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# Thermal Degradation of Certain Polymers under Oxidative Conditions

by

D. B. V. Parker

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ROYAL AIRCRAFT ESTABLISHMENT

Thermal degradation of certain polymers under  
oxidative conditions

by

D. B. V. Parker

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SUMMARY

The rate of loss of weight of a powdered polymer when heated in air was taken as an inverse measure of thermal stability under oxidative conditions.

A series of hydrocarbon polymers containing benzene nuclei formed from a homologous series of monomers has been prepared by Wurtz and Friedel-Crafts reactions, and results indicate that thermal stability diminishes as the series is ascended.

A number of other polymers and plastic materials has been examined using the same technique.

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## 1 Introduction

The thermosetting plastics at present in use in the aircraft industry have an upper temperature limitation which is too low for future requirements. The reasons for failure are twofold:

(i) Physical failure, i.e. the material loses strength or stiffness at elevated temperatures.

(ii) Chemical failure, i.e. fission of chemical bonds, with or without oxidation.

The first reason may be associated with the second or be independent of it, but it is obvious that a material cannot for long avoid physical failure if volatile matter is being lost as a result of chemical failure.

The presence of oxygen will accelerate the rate of chemical degradation in almost every case. It may be practicable to protect small plastic components from atmospheric oxygen, but this is hardly possible with structural plastics exposed to the combined effects of kinetic heating and rapid flow of air. In certain cases, for example where the material is porous, the resin may present a very large area per unit weight to the action of air (see paragraph 4.31).

The work to be described was begun to obtain some insight into the effect of molecular structure on the thermal stability of polymers. The polymers were heated in air under identical conditions and their rates of loss of weight recorded and compared. The main series of experiments (Series I) was on polymeric hydrocarbons, but in order to provide a basis for comparison the behaviour of a number of other polymers was also studied (Series II).

Similar work was performed by Sieffert and Schoenborn<sup>1</sup> using commercial plastic laminates, strips of which were heated in air and the weight loss noted periodically. However no work was done using resins alone.

## 2 Conditions of experiment

In order that the experiments should be comparable the physical size of polymer particles was standardised so that the ratio of surface area to volume might be the same in each case. The materials were ground and sieved between 40 and 120 mesh sieves, so that:

Maximum particle diameter } 0.0158 in. and  
Minimum particle diameter } 0.0047 in.

(except in the case of Polymer E, described in paragraph 3.1).

All polymers were heated, after sieving, for 24 hours at about 140°C.

The sieved and dried polymeric materials were spread thinly on a tared Petri-dish, weighed, and heated in an air oven at 300°C. Temperatures were maintained within  $\pm 3^\circ\text{C}$  (the thermometer bulb being placed as near as possible to the specimen) and the ventilation apertures on the oven were kept open. Periodically the samples were withdrawn from the oven, cooled in a desiccator and weighed before being replaced in the oven. The rate of loss of weight was thus determined.

The temperature used (300°C) was chosen to provide a reasonable rate of degradation without running the risk of ignition (see however, para. 4.31).

### 3 Series I - Hydrocarbon polymers

#### 3.1 Nature of the polymers examined

It may be expected that polymers containing benzene nuclei will be heat resistant since the resonance of such nuclei may prevent wide fluctuations of thermal energy. To produce a polymer, the benzene nuclei must be linked together, and the linkages will probably be points of attack or of scission.

It was therefore decided to prepare a series of polymers in which benzene rings are linked together by chains of methylene groups of varying length.

Polymer A - polyphenylene (no -CH<sub>2</sub>-groups between benzene nuclei). This material was prepared by means of a Wurtz reaction between sodium-potassium alloy and *p*-dichlorobenzene.

Polymer B - polymethylenephenylene (one -CH<sub>2</sub>-group between benzene nuclei): often referred to as "polybenzyl" in the literature<sup>4,11</sup>. This was prepared by the polycondensation of benzyl chloride by a Friedel-Crafts reaction.

Polymer C - polyethylenephenylene (-CH<sub>2</sub>-CH<sub>2</sub>- group between benzene nuclei): This was prepared by a Friedel-Crafts reaction.

Polymer D - polytrimethylenephenylene (-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>- group between benzene nuclei). This was prepared by a Friedel-Crafts reaction. Full details of the preparation of polymers A to D are given in Appendix I.

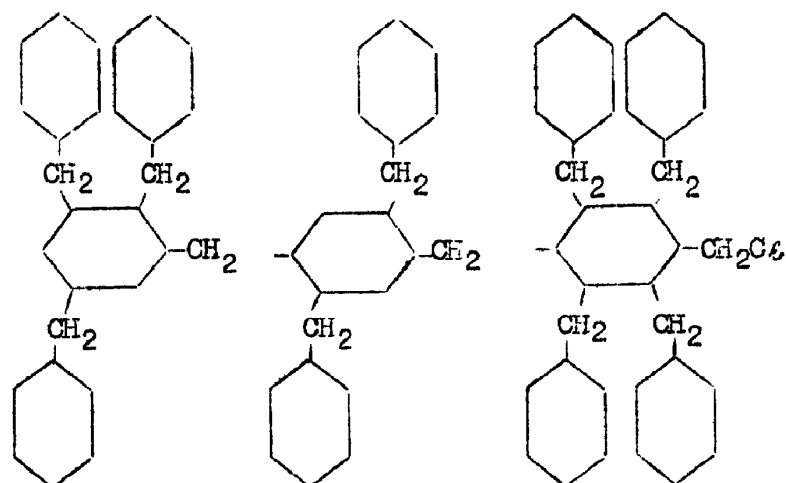
Polymer E - polyethylene. Commercial polythene powder was used. As the melting point is low, the granulation and sieving procedure used for the other polymers was inapplicable. The polythene powder was therefore sprinkled on to a Petri-dish so that when fused, the droplets would not coalesce. In spite of this, the ratio of area to volume of the polythene particles was probably smaller than in the case of the other polymers.

#### 3.2 Structure of the polymers

It is unlikely that polymer A consists solely of chains of benzene rings linked in the *para* positions. The rather drastic conditions of preparation render it likely that some branching has occurred.<sup>2</sup>

Polymers B to D prepared by the Friedel-Crafts reactions are likely to be highly branched, though it is uncertain whether the branching is random, as suggested by Flory<sup>3</sup>, or from a "backbone", as suggested by Haas, Livingston and Saunders<sup>4</sup>. The latter authors suppose that once a hydrogen atom on the benzene ring of a molecule of benzyl chloride has been substituted by a benzyl group, the remaining hydrogen atoms of the ring are activated and more likely to be substituted by further benzyl groups. Hence substitution is not random (in the Flory sense) and a typical structure built up may be depicted thus:





These considerations do not affect the argument that in polymers B to D the benzene nuclei are linked together by chains of one, two or three methylene groups respectively, and the experiments should show the effect of the linkages on heat resistance.

