

Feb. 14, 1967

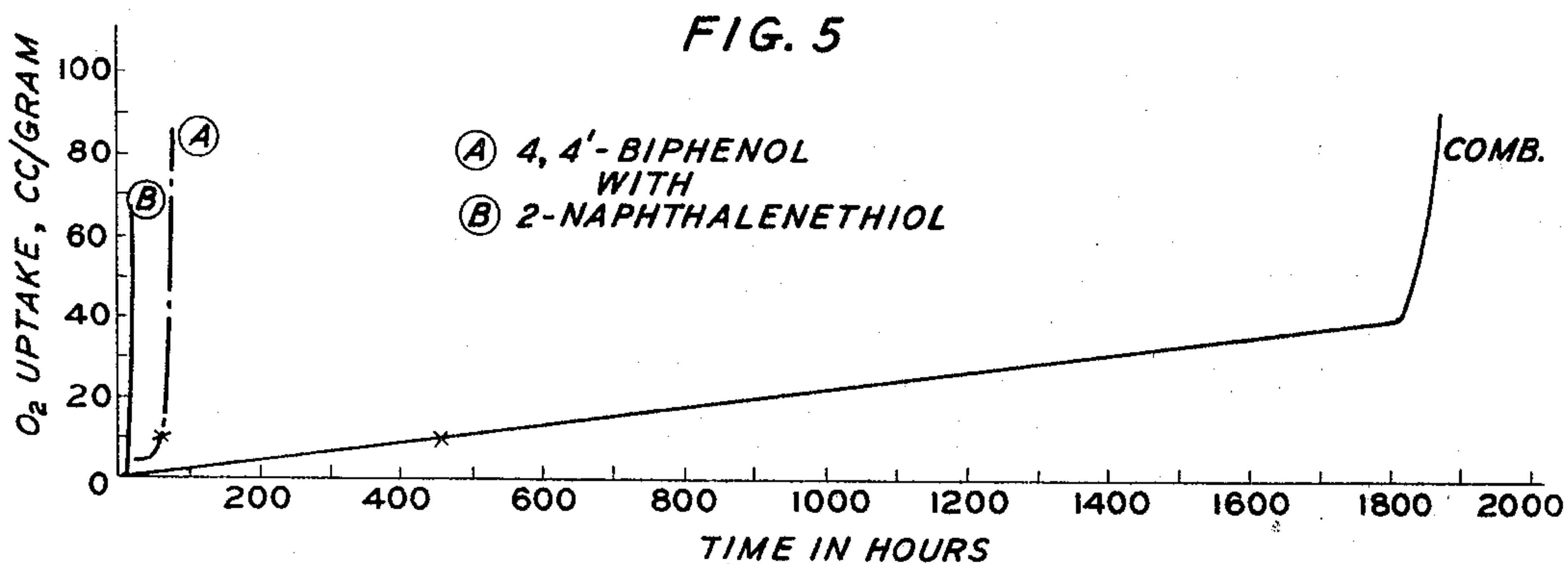
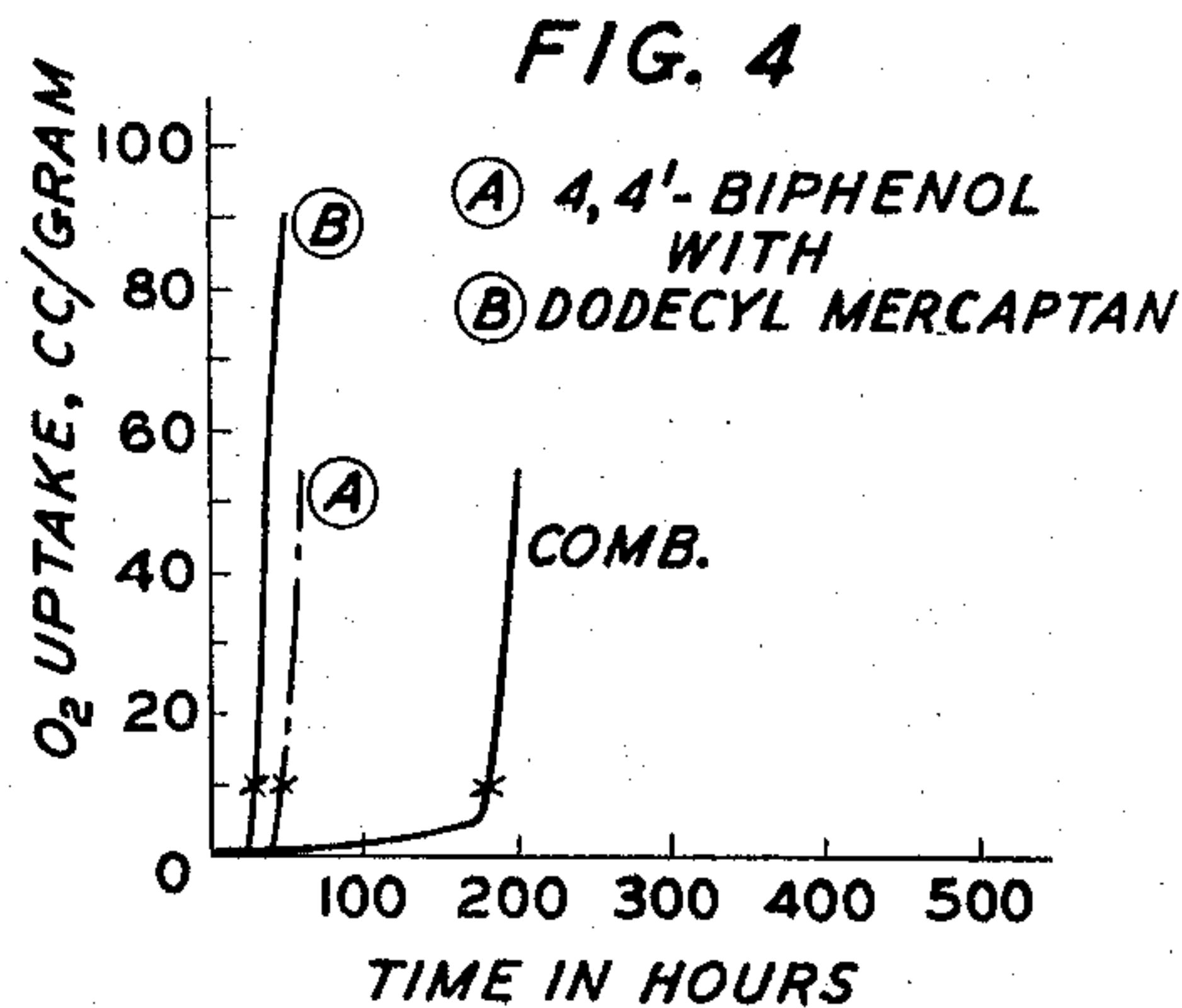
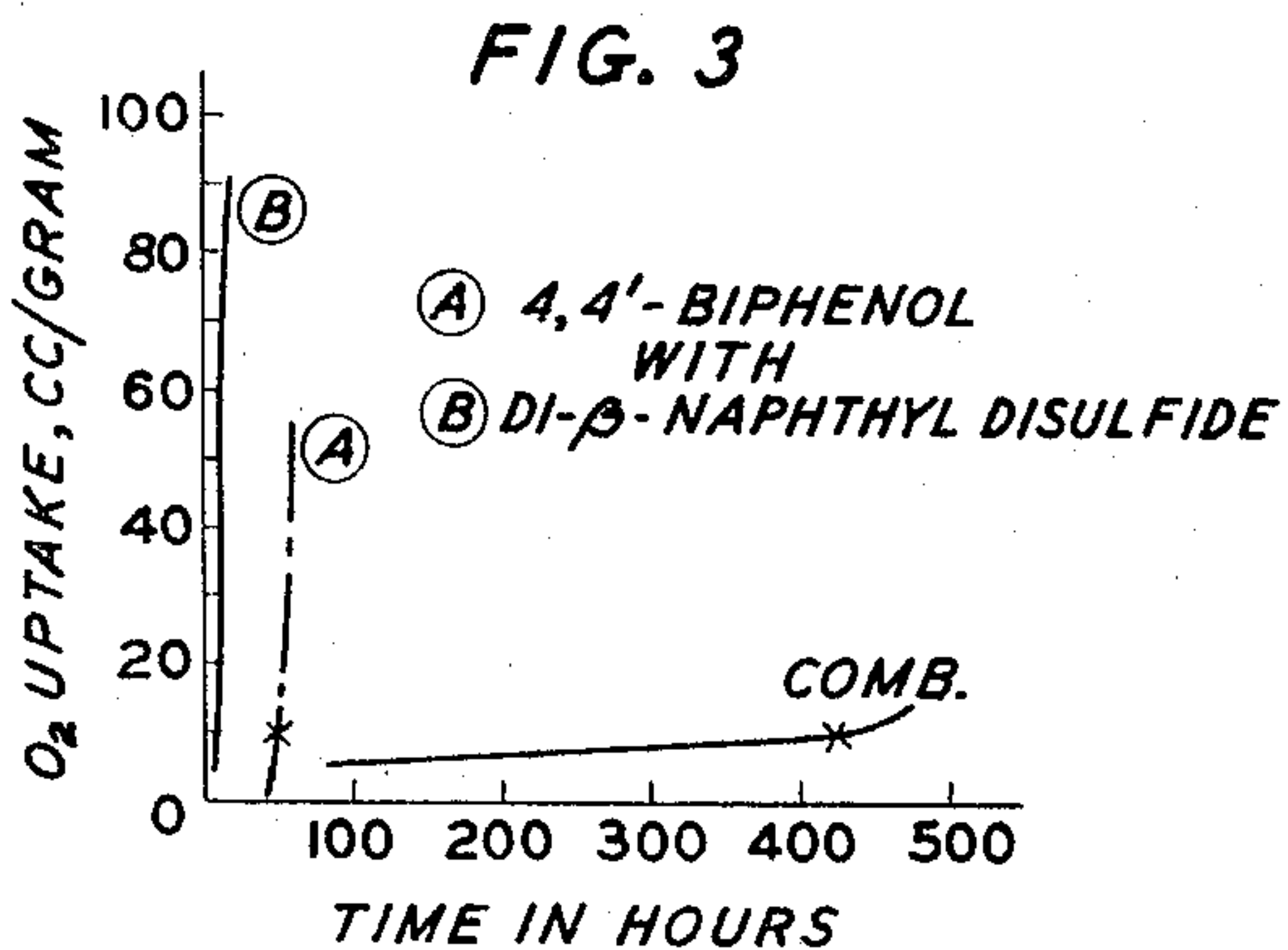
