THE AGING OF SBR VULCANIZATES

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THE AGING OF SBR VULCANIZATES

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Abstract

A literature survey was conducted on SBR aging. Being vulnerable to attack by the forces of nature (such as ozone, oxygen, heat and light), SBR vulcanizates requires the addition of chemicals to retard aging. Phenylamines were found to be the best type of antiaging additives. The effectiveness of other antiaging additives were examined. Although the mechanisms of aging are not perfectly understood; some theories and aging reactions are discussed.

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* Shelton and Wickham, Ind. and Eng. Chem. 49, 1277-81 (1957).

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* P. Lyon, K. A. Burgese and C. W. Sweitzer, Ind. and Eng. Chem. 48. 1544-6, (1956).

Introduction

The aging stability of SBR is influenced by heat, cold, light, and atmospheric conditions. Since SBR contains a large concentration of unsaturation available for chemical attack, the problem of protecting SBR is magnified. These bonds are especially vulnerable to attack by oxygen and ozone. In SBR, peroxides are initially formed and the rubber becomes hard and brittle. Intermediate free radicals are formed to set off repetitive reactive cycles.

Improvements in the resistance to attack by oxygen have been achieved by the incorporation of protective chemicals. Antioxidants may be separated into two broad classifications: aromatic amines and phenols. For SBR; the choice of the antioxidant is governed by the application. Some antioxidants have staining characteristics which do not interfere with their use in rubber compounds for tires, hoses, and belts. However, non staining antioxidants are required for light colored end products or rubber compounds with light colored surfaces.

Ozone cracking occurs especially when the SBR vulcanizate is subjected to high stress. Insoluble waxes bloom to the surface to prevent ozone attack; however, once the brittle waxes crack the wax becomes useless.

Presently the majority of commercial antiozonants contain substituted p-phenylene diamines. Mechanisms for antiozonant protection have been proposed; but currently none has been proven. The major principle involved is the preferential combination of the ozone with antiozonant instead of SBR.

Sunlight, primarily ultraviolet, has damaging effects on improperly formulated SBR vulcanizates. SBR attacked and damaged by U V light has a resinous or crazed appearance. It is interesting to note that antioxidants offer no protection against ultraviolet attack. If necessary, ultraviolet absorbing materials such as salicylates and benzotriazoles can be used in light colored products. Carbon black, however, offers excellent protection against sunlight.

Gamma radiation can damage SBR through a free radical mechanism which forms excessive crosslinks. Free radical traps offer sufficient protection.

The use of antiaging additive in SBR requires a considerable degree of skill in that the application as well as the environment in which the vulcanizate is to survive must be considered.

Rubber Antioxidant Applications

In order that the various applications for rubber antioxidants may be clarified, the following definitions are included:

A. Polymer stabilizers are added in the polymerization plant to inhibit the reaction with oxygen during storage and drying of the uncured resin.

B. Antioxidants - chemicals added during compounding to prevent oxidative changes which occur during processing.

C. Flex crack retarders - chemicals added to the rubber to prevent the growth of cracks while the rubber undergoes stress.

D. Antiozonants - substances which combat the reaction of the rubber with ozone.

Methods

Much can be written about various techniques employed to measure the variable which affect rubber aging. Many tests are used routinely but this section will survey some newer techniques.

McPherson (National Bureau of Standards) has summarized several methods in his work (1). (See his chapter on Deterioration of Rubber - 21 references).

A statistical method has been developed by Kase (2) who assume a certain tensile strength distribution.

Ozone attack can be measured by the use of a simplified apparatus.(3) A constant concentration of ozone is used. Of course the apparatus must be constructed of materials impervious to attack by ozone. A concentration of 2.7 centimeters per mole of air gives reproducible results. Photographs of samples are compared with standard photographs of SBR and butyl rubber.

A special jig can be used to hold dumbells in air aging ovens (4). Infrared spectra is a more sophisticated instrument used to follow the progress of SBR aging. One can measure the changes in the following bands: C=O, O-H, and C+C (5). Infrared spectra can be used to follow againg caused by heat and light by using the following equation: (6)

$$W = (k/B)(1 - e^{-Bn})(1 - V)$$

W = aging rate; V- oxidized concentration; k,B,n are constants.
The study of aging (reaction kinectics) can use similar equations. (7)
As an analytical tool, I.R. can be used to identify accelarators and antioxidants in compounded products. (8)

To evaluate the aging of SBR one can compare aged by unaged tensile strength data and oxidative crosslinking (volume swelling technique). (9) Some rubber is virtually unaffected by 120 hours at 177°C in an autoclave. One test method is to age thin films. Here various oxidizers such as HIO_3 can be used. (10)

Changes in the oxygen permeability of aged films can be measured. (11) If performed accurately, accelerated aging tests have tremendous commercial value. (12) Combined results show that an accelerating test should not be limited to one temperature. The rate of deterioration of a physical property depends on the composition of the individual vulcanizate. This is to be expected since the antiaging additive alone could be the difference. It appears that the logarithm of the time necessary to reduce the tensile strength is a function of the reciprocal of temperature. In another study, the correlation of accelerated tests was poor. (13) The weatherometer can be used to study SBR aging. However, it is not as useful as an ozone - air oven. (14)

An aluminum block with controlled heaters yields useful heat aging data. (15) (16) Pyrolysis of rubber yields useful data. (17) This type of degradation reveals heat resistance and general chemical composition. At temperatures approaching 400°F in a vacuum, SBR offers little resistance.