### 3.3 Results

The results are shown diagrammatically in Fig.1, in which loss of weight, as a percentage of original weight, is plotted against time. The curves show that the longer the chain of methylene groups between benzene nuclei, the lower the stability of the polymer to heat. The curve for polythene is given in Fig.1 for comparison with the curves for polymers containing benzene rings.

### 3.4 Discussion

The results suggest that the mode of degradation involves the link between benzene rings and that in a polymer the higher the ratio of aromatic bonds to aliphatic, the more likely is the polymer to be heat resistant. The relatively good performance of polymer B (polymethylene-phenylene) is interesting in view of the reactivity of the single methylene group between benzene rings. For example diphenylmethane is easily oxidised to the ketone.

The form of the curves obtained raises many questions as to the mechanism of weight loss. The simplest law which can be postulated is that the rate of loss is directly proportional to the weight of polymer present at any given time, i.e.

$$-dW/dt = \text{constant} \times W$$

where  $W$  is the weight actually present at a given time.

Comparison of the experimental curves (Fig.1), with curves of constant rate of weight loss (Fig.2) emphasises the fact that the polymers lose weight at a much higher rate in the early stages of heating than they do in later stages. This may be due to the molecular weight distribution of the polymers used, or to a "curing" (cross-linking) reaction accompanying the degrading process.

Were the losses due solely to oxidation, degradation might well take place on the surface of the particles. If this were so the rate of loss would be affected by the rate of reduction of surface area of the particles. Equally thick skins of material would be removed in equal intervals of time,

i.e.  $- dr/dt = \text{constant},$

where  $r$  is the radius of the particle.

From this  $- dW/dt = \text{constant} \times W^{2/3}.$

Curves of constant radius loss (Fig.3) fit the experimental data no better than those of constant weight loss.

### 3.5 Conclusion - Series I

In spite of the good performance of polymer A, it is probable that the preparative and manipulative difficulties will rule out development of this polymer as a plastic material.

Future work on heat resisting hydrocarbons should therefore be directed to the development of polymers consisting of simple or fused benzene nuclei linked by single methylene groups.

The mechanism of the release of volatile material from these polymers is as yet unknown.

## 4 Series II - Miscellaneous plastic materials and polymers

### 4.1 Nature of materials examined

Following the experiments with the polymers of Series I, attention was paid to certain miscellaneous plastic materials and polymers. Table I summarises the type and origin of these materials. All resins were given their usual or recommended cure cycles before sieving, and were dried at 1400 after sieving.

### 4.2 Results

The results are illustrated in Figures 4 to 9. The experimental procedure was as described in paragraph 2.

### 4.3 Discussion

Non of the types of material has been examined exhaustively, and therefore only limited deductions should be drawn from the data.

#### 4.31 Phenol-formaldehyde resins

Two of the four phenolic resins examined (G and H) gave good results, and two (F and Q) gave poorer results (Fig.4). The best results are little worse than those for polymer B, which is interesting in view of the probable similarity between the structure of a phenolic resin and that of polymethylene-phenylene. Both the resins which gave good results were ammonia catalysed. One at least of the poorer resins is known to be catalysed by sodium hydroxide. The other, probably also catalysed by sodium hydroxide, was extracted from a commercial resin-impregnated asbestos felt. It is noteworthy that pieces of this impregnated felt cured under "no pressure" conditions, inflamed spontaneously when heated in air at 300°C, the resin being burnt off completely in about 15 minutes. This phenomenon may be due to the extreme porosity of the material

giving a large area of exposure to oxygen, or to a catalytic effect of the asbestos. Indications, from a single experiment, are that the rate of loss of weight could probably be greatly slowed down, and the incandescence suppressed, by impregnating the cured felt in silicone varnish.

An alcoholic solution of an ammonia catalysed resin was prepared and solid sodium hydroxide was dissolved in it to give a concentration of 1 per cent on the resin. The solution was evaporated to small bulk and the resin cured. The behaviour of this sodium hydroxide treated resin (V) at 300°C was significantly worse than the original ammonia catalysed resin (G).

Modification of phenolic hydroxyl groups in phenol-formaldehyde resins by methylation at the 'A' stage (using dimethyl sulphate) improved the performance of the caustic soda catalysed resin, but hardly affected the performance of an ammonia catalysed one (see Fig.5). The rate of cure of methylated resins is very slow.

#### 4.32 Melamine-formaldehyde resins

The weight loss of a cured trimethylol melamine was initially high though the rate fell to a low value (Fig.8). A melamine resin containing a lower methylol content (K) gave better results. It is interesting to note that the strength of laminates using conventional melamine resins also shows a large drop during the early stages of heating<sup>5</sup>. Analysis of the residue left after heating melamine resin J for 144 hours at 300°C gave the following results:

Carbon	44.4%
Hydrogen	3.4%
Nitrogen	43.0%

These figures suggest that the triazine ring of the melamine molecule is intact. The high initial loss of weight on heating may be due to loss of volatiles leading in turn to "tighter" condensation of the triazine nuclei.

A modified melamine resin (U) of unknown composition gave good results in the early stages.

#### 4.33 Ethylenephénylene polymers

Most of the work recorded in the literature on ethylenephénylene polymers has been with reference to the "poly-p-xylylene" discussed by Szwarc<sup>6</sup>. The monomer is produced by pyrolysis of p-xylene, and may be considered to be:



or the free radical:



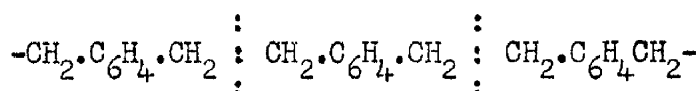
The polymer produced by combination of these monomers may be linear but is likely to be cross-linked<sup>7</sup> in view of its insolubility. It is reported to have good heat resistance, and patents on its manufacture exist<sup>8</sup>.

A sample of this polymer (L) was heated at 300°C in the usual way. It showed very considerable loss of weight (Fig.6).

A similar polymer was prepared by a Wurtz reaction with *o,o'*-dibromo-*p*-xylene (S). This gave similar though worse results. The molecular weight of polymer S is thought to be low.

Figure 6 also shows the behaviour of polymer C (described in paragraph 3 - Series I) which is an ethylenephenylene polymer prepared by a Friedel-Crafts reaction. Its behaviour is also similar to, though better than "poly-*p*-xylylene."

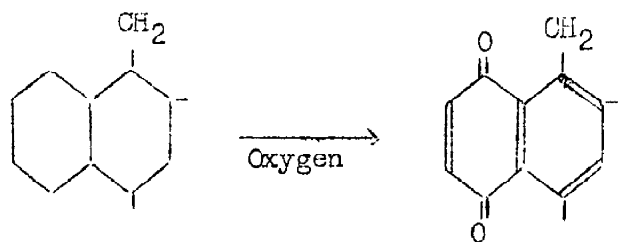
The behaviour of these polymers is considerably worse than that of "polybenzyl." This is to be expected since a polymer of structure:



can split symmetrically into radicals  $\text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2$  which must be fairly stable in view of the method of preparation of "poly-*p*-xylylene."