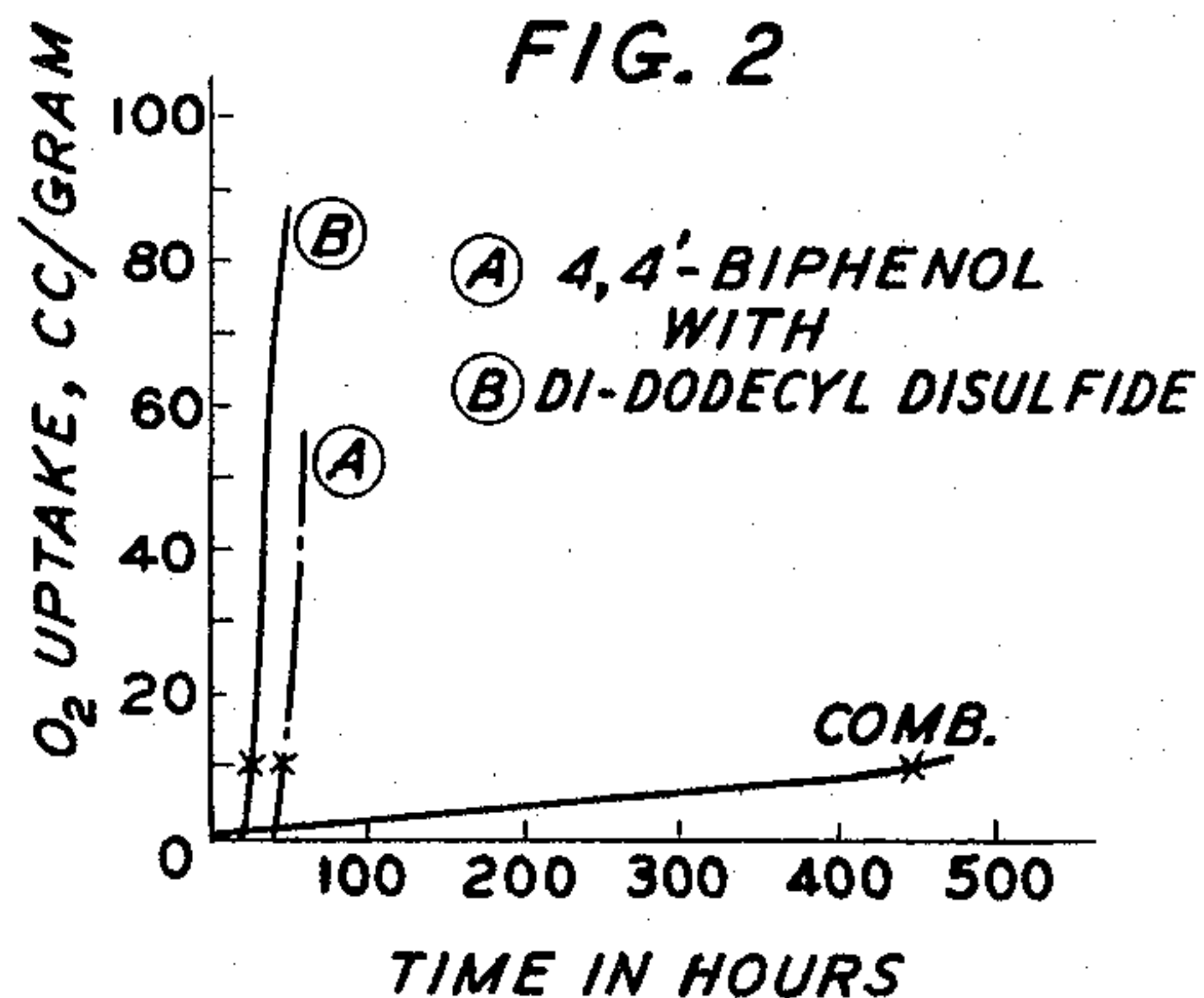
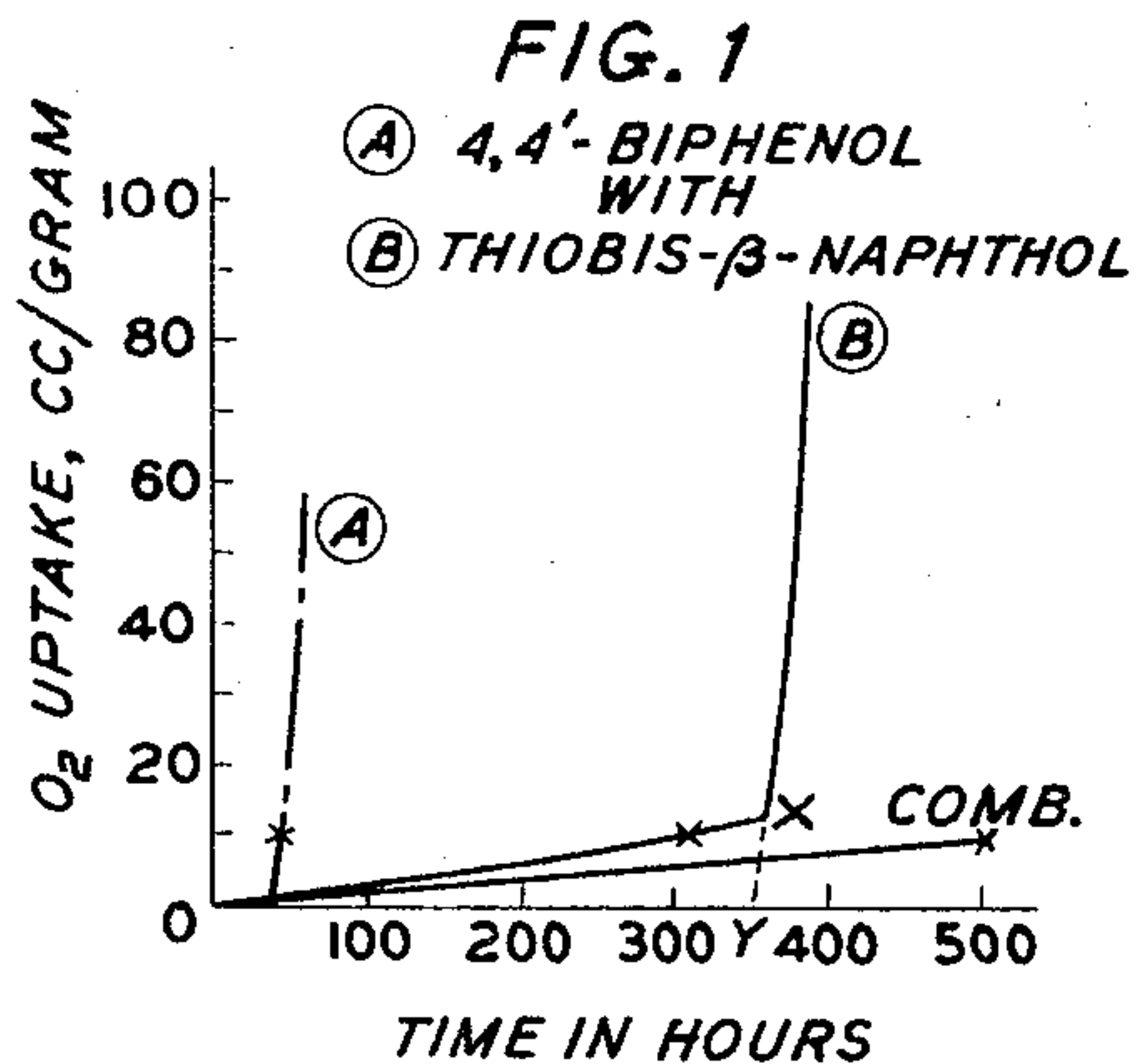
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3,304,283

