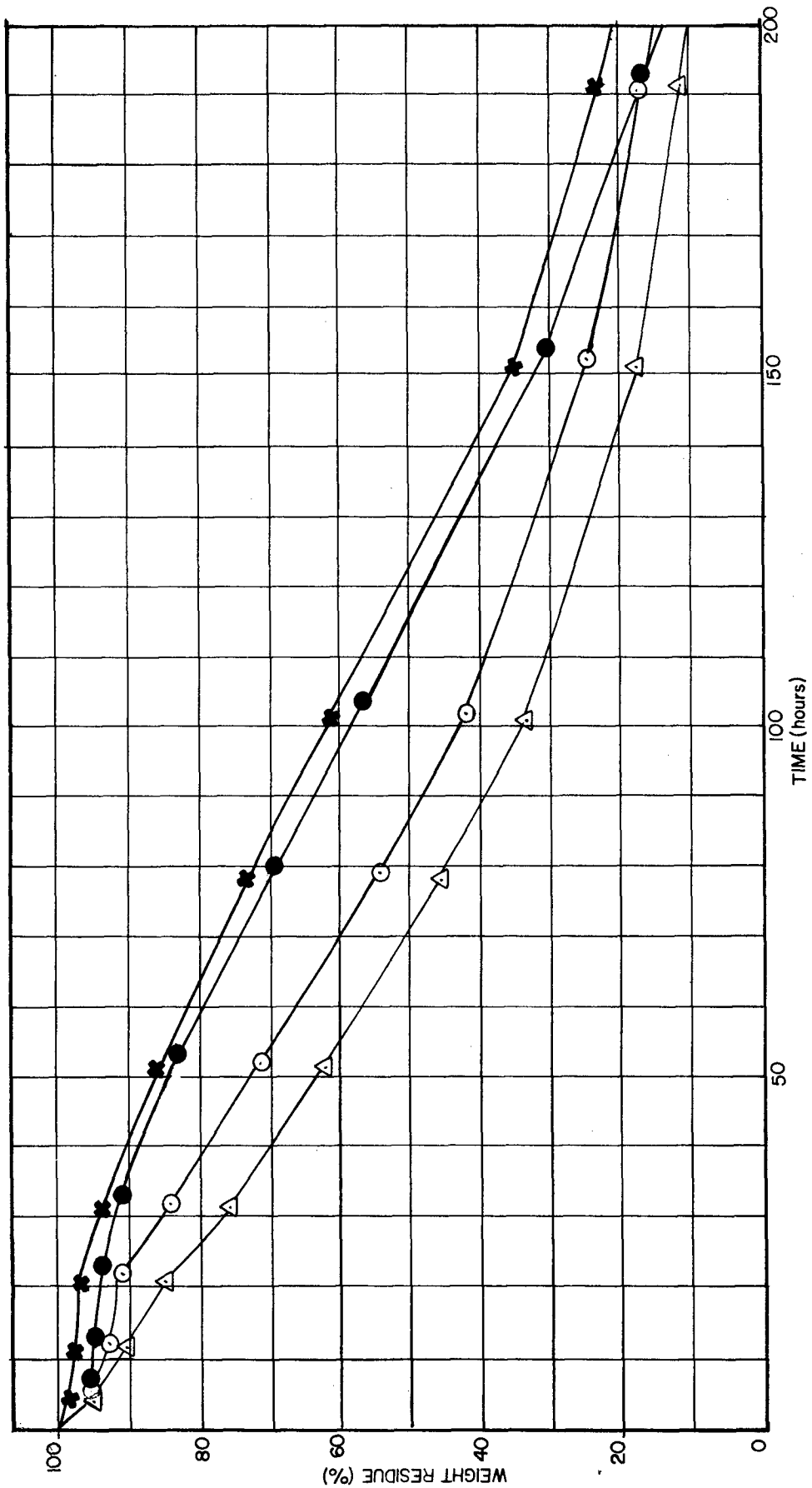


Figure 2. Composite Plot from 343°C Isothermal Aging Runs