#### 4.34 Polymethylenenaphthylene

1-Chloromethylnaphthalene was prepared and polymerised by a Friedel-Crafts reaction in the manner described in Appendix I. The physical appearance of the polymer was similar to that of polymethylenephenylene. The behaviour on heating at 300°C was interesting (Fig.7). A maximum occurred in the early part of the curve (noticed in more than one run) due possibly to oxidation without scission. Possibly naphthaquinones are formed:



The later part of the curve is very similar to that given by polymer B.

#### 4.35 Miscellaneous polymers

The behaviour of the other polymers is shown in Figure 9. Polymer M is a polyester resin crosslinked by styrene. The material loses styrene disastrously at 300°C, leaving a hard, black, fairly heat resistant residue. Polymer T is a "heat resistant" polyester resin cross-linked by triallyl cyanurate. Polymer R is a silicone resin.

The silicone resin is the most thermally stable polymer studied so far. At the end of 150 hours at 300°C it was not even discoloured. It was, however, quite rubbery at 300°C though brittle at room temperature, a fact which emphasises the lack of correlation between chemical stability and retention of physical properties at high temperatures.

#### 4.4 Conclusions - Series II

The method of determining curves for rate of weight loss by heating finely divided plastic material at high temperatures is useful for preliminary examination of materials before lengthy physical testing is begun.

The results obtained for melamine resins, and the widespread use of triallyl cyanurate as a cross-linking agent for heat resistant polyester resins suggests that more detailed investigation of polymers containing the triazine ring might be rewarding.

Phenolic resins, although among the earliest polymers in commercial use, are still among the most heat resistant. The effect of metallic oxides and asbestos on their behaviour at high temperatures should be investigated in more detail. Methods for the protection of phenolic resins by others more chemically stable if less strong physically (e.g. silicones) may be capable of development.

#### Acknowledgments

It is desired to acknowledge the assistance given by Mr. D. Clark, for X-ray crystallography; Mr. T.R.F.W. Fennell and the staff of the Analytical Section, for analyses; Mr. D. Sheehan who provided the sample of polyphenylene used; and also the following firms, who provided resins and information: Bakelite Ltd., British Oxygen Co., Ltd., Imperial Chemical Industries, Ltd.

The sample of poly-p-xylylene was provided by D.M.X.R.D.

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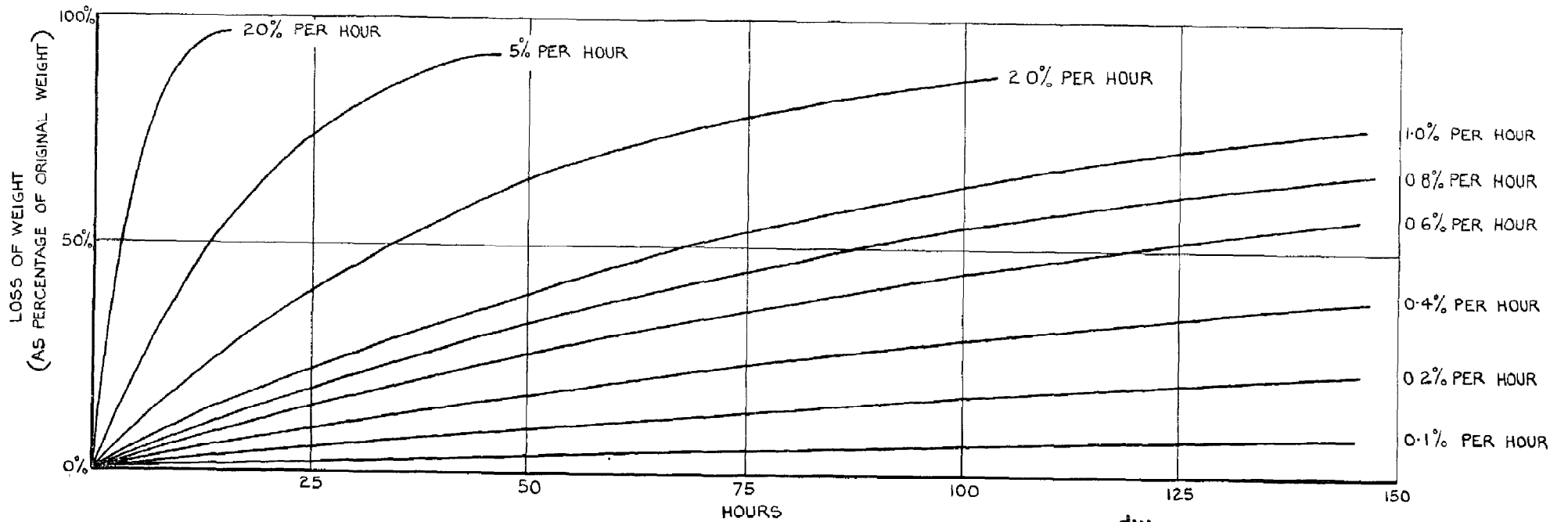