STABILIZED ALPHA-MONO-OLEFINIC POLYMERS

Original Filed May 12, 1960

3 Sheets-Sheet 1



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STABILIZED ALPHA-MONO-OLEFINIC POLYMERS

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FIG. 6

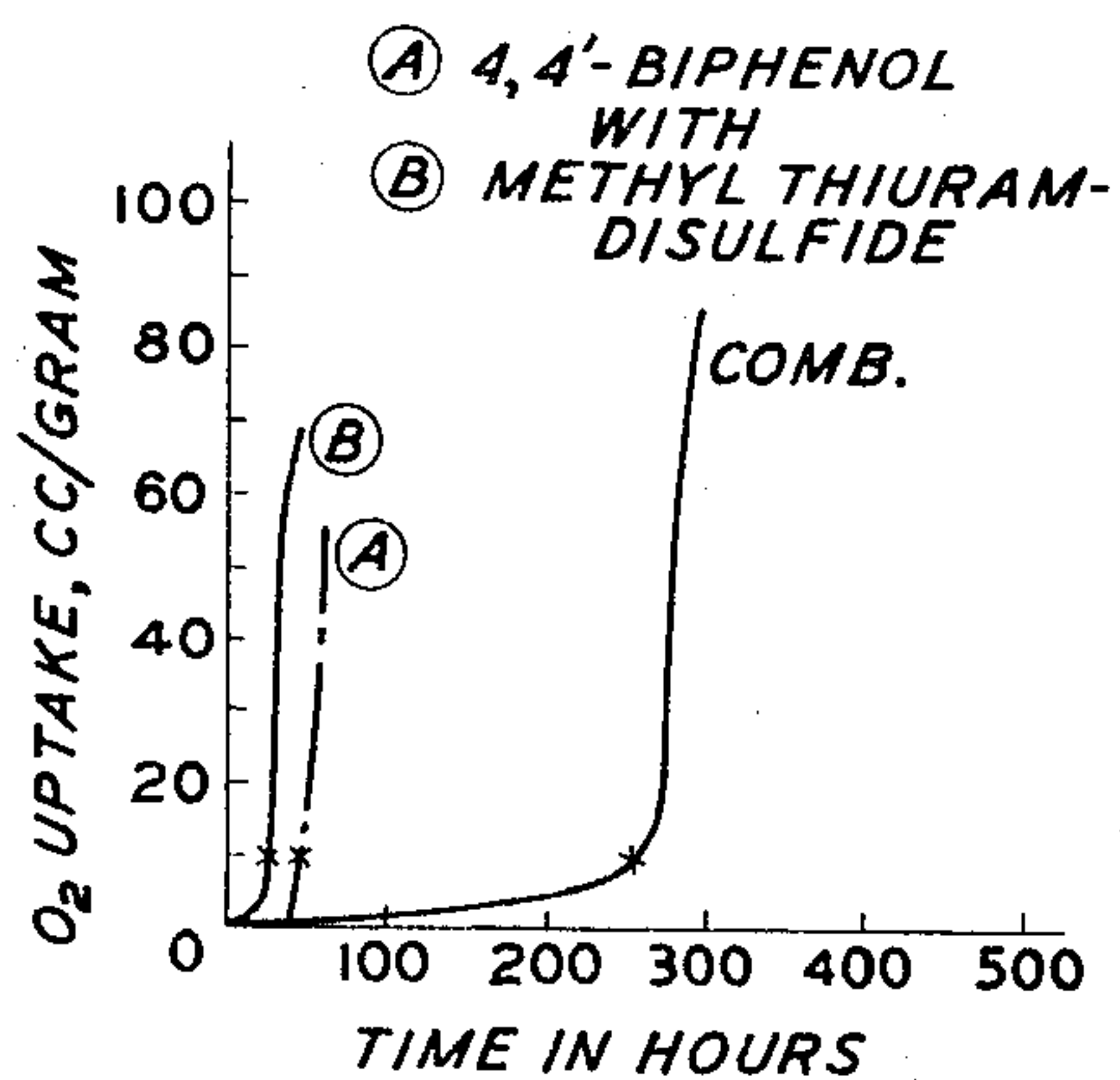