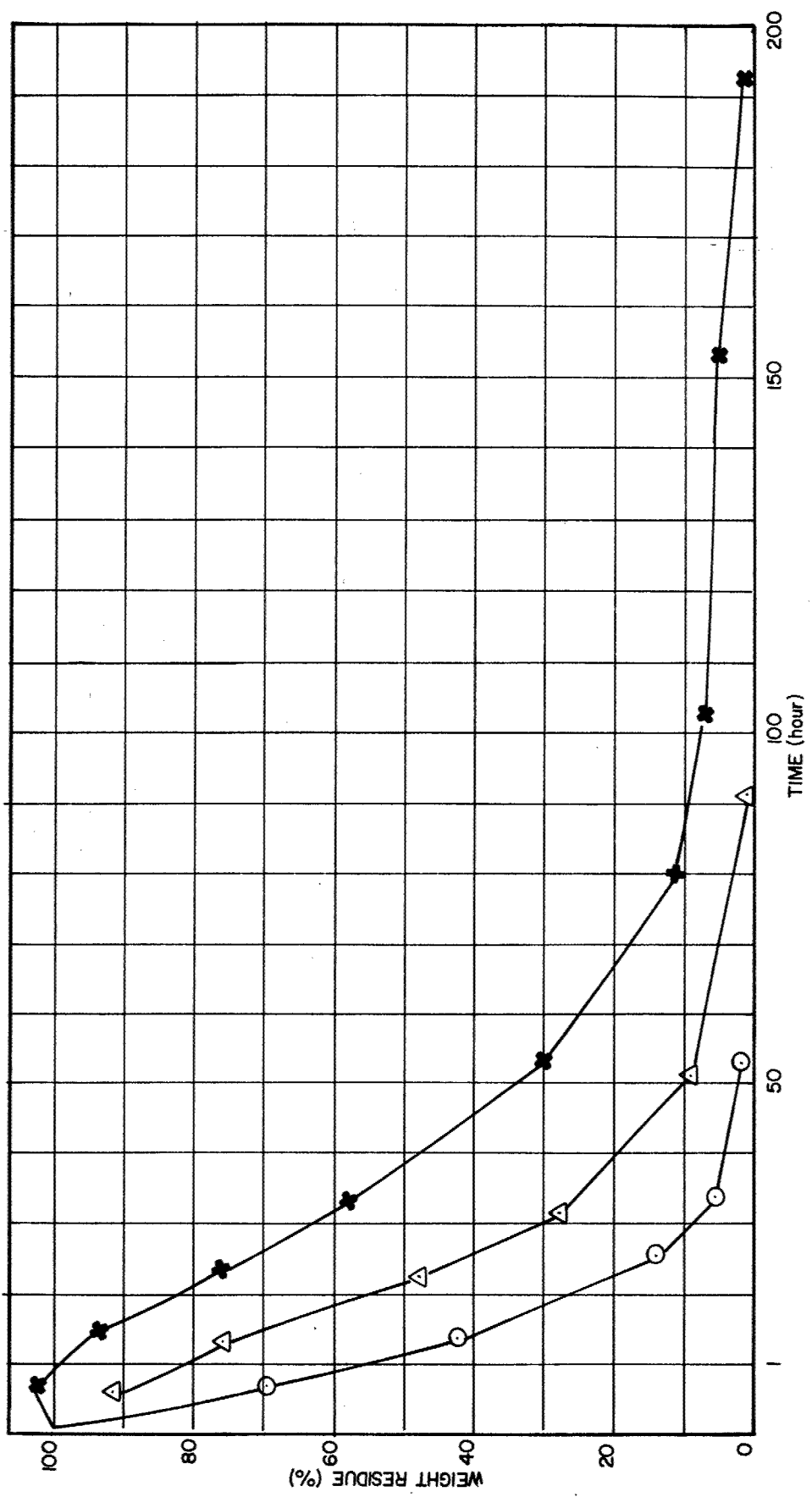


Figure 3. Composite Plot from 371°C Isothermal Aging Runs