FIG. 2. LOSS OF WEIGHT AGAINST TIME ASSUMING  $-\frac{dw}{dt} \propto W$

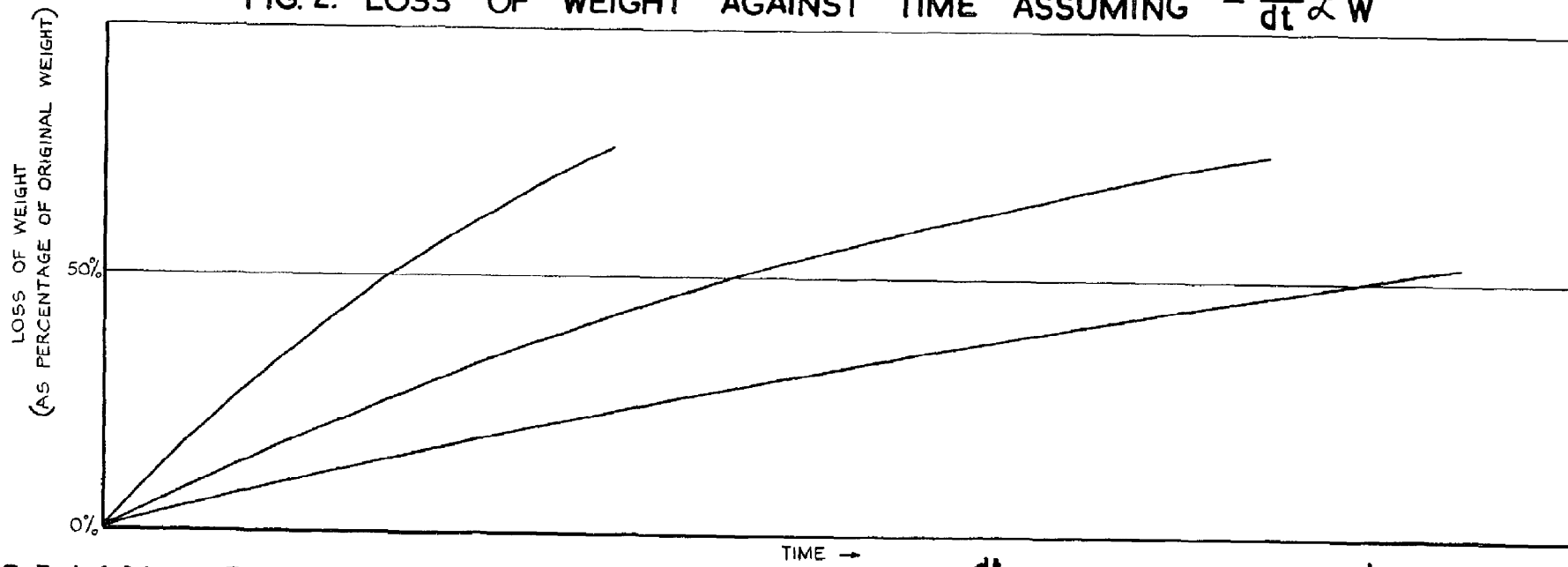


FIG. 3. LOSS OF WEIGHT AGAINST TIME ASSUMING  $-\frac{dw}{dt} = \text{CONSTANT}$ ,  $\therefore -\frac{dw}{dt} \propto W^{2/3}$

## APPENDIX I

### Preparation of Hydrocarbon Polymers

#### Polymers from Wurtz reactions

##### Polyphenylene (Polymer A)

Polymer A was prepared by means of a Wurtz type reaction between *p*-dichlorobenzene and sodium/potassium alloy. The reaction was carried out under nitrogen in boiling diphenyl, the temperature of which was sufficient to cause the reaction to proceed moderately quickly. The tan brown produce was extracted with benzene to remove material of low molecular weight. By analysis of end groups, the average chain length of the polymer used for thermal degradation experiments was thirty-five benzene rings.

Full details of the preparation are given by Sheehan<sup>9</sup>.

##### Polyethylenephenylene (polymer S)

Polymer S was prepared in a similar way by a reaction between  $\omega,\omega'$  dibromo-*p*-xylene and sodium metal in boiling xylene. The reaction was continued for 24 hours after which the buff coloured solid product was extracted first with water and then benzene.

#### Polymers from Friedel-Crafts reactions

##### Introduction

Early work on the formation of polymers by Friedel-Crafts reactions is described by Jacobson<sup>10</sup>. When benzyl chloride is treated with anhydrous aluminium chloride in the cold, and in the absence of solvents, a vigorous reaction ensues with the evolution of hydrogen chloride. The product consists of an insoluble, infusible, buff coloured solid, together with another material, soluble in benzene and other solvents, and melting about 80°C. Jacobson (loc.cit.) mentions that the proportion of soluble to insoluble polymer varies with the proportion of aluminium chloride used and also stated that the presence of a solvent affects the product.

Shriner and Berger<sup>11</sup> describe a polymer obtained by the action of concentrated sulphuric acid on benzyl alcohol. The product appears to be similar to Jacobson's "insoluble" polymer.

Haas, Livingston and Saunders<sup>4</sup> obtained a soluble form of polymer by the action of ferric oxide on benzyl chloride and examined its structure by physical methods.

Records of similar work with starting materials other than benzyl chloride are sparse. The production of polyethylenephenylene polymers by the action of aluminium chloride on ethylene chloride and benzene is mentioned by Szwarc<sup>6</sup>.

For the thermal degradation experiments described in the body of this Note, the "infusible" polymers were, of course, required.

It has been found by the author that the maximum yield of "infusible" polymer can be obtained by carrying out the condensation of the benzyl chloride in solution in carbon disulphide in the presence of aluminium

chloride. If nitrobenzene is used as a solvent, the reaction is more vigorous and the polymer obtained is of the soluble type. The most convenient way of obtaining the soluble polymer is to heat benzyl chloride with a small quantity of boron trifluoride (as etherate). A brown glassy solid, melting point about 90°C is obtained. End group analysis (for chlorine) indicates that the polymer molecule is composed of about 40 benzyl groups, (agreeing with Jacobson). Analysis of the "insoluble" polymer gave a calculated molecular weight only about 20% higher but this result is considered unreliable in view of the difficulty of removing ionic chlorine from the insoluble polymer. Both polymers proved to be amorphous when examined by X-ray crystallographic methods.

The reactions were found to be general and gave similar polymers when carried out with 1-chloromethylnaphthalene, and with the homologues of benzyl chloride, 2-chloroethylbenzene and 3-chloropropylbenzene.

#### Experimental procedure for the 'infusible' polymer

Fifty one grams (0.47 mol.) of benzyl chloride were dissolved in 150 ml. of carbon disulphide. Powered anhydrous aluminium chloride (0.5g) was added. The mixture was allowed to stand in the cold for seven days, being shaken occasionally. Most of the solvent was then decanted from the solid matter and the latter washed with a little more carbon disulphide, which was also decanted. A small quantity (about 10g) of ice was then added, followed by concentrated hydrochloric acid (1 ml.). After the mixture had been shaken thoroughly, it was exposed in the open air for a while to allow carbon disulphide to escape, and the solid was then filtered off and washed with water. The product, a biscuit-coloured granular material, was ground up and boiled several times with distilled water to which a little wetting agent had been added. Yield about 28g. (80%).

The same procedure may be followed with 1-chloromethylnaphthalene, 2-chloroethylbenzene, or 3-chloropropylbenzene. In the case of the last two, the yields are lower. 2-Chloroethylbenzene gives red polymer; 3-chloropropylbenzene a green one.

#### Polymethylenephénylene (Polymer B) and Polyethylenephénylene (Polymer C)

Polymers B and C were prepared using commercial benzyl chloride and commercial 2-chloroethylbenzene respectively.

#### Polytrimethylenephénylene (Polymer D)

For the preparation of polymer D, the required monomer, 3-chloropropylbenzene had first to be prepared. Following Strauss and Berkow<sup>12</sup>, cinnamyl alcohol was reduced with sodium amalgam and water and the hydrocinnamyl alcohol was recovered and distilled (b.p. 118°-120° at 12 mm). The hydrocinnamyl alcohol was then chlorinated using thionyl chloride in pyridine. The product was extracted with ether, and the ethereal solution was washed with sodium bicarbonate solution and water. After removal of the ether, the dried product was distilled at reduced pressure, and on redistillation a fraction (b.p. 65°-70° at 1.5 mm Hg) was collected. A further fractionation gave a product boiling between 92° and 94°C at 10 mm Hg. Suter and Evans<sup>13</sup>, who prepared the substance by the action of chloroethyl sulphate on benzyl magnesium chloride, give the boiling point as 93.5°-95°C (11 mm Hg).

The polycondensation of 3-chloropropylbenzene resulted largely in the fusible polymer, only a small yield of "infusible" polymer being obtained.



Polymethylenenaphthylene (Polymer N)

Polymer N was prepared from 1-chloromethylnaphthalene, which was made as described by Grummit and Buck<sup>14</sup>. The monomer was polycondensed in the same way as described above for benzyl chloride. A slightly greater yield was obtained.