FIG. 8

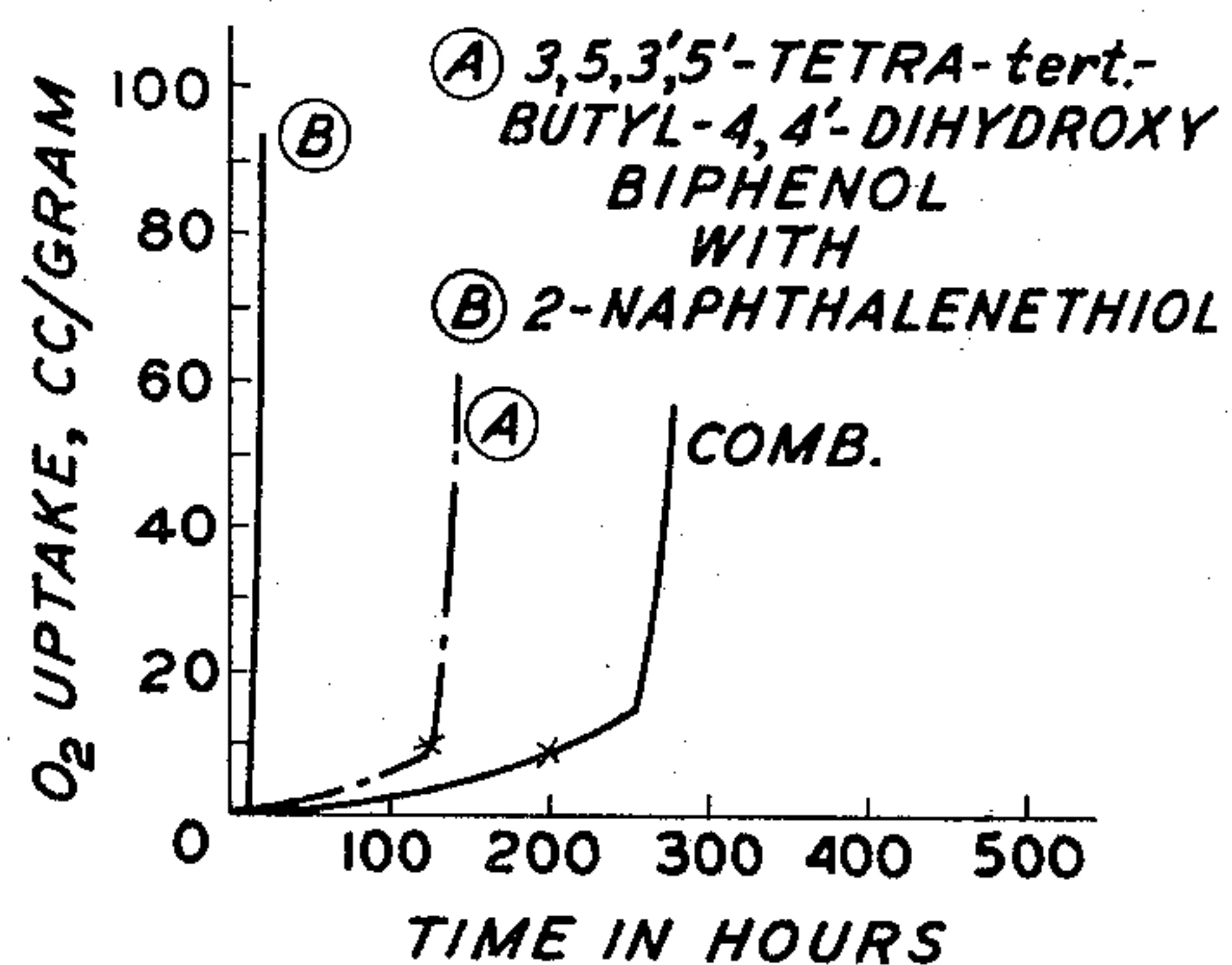


FIG. 7

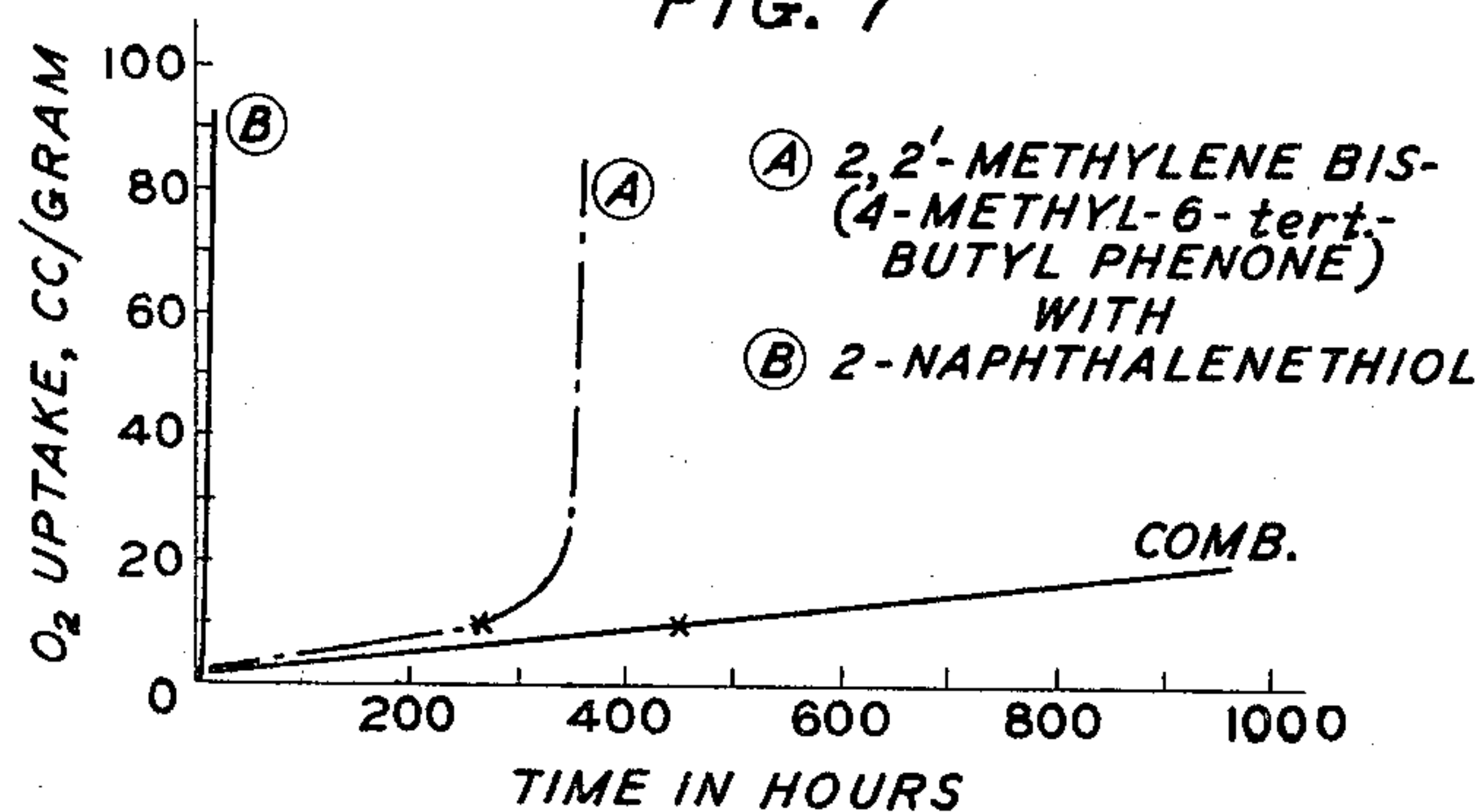
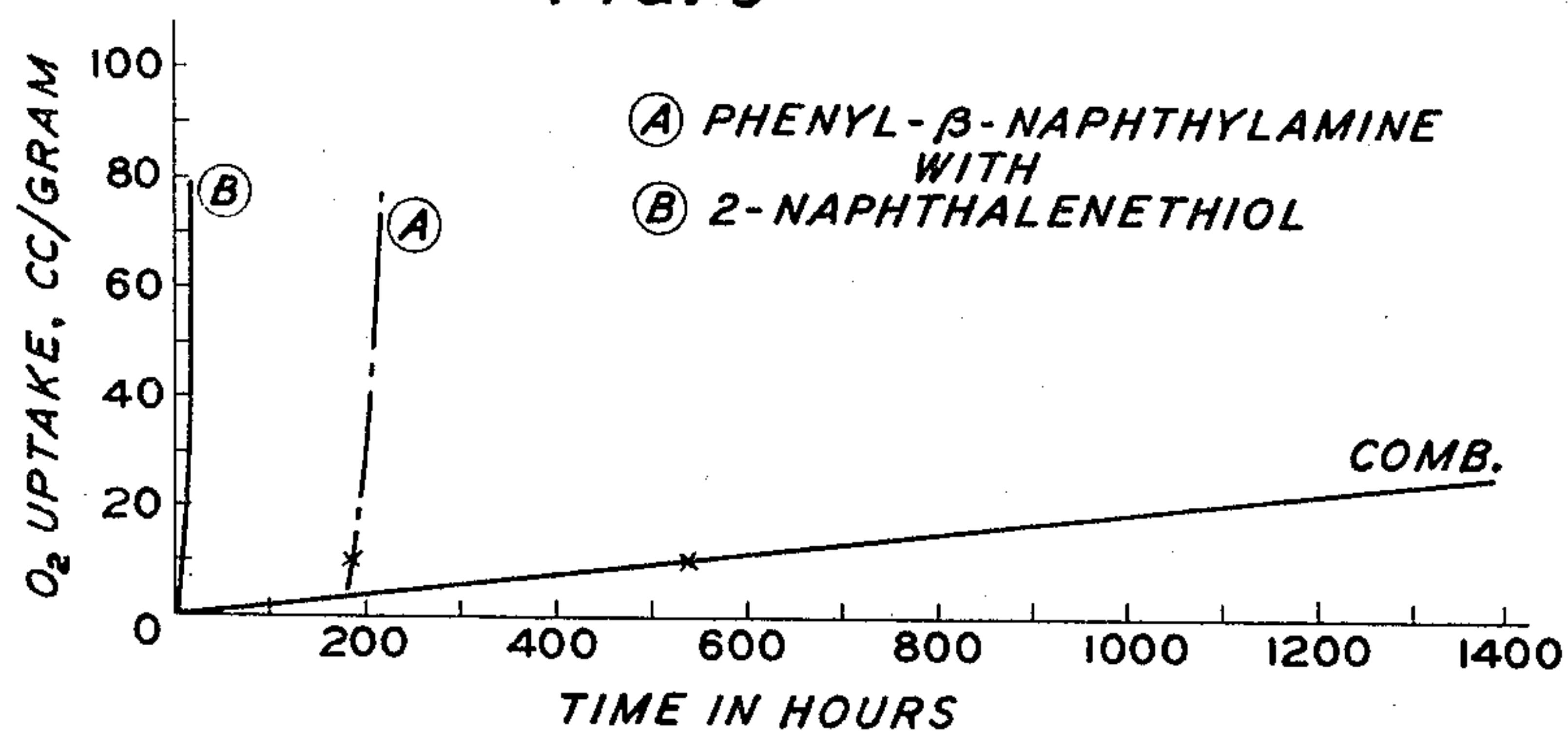


FIG. 9



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STABILIZED ALPHA-MONO-OLEFINIC POLYMERS

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FIG. 10

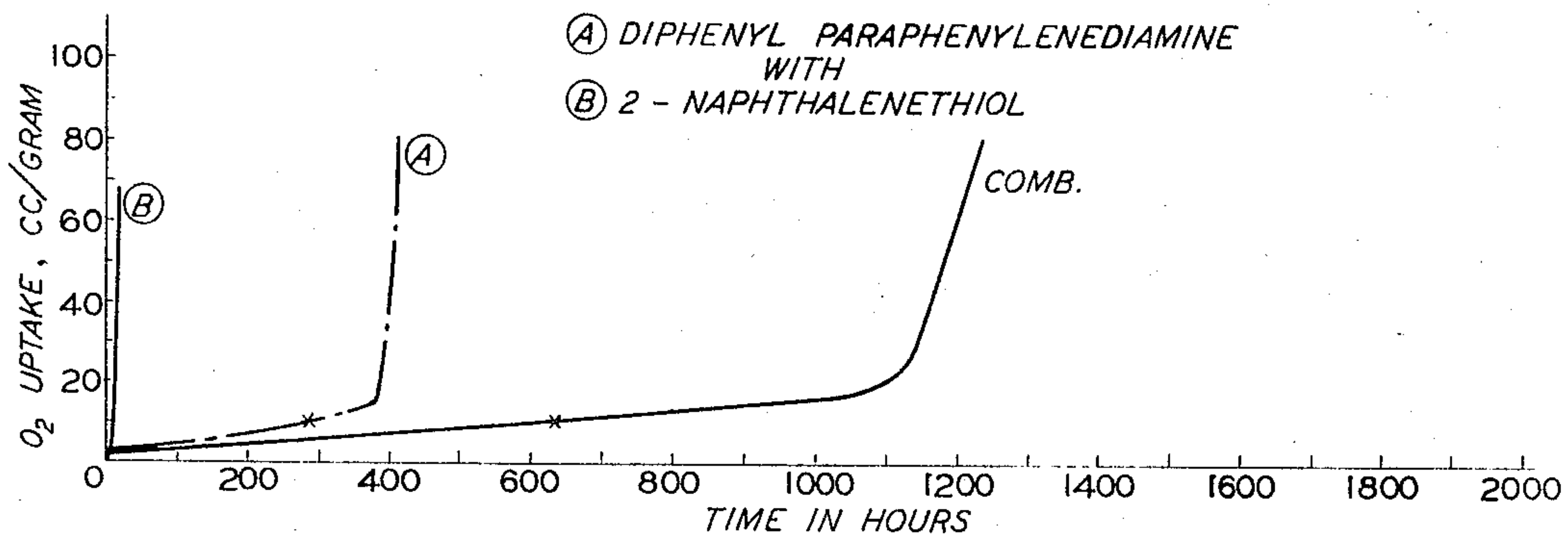


FIG. 11

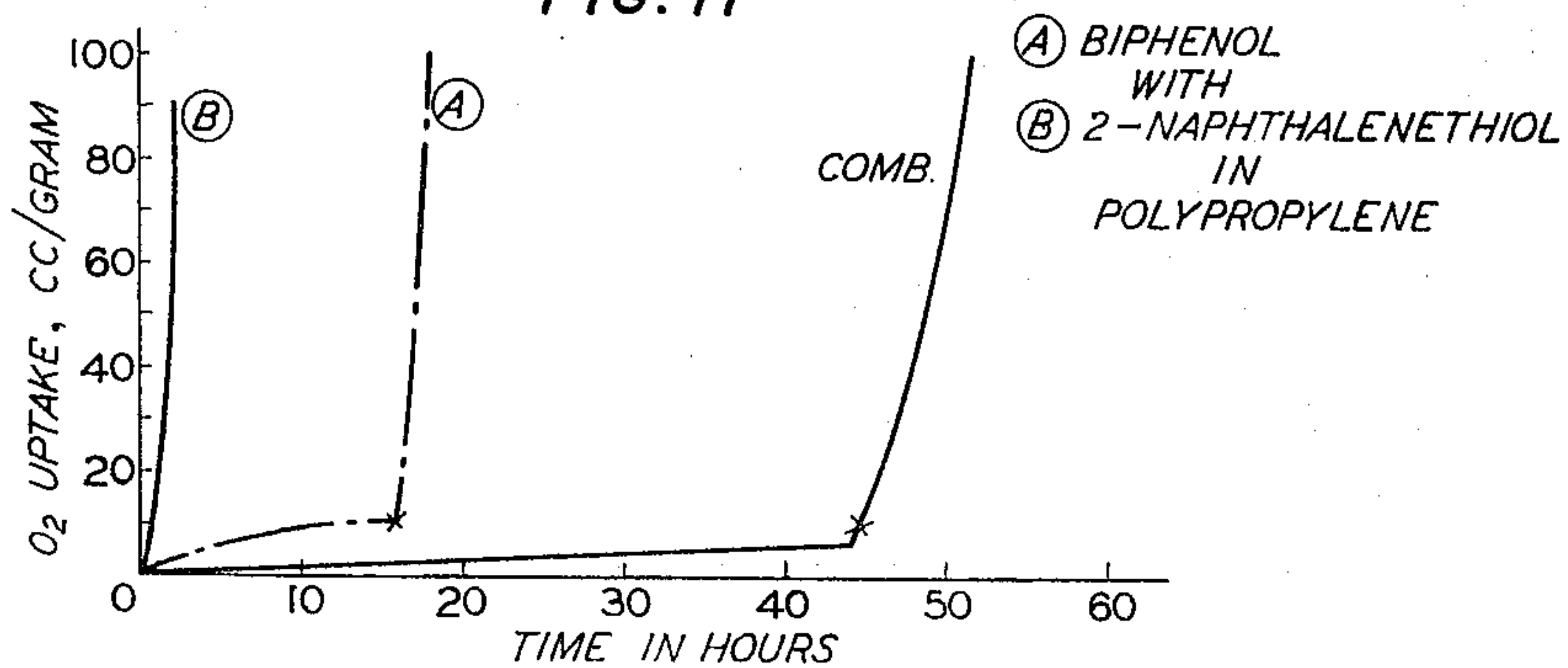


FIG. 12

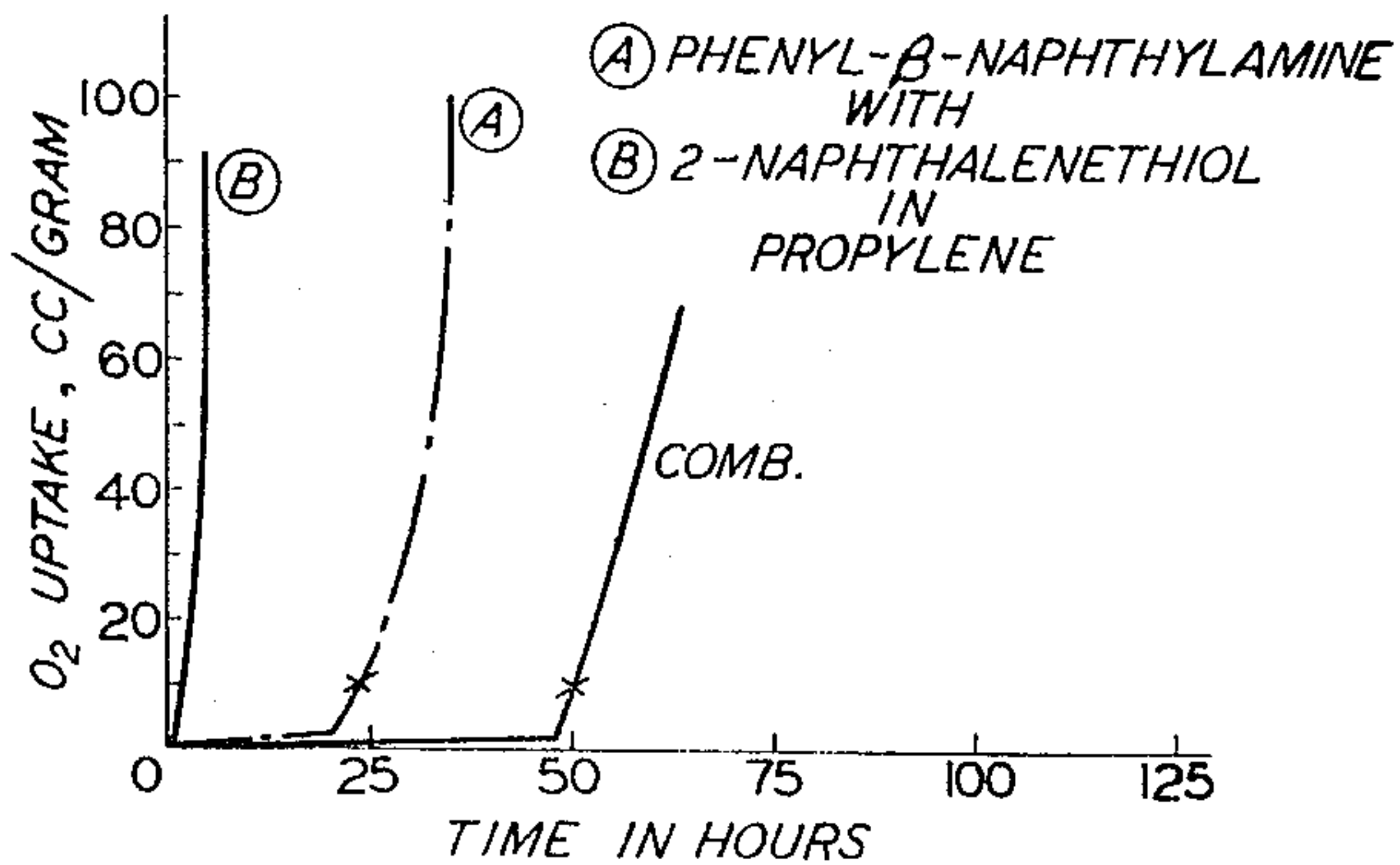
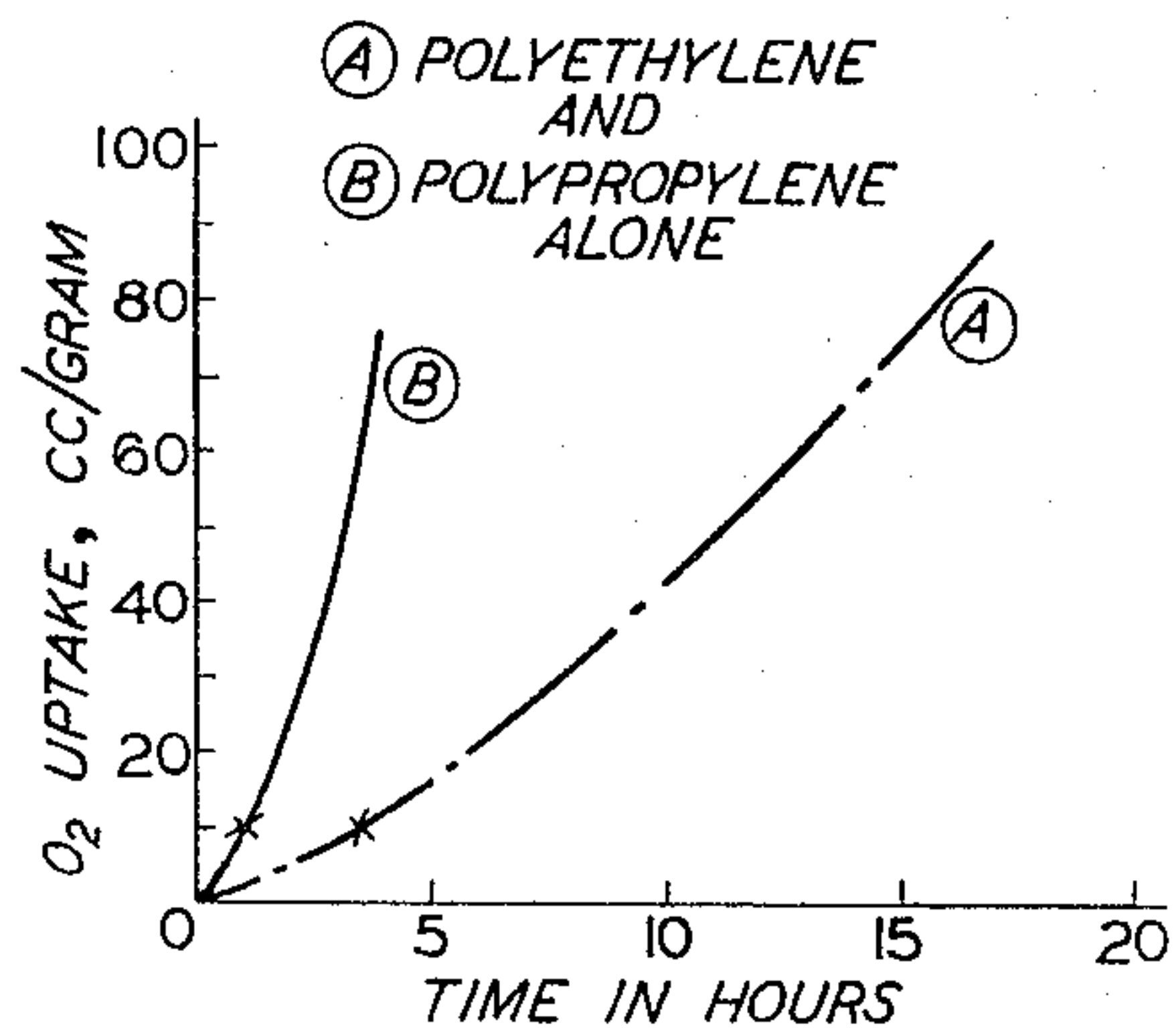