---



TABLE I

Miscellaneous plastic materials and polymers

Key to Serial letters used in the text

Serial Letter*	Type of polymer	Remarks
F	Phenolic resin	Caustic soda catalysed. Phenol to formaldehyde ratio, 1:1.3 Prepared in laboratory.
G	Phenolic resin	Commercial resin Ammonia catalysed.
H	Cresylic resin	Commercial resin Ammonia catalysed.
J	Melamine resin	Commercial resin Melamine to formaldehyde ratio, 1:3
K	Melamine resin	Prepared in the laboratory. Melamine to formaldehyde ratio, 1:1.75
L	'Poly-p-xylylene'	Prepared by Szwarc method. Supplied by M. of Supply, D.M.X.R.D.
M	Polyester resin, styrene cross-linked	Commercial resin
N	Polymethylenenaphthylene	Prepared by Friedel-Crafts synthesis (See Appendix I).
O	Methylated phenolic resin	Polymer F methylated at the 'A' stage
P	Methylated phenolic resin	Polymer G methylated at the 'A' stage
Q	Phenolic resin	Extracted by alcohol from impregnated asbestos felt
R	Silicone resin	
S	Polyethylenephenylene	Made by Wurtz synthesis (See Appendix I).
T	Polyester resin, T.A.C. cross linked	
U	Melamine resin	Commercial experimental resin
V	Phenolic resin	Resin G, with 1 per cent sodium hydroxide added.

\*Polymers A to E are described in paragraph 3.



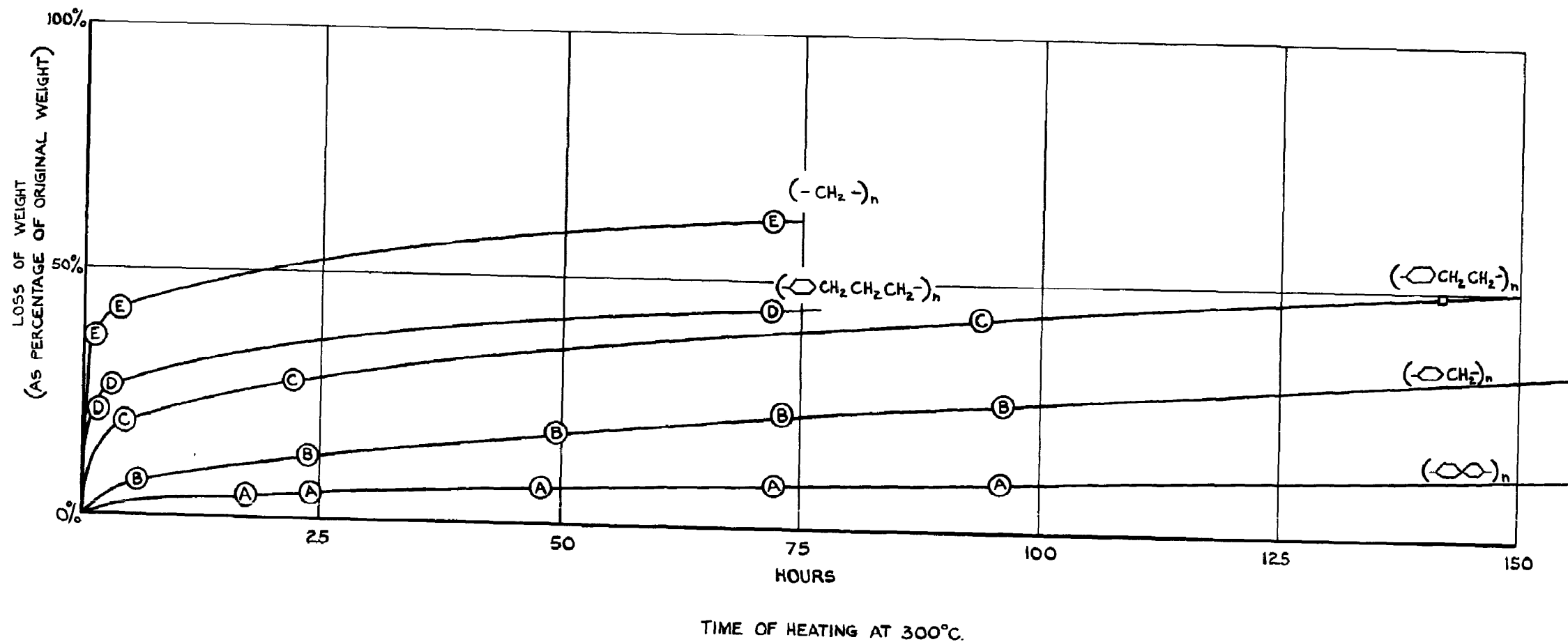


FIG. I. LOSS OF WEIGHT BY POLYMERIC HYDROCARBONS ON HEATING IN AIR.

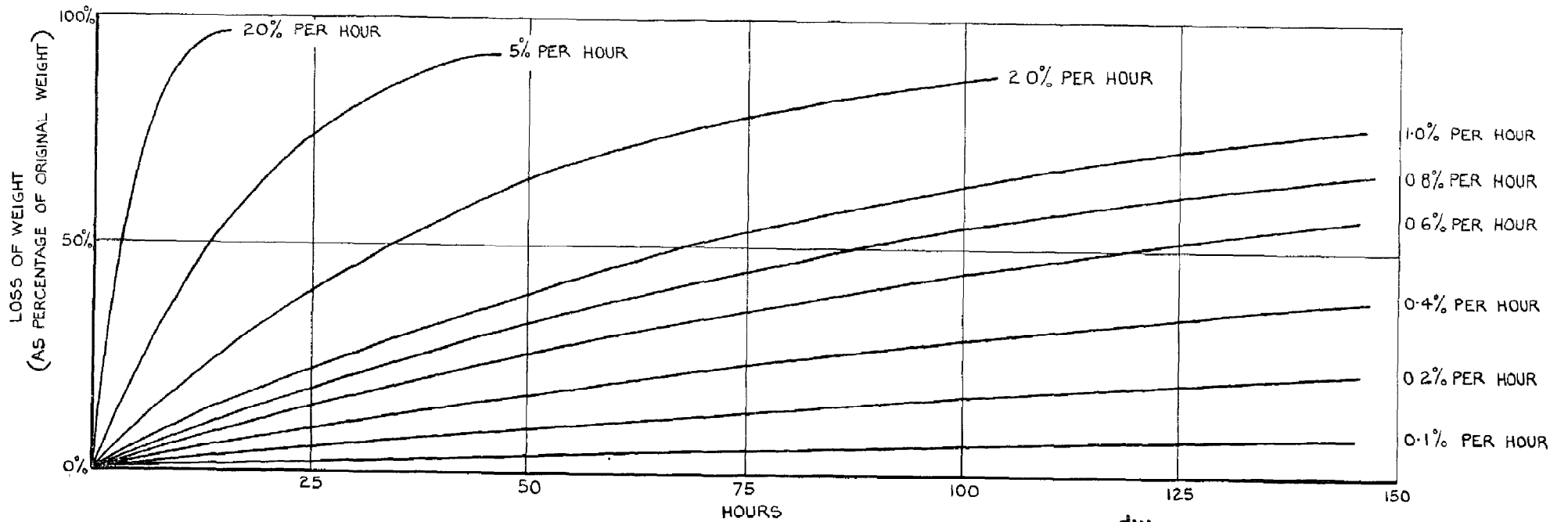


FIG. 2. LOSS OF WEIGHT AGAINST TIME ASSUMING  $-\frac{dw}{dt} \propto W$

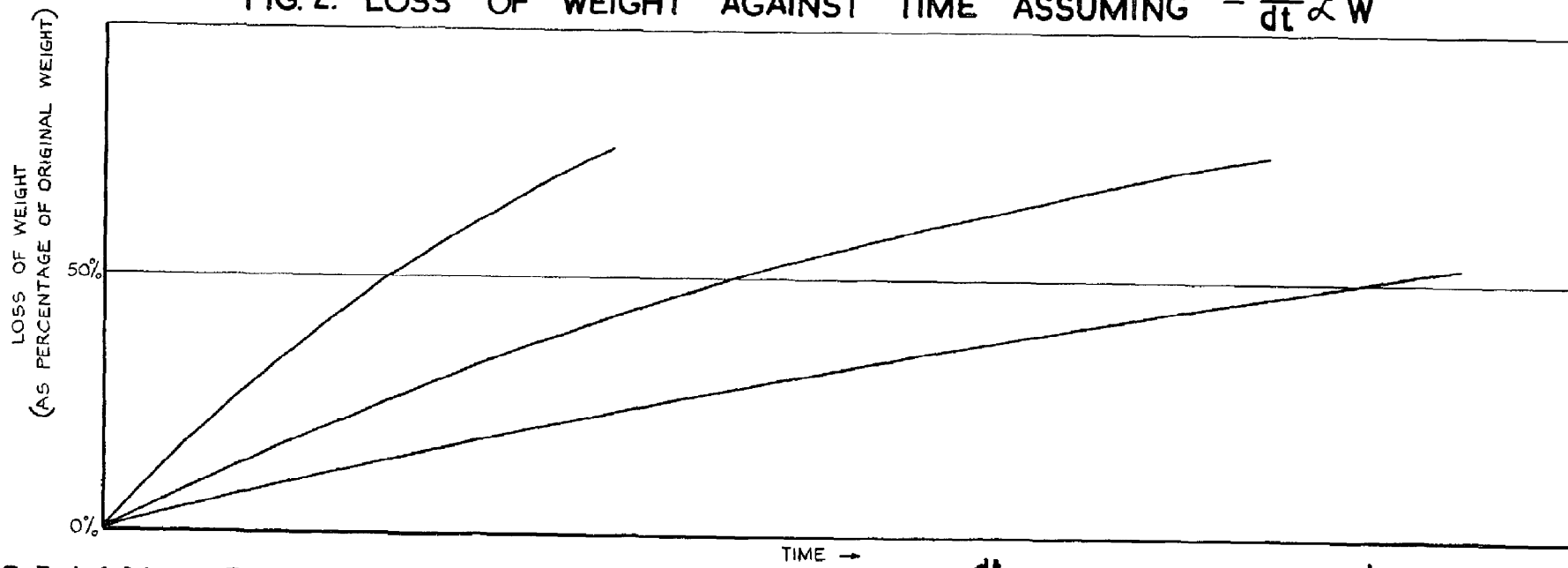


FIG. 3. LOSS OF WEIGHT AGAINST TIME ASSUMING  $-\frac{dw}{dt} = \text{CONSTANT}$ ,  $\therefore -\frac{dw}{dt} \propto W^{2/3}$

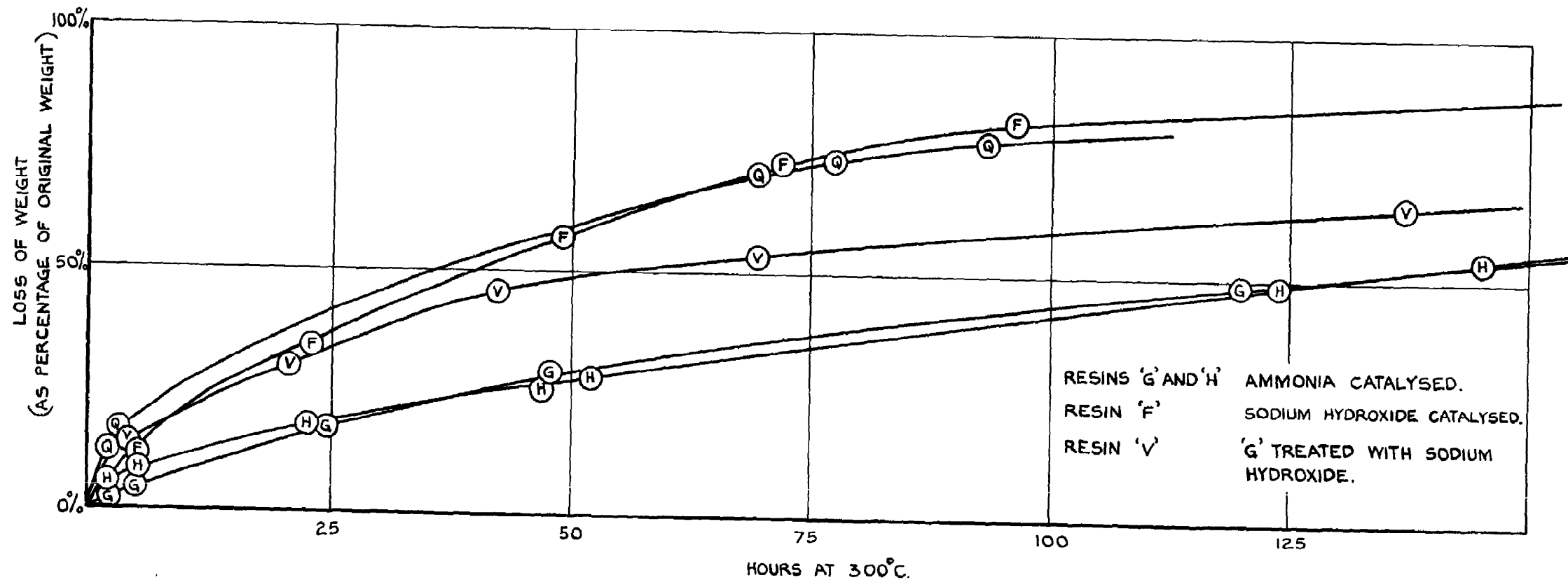


FIG. 4. LOSS OF WEIGHT ON HEATING IN AIR. PHENOLIC RESINS.