FIG. 13



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3,304,283
**STABILIZED ALPHA-MONO-OLEFINIC
POLYMERS**

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Continuation of application Ser. No. 28,734, May 12,
1960. This application Apr. 24, 1964, Ser. No. 364,881
19 Claims. (Cl. 260—45.9)

This invention relates to stabilized polymeric materials. Further, it relates to essentially saturated hydrocarbon polymeric materials having included therein small amounts of additives which have been found to exhibit a retarding effect on deleterious oxidation of the material. This invention is primarily directed to inhibiting so-called thermal oxidation in polymers by the addition of certain combinations of organic materials which have been found to produce a synergistic effect.

This application is a continuation of copending application Serial No. 28,734 filed May 12, 1960, now abandoned.

Considerable study has been devoted to the effects and prevention of thermal oxidation in the more common saturated polymers, particularly polyethylene and polypropylene. Thermal oxidation, as concerned with here, is oxidation normally occurring in ordinary atmospheres essentially independent of ultraviolet light which varies or accelerates with increasing temperature. "Antioxidant" materials have consequently been developed which provide a marked retardation of thermal oxidation. Such antioxidants as known in the prior art characteristically required an antioxidant radical such as a secondary amino group or a hydroxyl group attached to an aromatic ring. These compounds result in a resonant stabilized structure. Typically, such compounds further contain additional substituents such as branched or normal aliphatic groups. A more thorough treatment of antioxidant materials and mechanism can be found in G. W. Wheland's "Advanced Organic Chemistry," 2nd edition, chapters 9 and 10.

The particular polymeric materials adapted to be treated by this invention are polymers containing tertiary hydrogen atoms. Such polymers are of two general types: those containing random numbers and spacing of tertiary hydrogen atoms such as polyethylene and those containing ordered hydrogen atoms such as polypropylene. This invention concerns either type and mixtures thereof or copolymers containing one or more of either type. Specific compounds appropriate for this invention are polymers of olefins such as polyethylene, both conventional and the newer higher density materials, polypropylene, polybutene-1, poly-3-methyl butene-1, poly-4-methyl pentene-1, poly-4,4-dimethyl pentene-1, polydodecene-1 and poly-3-methyl pentene-1.

Although the most common polymeric materials falling within the class above outlined are the polymerization products of monomers containing four or fewer carbon atoms, polymerized products of higher order monomers, and copolymers and mixtures containing such polymers may also be stabilized in accordance with this invention. For a discussion of the oxidative mechanism against which protection is imparted in accordance with this invention, see Modern Plastics, volume 31, pages 121 to 124, September 1953.

Some of the polymeric materials included in the class above set forth have already attained considerable commercial importance; notably, polypropylene and the various types of polyethylene. Some of the other materials in this class have excellent electrical and mechanical properties and will doubtlessly find widespread use in the near future.

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Many of the most important applications of polyethylene such as its use in cable sheathings, depend on its very good mechanical properties such as high tensile strength and abrasion resistance coupled with its resistant properties against water and water vapor. Other uses take advantage of its high dielectric strength in applications such as primary insulation of wire conductors. The consequences of thermal oxidation in such polymers are increased in temperature of low brittle point, impairment of tensile strength and poorer dielectric properties. Accordingly, successful use of these materials in applications now contemplated requires the use of good antioxidant materials.

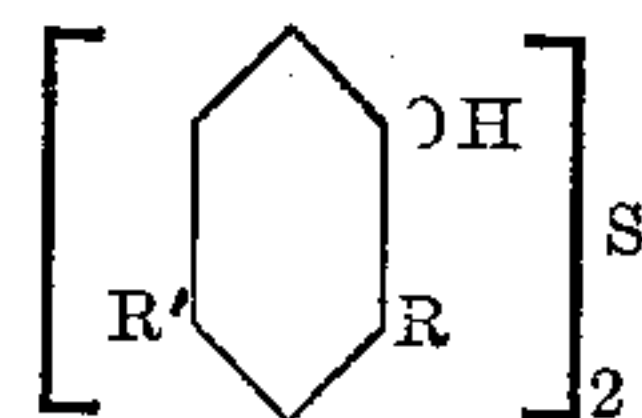
It has previously been found that certain classes of sulfur compounds when combined with various other specific materials and incorporated in small amounts in a polymeric material exhibit a synergistic antioxidant effect. Many of these combinations compare favorably with the best commercial antioxidants. This is set forth in copending applications of Hawkins et al. which were filed November 29, 1956, and issued January 10, 1961, Serial No. 625,577, now United States Patent No. 2,967,850; Serial No. 625,068, now United States Patent No. 2,967,846; Serial No. 625,110, now United States Patent No. 2,967,849; Serial No. 625,109, now United States Patent No. 2,967,848; Serial No. 625,108, now United States Patent No. 2,967,847; Serial No. 672,062, which was filed July 15, 1957, now United States Patent No. 2,889,306, issued June 2, 1959; and Serial No. 625,184, which was filed November 29, 1956, now abandoned.

We have now discovered that two additional types of compounds synergize these same classes of sulfur compounds. These are biphenols and related phenols and aromatic amines each of a specific nature as hereinafter defined.

The sulfur compounds which are synergized by these newly discovered compounds are those previously found to be synergized with carbon black and certain conjugated materials in the copending applications of Hawkins et al. above set forth. It is this class of compounds which is intended to be within the scope of the present invention. This class encompasses generally: various aromatic thioethers, aliphatic and aromatic disulfides, aromatic and aliphatic mercaptans and aliphatic thiuramdisulfides.

More specifically the compounds are as follows:

The specific aromatic thioethers are here distinguished by two groups, aromatic phenolic thioethers and diaryl thioethers. The aromatic phenolic thioethers all contain as substituents in addition to one or more hydroxyl groupings at least one normal or branched alkyl grouping which probably serves the function of sterically hindering the antioxidant functional group. The general formula for these antioxidants which, when combined with the conjugated compound in a polymeric material such as polyethylene, comprises this invention is:



(1)

in which R is a normal alkyl group containing from 6 to 20 carbon atoms or a branched alkyl group containing from 3 to 6 carbon atoms and R' is either hydrogen or normal alkyl group containing up to 6 carbon atoms. In the general formula above, the total number of carbon atoms contained in an entire moiety of the molecule should not exceed about 30 since a greater number of carbon atoms results in impractical compounds difficult and expensive to obtain. Examples of compounds falling within the scope of the general formula above may be found in copending application Serial No. 625,184 of Hawkins et al., now abandoned, which application also

contains a more thorough treatment of this group. Aromatic thioethers of this invention also include the diaryl monosulfides of the general formula A_r-S-A_r' in which A_r and A_r' are fused aromatic ring structures, such as naphthyl or anthryl containing at least one ring substituent selected from the group consisting of hydroxyl radicals and secondary amine radicals and which may contain one or more additional ring substituents such as, for example, hydrocarbon radicals containing up to 20 carbon atoms, however, again with a proviso that the total number of carbon atoms in either moiety including substituents shall not exceed 30. Examples of this group of compounds can be found in Hawkins et al. Serial No. 625,068, now U.S. Patent No. 2,967,846, issued January 10, 1961.

The aliphatic disulfides fall within the general formula $(R-S-S-R')_x$ in which R and R' are aliphatic radicals such as for example, butyl or higher order homologues of the alkyl series and in which one or more hydrogen atoms may be replaced by a hydrocarbon substituent or non-hydrocarbon substituent known to be inert with respect to the polymer to be stabilized such as nitrogen, and x is an integer of at least 1. The R and R' moieties of these compounds may be identical or not, the only requirement additional to those set forth being a restriction of the number of carbon atoms in each moiety including substituents in the exclusive range of from 4 to 30. The lower limit of 4 carbon atoms is necessitated by the high vapor pressure of compounds of this class containing fewer carbons resulting in practical difficulty in introducing the material into the polymer, while the upper limit of 30 carbons is directed primarily to ease of compounding the polymeric materials and to dilution of the antioxidant effect based on the weight percentage range which is practical. A more thorough treatment of these compounds and examples thereof appears in copending application Serial No. 625,108, filed November 29, 1956, now U.S. Patent No. 2,967,847, issued January 10, 1961.