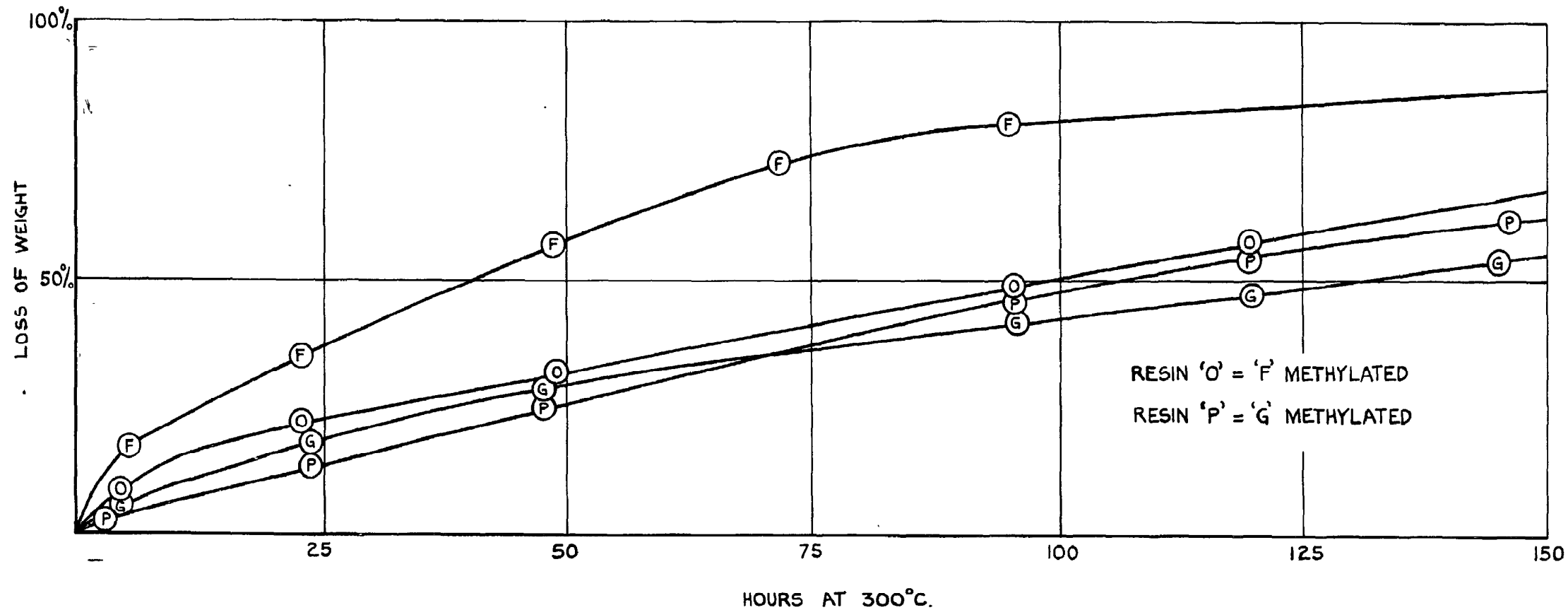


FIG.5. LOSS OF WEIGHT ON HEATING IN AIR  
EFFECT OF METHYLATION ON HEAT  
RESISTANCE OF P. F. RESINS.



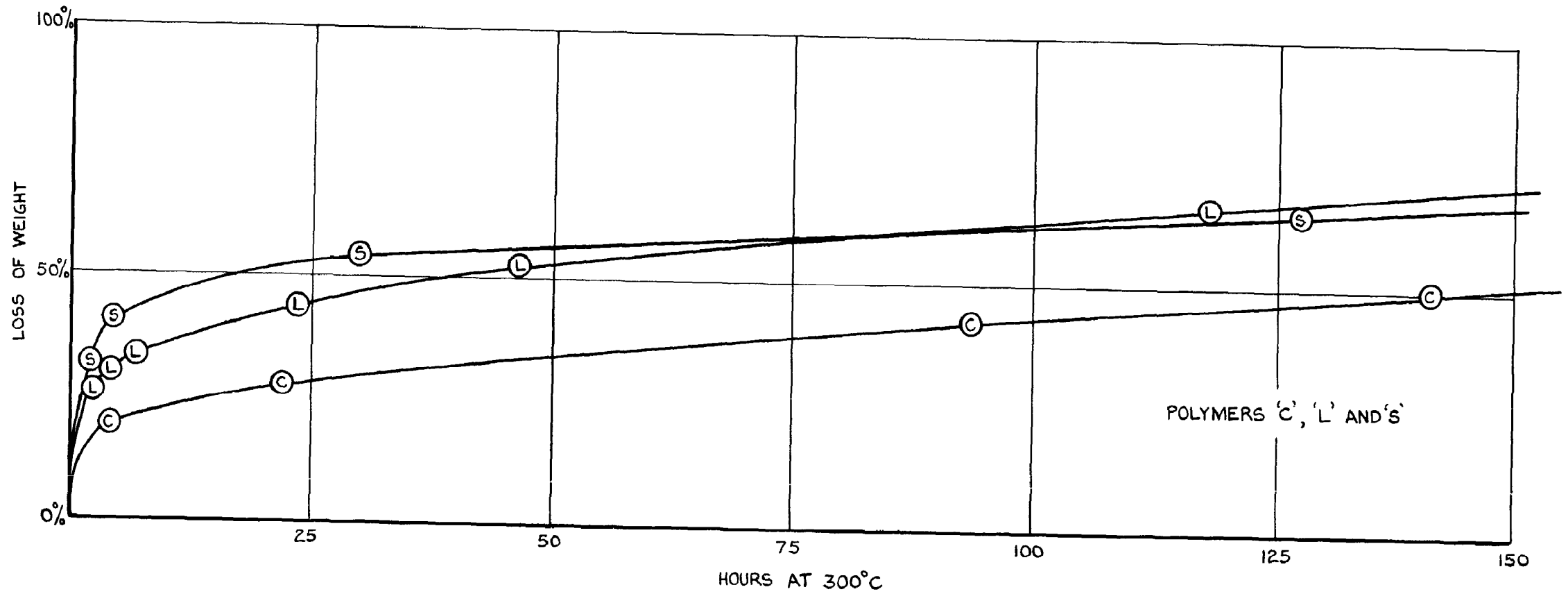


FIG. 6. LOSS OF WEIGHT ON HEATING IN AIR  
ETHYLENEPHENYLENE POLYMERS.

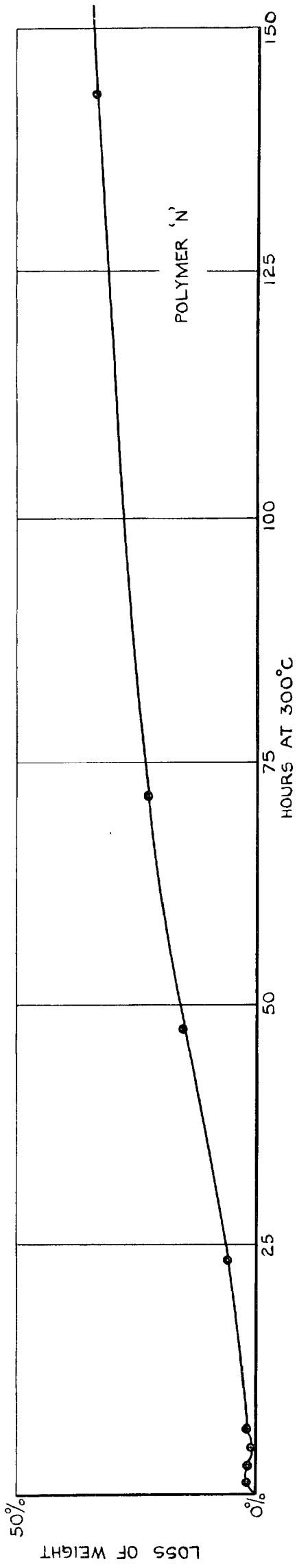


FIG. 7. LOSS OF WEIGHT ON HEATING IN AIR — METHYLENENAPHTHYLENE POLYMER.

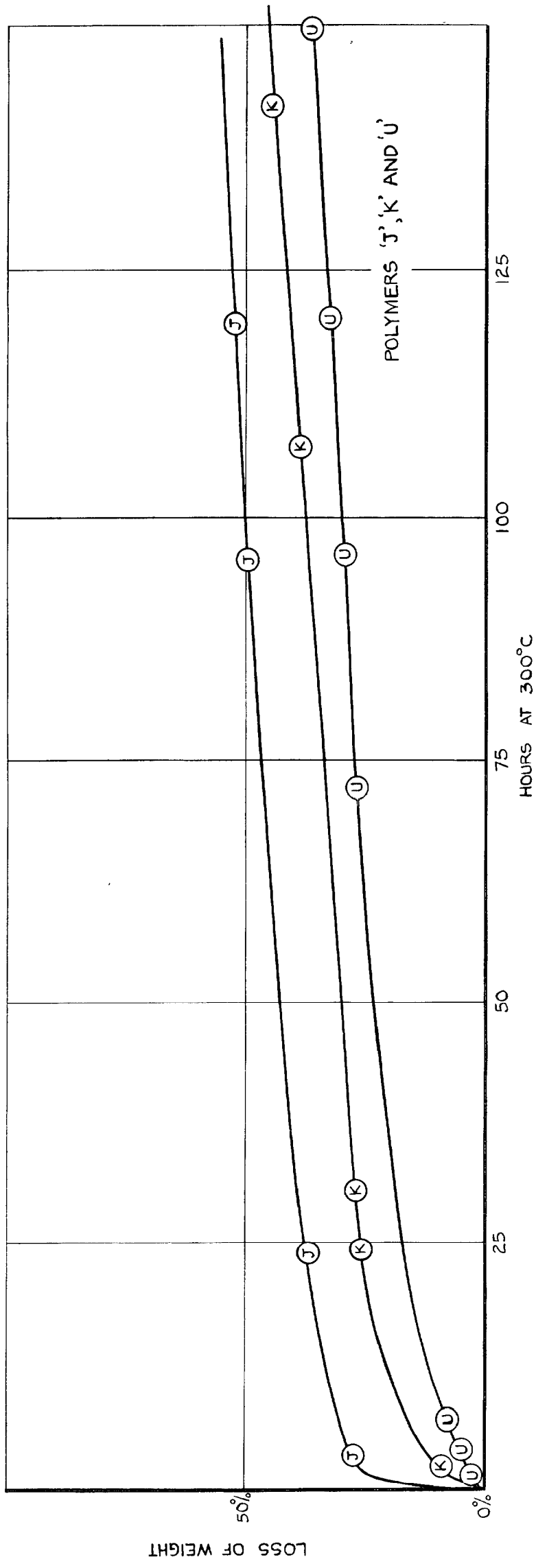


FIG. 8. LOSS OF WEIGHT ON HEATING IN AIR — MELAMINE RESINS.

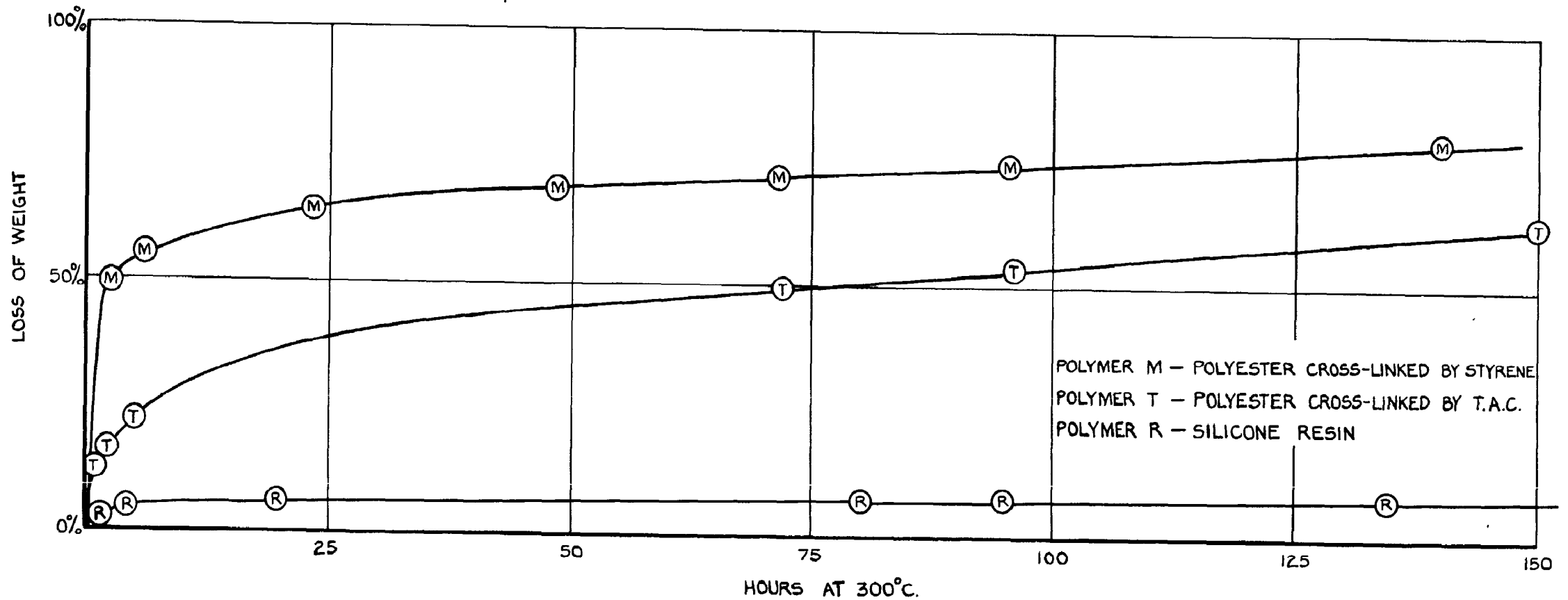


FIG. 9. LOSS OF WEIGHT ON HEATING IN AIR  
 MISCELLANEOUS POLYMERS.





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