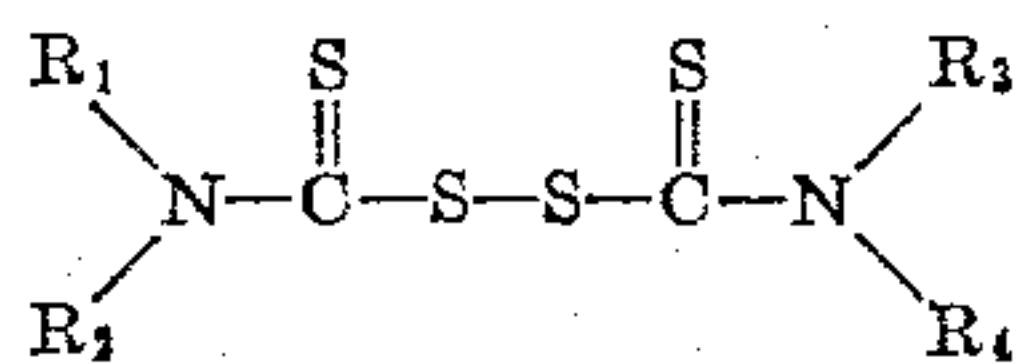
The aromatic disulfides of this invention include the dicyclic-disulfides falling within the general formula



in which R and R' are ring structures such for example as phenyl, naphthyl, anthryl, thiazole or other aromatic or heterocyclic radicals and S is a sulfur atom. Either or both of the cyclic moieties of these compounds may additionally contain one or more aliphatic substituents providing that the total maximum number of carbon atoms in the moiety is 30. Examples of compounds falling within this group may be found in copending application Serial No. 625,577, Hawkins et al., now U.S. Patent No. 2,967,850, issued January 10, 1961.

The mercaptans within the scope of this invention fall within the general formula $R-(SH)_x$. R is either an aliphatic radical having from 6 to 30 carbon atoms including substituents or an aromatic ring structure, for instance, phenyl, naphthyl, anthryl, thiazole or other aromatic or heterocyclic groups, having a maximum of 30 carbon atoms in the molecule. A more complete treatment of this group of compounds and examples thereof can be found in copending applications of Hawkins et al., Serial No. 625,109, now U.S. Patent No. 2,967,848, issued January 10, 1961, and Serial No. 625,110, now U.S. Patent No. 2,967,849, issued January 10, 1961.

The aliphatic thiuramdisulfides appropriate to the invention fall within the general formula



in which R_1 , R_2 and R_3 , R_4 are aliphatic radicals such as, for example, methyl or higher order homologues of the alkyl series and in which one or more hydrogen atoms may be replaced by a hydrocarbon substituent or other substituent, such as nitrogen, known to be inert with respect to the polymer to be stabilized. The R_1 , R_2 , R_3 and

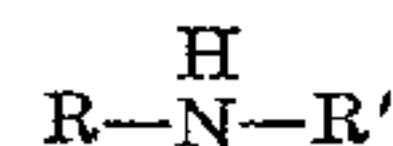
R_4 substituents of these compounds may be identical or not, the only additional requirement being that the sum of carbon atoms contained in each of the paired substituents R_1 , R_2 and R_3 , R_4 be no greater than 30. The maximum imposed on the number of carbon atoms contained in the substituents is directed primarily to ease of compounding the polymeric materials and to dilution of the antioxidant effect based on the weight percentage range which is practical. Examples of compounds falling within this group may be found in copending application Serial No. 672,062, Hawkins et al., now Patent 2,889,306, issued June 2, 1959.

Although in many instances symmetrical sulfur compounds are set forth in the above-referred-to copending applications, it should be understood that unsymmetrical compounds of the same nature are also effective.

The second component of the synergistic mixture according to the invention is at least one compound selected from the following: Biphenols having the general formula



where X is a CH_2 group or a single bond and R and R' are aromatic rings. This invention also includes the derivatives of this formula which include at least this structure. Accordingly, each radical may have additional substituents or condensed rings and the intermediate methyl group may be substituted. The hydroxyl groups may be at any position as long as there is one for each radical; aromatic amines having the general formula



where R and R' are either benzene or naphthylene rings; and those derivatives of this formula which include at least this structure. Accordingly either radical may be substituted or another phenyl group may be attached to either radical (or both radicals) through an amino group as in diphenyl-p-phenylenediamine.

Combinations of these two classes of compounds show a synergistic antioxidant effect which can be appreciated from an examination of the accompanying FIGURES 1-13. Each figure is a plot of accelerated oxidation tests on a polymeric material of the designated class protected with a particular synergistic mixture according to the invention. Each figure contains three curves, one showing the polymer containing only a sulfur compound according to the invention, one showing the polymer containing a phenol or amine according to the invention, and a third showing the polymer protected with the synergistic mixture of both of these compounds. Also, control curves for the unprotected polymers have been included. The procedure used for these accelerated tests is hereinafter described.

The coordinates on each figure are oxygen uptake and grams per cubic centimeter of the sample (ordinate) versus time in hours (abscissa). The oxygen uptake rate is a measure of oxidative degradation of the sample. Each of FIGS. 1-12 illustrates the antioxidant properties of one combination according to the invention. The curves designated A and B are control curves showing the stabilizing effect of each material separately. The letters A and B on the curves correspond to the compounds similarly marked. The third curve in each instance designated "COMB" is of course the synergistic combination of compounds A and B according to the invention. FIG. 13 is included as a control curve showing uninhibited polyethylene and polypropylene. FIGS. 1-6 are concerned with the various sulfur containing components while FIGS. 7-12 show the various amine or phenol according to the invention. In FIGS. 1-6, each type of sulfur containing compound was tested with a typical phenol, namely, 4,4' biphenol. In each of FIGS. 7-12, various amines and phenols were tested with a single sulfur containing material, specifically, 2 naphthalenethiol.

The specific combinations of compounds illustrated by each figure are:

FIG. 1, 4,4' biphenol with an aromatic phenolic thioether specifically thiobis- β -naphthol;

FIG. 2, 4,4' biphenol with an aliphatic disulfide specifically di-dodecyl disulfide;

FIG. 3, 4,4' biphenol with an aryl disulfide specifically di- β -naphthyl disulfide;

FIG. 4, 4,4' biphenol with an aliphatic mercaptan specifically dodecyl mercaptan;

FIG. 5, 4,4' biphenol with an aromatic mercaptan specifically 2-naphthalenethiol;

FIG. 6, 4,4' biphenol with a thiuram disulfide specifically methyl thiuramdisulfide;

FIG. 7, 2,2' methylenebis - (4 - methyl - 6 - tert - butyl phenol); with 2-naphthalenethiol;

FIG. 8, 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxy biphenyl with 2-naphthalenethiol;

FIG. 9, phenyl- β -naphthylamine with 2-naphthalenethiol;

FIG. 10, diphenylparaphenylenediamine with 2-naphthalenethiol;

FIG. 11, 4,4' biphenol with 2-naphthalenethiol in polypropylene;

FIG. 12, phenyl- β -naphthylamine with 2-naphthalenethiol in polypropylene;

FIG. 13, uninhibited pure polyethylene and uninhibited pure polypropylene alone.

In FIGS. 1-10 above the polymeric material treated was polyethylene. In order to illustrate the adaptation of the antioxidant materials of this invention to the higher order polymers, two runs are reported for polypropylene. The plot for these runs appears in FIGS. 11 and 12.

The amounts of each component of the synergistic mixture are not critical, however, a minimum of 0.01% by weight of each is necessary, for significant antioxidant effect. A maximum of 10% by weight of the mixture is a practical upper limit beyond which the polymer fails to retain sufficient mechanical strength. However, for economical reasons a maximum of 5% of the mixture is preferred. There is no requirement that the two components of the mixture be used in equal proportion; however, in all the examples appearing herein, 0.1% by weight of each component was used.

It was found expeditious in the experimental procedure to employ equal weight measures of each component; however, it is obvious that for each combination of components a particular weight ratio based on molecular formulas results in optimum effectiveness for a minimum of material used; however, any mixture falling within the limits above delineated—0.01% by weight of each component to a combined weight of 10%—falls within the scope of this invention.

The figures presented are representative of data taken from a standard accelerated aging test for polymeric materials. Such tests are well known and data taken therefrom is of known significance. To aid the description of this invention an outline of the accelerated testing procedure is as follows:

The saturated hydrocarbon polymer, together with a mixture of each component of the classes set forth above, was prepared by mill massing on a 6 inch by 12 inch 2 roll mill having roll speeds of approximately 25 and 35 r.p.m. with the rolls at a temperature of about 120° C. One tenth percent of each retarder was incorporated into the polymer being tested. The polyethylene used in these studies was of commercial high molecular weight, high pressure polymer supplied by the Bakelite Company as DYNK. The polypropylene used was Profax-6501 made by Hercules Powder Company which is a virgin, uninhibited polypropylene.

Test samples weighing 0.1 gram in the form of strips approximately 10 mils thick were cut from the polymeric material containing the antioxidant mixture. These strips were placed in a Pyrex glass tube attached to a mercury monometer together with about 2 grams of

type 5-A Linde Molecular Sieve, a synthetic zeolite absorbent. The reaction vessel, after being successively evacuated and filled with oxygen to assure a complete oxygen environment, was again filled with oxygen and was placed in the air-circulating strip-heater oven maintained at 140° C. and of such design to insure a variation of no more than 1° C. throughout the volume in the oven. The reaction vessel was immediately connected to an oxygen gas burette with a short length of polyvinyl chloride tubing. After reaching a temperature equilibrium at the said temperature of about 140° C., which took about 15 minutes, the system was adjusted to zero reading at atmospheric pressure. Readings of oxygen uptake were made as required at atmospheric pressure, one such reading being taken every 4 to 12 hours.

Referring again to the figures, the coordinates are oxygen-absorbed in cubic centimeters per gram of sample (as measured on the mercury-filled monometer) on the ordinate and time in hours on the abscissa. The plotted data was taken from a run in which the polymeric samples were maintained at a temperature of 140° C.

In interpreting curves such as these, it is here assumed that the useful properties of polyethylene and other polymeric materials included in the class previously set forth are not critically affected until the amount of oxygen absorbed by the polymer is of the order of .5% by weight. This is equivalent to about 10 cubic centimeters of oxygen absorbed in the ordinate units. Using this value of 10 cc./gram sample which is denoted by a cross on each figure it is readily apparent that each figure shows a significant synergistic effect in the curve representing the mixture of compounds according to the invention.

Another factor often considered in evaluating antioxidant action is the length of the "induction" period. This is the period at which the antioxidant appears to break down completely offering no further effect so that the polymer appears to absorb oxygen at its normal uninhibited rate. The induction period is obtained by extrapolating the curve beyond the point where a significant upswing in O₂ absorption occurs, i.e., point X in FIG. 1, back to the abscissa. The value obtained, Y in FIG. 1, about 350 hours, is a measure of the length of time the antioxidant is effective. As is seen, some of the figures show curves which fail to show an induction period. However, in many of the curves it is evident that the synergism reflected by the increase in induction periods is even greater than that reflected in the other standard, i.e., oxygen absorption of 10 cc./gram of sample.

Whereas specific compounds and groups of compounds have been herein set forth as appropriate for either component of the inventive synergistic antioxidant mixture, they are not intended as limiting the scope of this invention. It will be apparent to those skilled in the art that any compound having the same general character as those specifically set forth can be employed without departing from the scope of the appended claims.

What is claimed is:

1. A composition stabilized against oxidative degradation comprising a polymer of an alpha-mono-olefin having 2 to 12 carbon atoms and a stabilizer consisting of two components, each of said components being included in an amount of at least 0.1% by weight and the maximum amount of both components together being 10% by weight, a first component selected from the group consisting of

aromatic disulfides having the general formula



in which R and R' are ring structures each containing at least one carbon atom and in which the maximum number of carbon atoms in each of the said ring structures including substituents is 30,

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alkyl disulfides having the general formula



in which R and R' are alkyl radicals each containing from 4 to 30 carbon atoms

aromatic mercaptans having the general formula R—SH

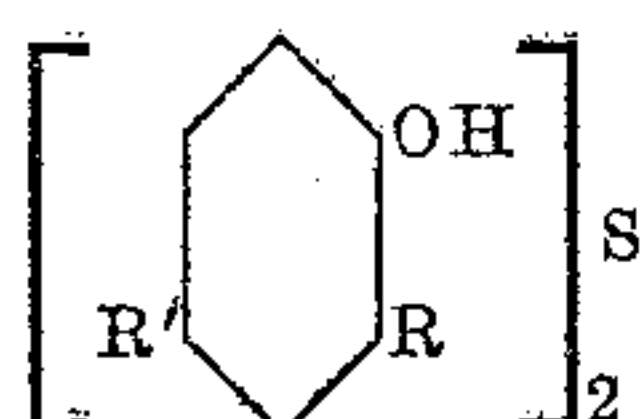
in which R is a ring structure containing from 1 to 30 carbon atoms,

aliphatic mercaptans having the general formula



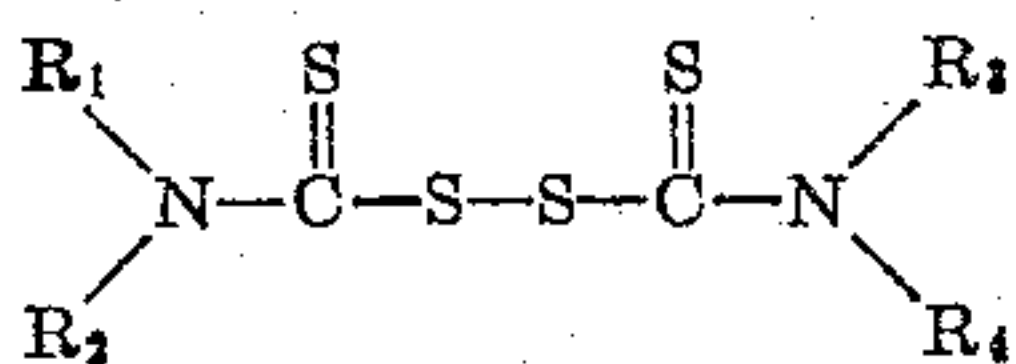
in which R is an alkyl radical containing from 6 to 30 carbon atoms, and x is an integer having a maximum value of two,

aromatic thioethers having the general formula:



R is selected from the group consisting of a normal alkyl group containing from 6 to 20 carbon atoms and a branched alkyl group containing from 3 to 6 carbon atoms, and R' is selected from the group consisting of hydrogen and a normal alkyl group containing up to 6 carbon atoms, and the total number of carbon atoms in R and R' does not exceed 30, diaryl thioethers having the general formula Ar—S—Ar' in which Ar and Ar' are fused ring carbocyclic benzenoid aromatic radicals containing at least one substituent selected from the group consisting of hydroxyl radicals and secondary amine radicals and further in which compound the maximum number of carbon atoms in each fused ring moiety including substituents is 30

aliphatic thiuramdisulfides having the structure



in which R₁, R₂, R₃ and R₄ are aliphatic groups and in which the total number of carbon atoms contained in each of the substituent pairs R₁, R₂ and R₃, R₄ is from 2 to 30,

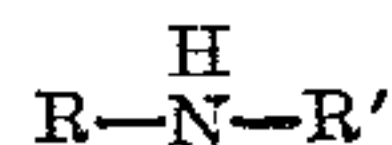
and a second component selected from the group consisting of

phenols which are characterized by the general formula:



where X is selected from the group consisting of a CH₂ group and a single bond, and R and R' are aromatic rings,

amines which are characterized by the general formula:



where R and R' are selected from the group consisting of benzene and naphthylene rings.

2. The composition of claim 1 wherein the first component is an aromatic disulfide.

3. The composition of claim 1 wherein the first component is an alkyl disulfide.

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4. The composition of claim 1 wherein the first component is an aromatic mercaptan.

5. The composition of claim 1 wherein the first component is an aliphatic mercaptan.

6. The composition of claim 1 wherein the first component is an aromatic thioether.

7. The composition of claim 1 wherein the first component is a diaryl thioether.

8. The composition of claim 1 wherein the second component is a phenol.

9. The composition of claim 1 wherein the second component is an amine.

10. The composition of claim 1 wherein the hydrocarbon polymeric material comprises polyethylene.

11. The composition of claim 1 wherein the hydrocarbon polymeric material comprises polypropylene.

12. The composition of claim 1 wherein the first component is naphthalenethiol.

13. The composition of claim 1 wherein the first component is di-dodecyl disulfide.

14. The composition of claim 1 wherein the first component is di-β-naphthyl disulfide.

15. The composition of claim 1 wherein the first component is thiobis-β-naphthol.

16. The composition of claim 1 wherein the second component is 4,4'-biphenol.

17. The composition of claim 1 wherein the second component is phenyl-β-naphthylamine.

18. The composition of claim 1 wherein the second component is diphenyl paraphenylene-diamine.

19. A stabilized polymeric composition comprising a polymer of an alpha-mono-olefin having from 2 to 12 carbon atoms and a stabilizer consisting of two components, each of said components being included in an amount of at least 0.1% by weight, and the maximum amount of both components being 10% by weight, the first component selected from the group consisting of thiobis-β-naphthol, di-dodecyl disulfide, di-β-naphthyl disulfide, dodecyl mercaptan, naphthalenethiol and mixtures thereof, and the second component selected from the group consisting of biphenol, 3,5,3',5'-tetra-tert.-butyl-4,4'-dihydroxy biphenol, 2,2'-methylene-bis-(4-methyl-6-tert.-butyl phenol), phenyl-β-naphthylamine, diphenyl paraphenylenediamine and mixtures thereof.

References Cited by the Examiner

UNITED STATES PATENTS

2,479,948	8/1949	Luten	260—45.95
2,543,329	2/1951	Myers et al.	260—45.9
2,829,121	4/1958	Leeper	260—45.9
2,889,306	6/1959	Hawkins et al.	260—41
2,967,845	6/1959	Hawkins et al.	260—41
2,967,846	6/1959	Hawkins et al.	260—41
2,967,847	6/1959	Hawkins et al.	260—41
2,967,848	6/1959	Hawkins et al.	260—41
2,967,849	6/1959	Hawkins et al.	260—41
2,967,850	6/1959	Hawkins et al.	260—41
2,985,617	5/1961	Salzer et al.	260—45.9
3,004,949	10/1961	Chevassus	260—45.75

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