Excess antioxidant hurts the aging properties of SBR as measured by the change of oxygen absorption and the deterioration of physical properties. (18)

Viscosity changes are valuable in the evaluation of antiozonants. (19)

A solution is prepared by dissolving 0.5 grams of SBR vulcanizate in an appropriate hydrocarbon solution (e.g. toluene). Ozone is passed through the solution and the resulting change in viscosity is noted.

In another evaluation of various antioxidants. Oxygen is passed through a solution of vulcanizate dissolved in dipentene. (20)

Classification of Antiaging Additives

In the appendix several tables classifying the various antiaging additives have been included. Antiaging materials can be categorized (1) by function (antioxidants, antiozonants, and anticracking); (2) by commercial applications; (3) by chemical groups. The lists found in the appendix are rather comprehensive. Some additives have been used widely in SBR vulcanizate applications, but others are simply laboratory curiosities.

Amine antioxidants have been divided into the following categories:

I. Secondary diarylamines:
    A. Phenylnaphthylamine
    B. Substituted diphenylamines
    C. Para - phenylenediamines
II. Ketone - amine condensates.
III. Aldehyde - amine condensates.
IV. Alkyl - aryl secondary amines.
V. Primary arylamine.

Phenolic antioxidants may be classified as follows:

VI. Hindered Phenols.
VII. Hindered Thiophenols.
VIII. Hindered Bisphenols.
IX. Polyhydroxy Phenols.

I. Secondary diarylamines A) N - Phenyl and N - 1 - naphthylamines are widely used as antioxidants and are found to perform well for a wide variety of applications. B) Substituted diphenylamines. These antioxidants are to volatile for practical use. The octylated and nonylated derivatives are available commercially. C) Paraphenylenediamines. $N - N^1$ - Diphenyl - p - phenylenediamine is used in combination with other amines due to its low solubility in SBR. A mixed diaryl - p - phenylenediamine is very effective in inhibiting oxidation and flex cracking.

II. Ketone amine condensates: this group is particularly effective at elevated temperatures; many compounds in this group are complex and identification has not been made.

III. Aldehyde Amine Condensates: Heat aging is the best feature of this group, which gives moderate antioxidant activity.

Classes IV and V have little commercial value. VI. Hindered Phenols - this group includes 2,4,6 trialkylphenols which exhibit considerable antioxidant activity. However, bulky groups located in the ortho position can reduce the effectiveness of the antioxidants.

VII. Hindered thiobisphenols - these materials are slightly more active than those in group VI; but stain a little more.

VIII. Alkylidene bisphenols - An extremely important group which offers activity without staining; these compounds have many applications. However, one disadvantage is their rather poor protection against flex cracking.

IX. Polyhydroxy Phenols - Some members of this group have been used as polymer stabilizers.

Antioxidant - Antiozonant Evaluation

Since there exists a myriad of candidate materials which could serve as SBR antiaging additives; it is important to determine the effectiveness of these materials efficiently. In most cases the rubber technologist wishes to test these chemicals in the SBR vulcanizate to obtain the ultimate limits quickly. (Tests could be performed at elevated temperature under adverse conditions). The American Society for Testing Materials (ASTM) has designated some standard tests to be used for this evaluation. Generally, SBR vulcanizates should be exposed to all common degradative conditions, including UV light, ozone, oxygen, oxygen at elevated temperature, and gamma radiation.

Shelf and Heat Aging Tests: Accelerated tests for shelf and static aging are based on ASTM tests D573 - 53 and D865 - 62. SBR vulcanizates are subjected to heat aging at 70°C for seven days. Two other tests, ASTM D572 - 67 and ASTM D454 - 53 involve conditions of 70°C at 300 psi oxygen and 127°C at 180 psi air pressure.

The physical properties should be compared before and after heat aging to indicate the effectiveness of the additive.

Flex Cracking

Under constant stress, cracks can develop on the surface. Although there are numerous tests for the evaluation of anticracking additives; it is difficult to separate the affects of flex cracking from fatigue cracking, weather checking, and ozone cracking. The specimens are flexed through a series of cycles and rated against standard specimens.

Polymer Stabilizer Evaluation

To evaluate the effectiveness of a polymer stabilizer, the change in the following properties are observed:

A. viscosity
B. color
c. gel formation
D. surface texture
E. reversion

Viscosity as measured typically by the Mooney Viscometer could increase or decrease when the polymer is under oxygen attack. Oxygen degradation decreases viscosity; but crosslinking produces the opposite effect. However, if both effects would balance simultaneously, then the net change in viscosity would be nil.

Antiaging Additives

The following sections survey the various antiaging additives which can be used for SBR. It is important to recognize that different antiaging additives protect in different ways. An additive effective against heat aging may be ineffective against ozone attack. A material can act as an antioxidant under one set of conditions only to be ineffective under other conditions. Generally, amine antioxidants act by reacting with free radicals and by cleaoing peroxider. Phenolic antioxidants react mainly as free radical traps or chain stoppers. Phosphates function by reacting with free peroxides. Since the chemistry of aging is complex and not understood completely; a combination of additives can have much greater affect than single additives.

Carbon Black As Antiaging Additives

Carbon black is a major part of virtually every SBR formulation. It has been found that carbon black, in addition to acting as a reinforcing agent (giving the vulcanizate improved physical properties) has antiaging character (1, 2, 3, 4). As Lyons, Burgess and Sweltzer (1) indicate in their article, if one could understand all the complicated interactions of carbon black with respect to polymer oxidation and cure mechanisms; it would be possible to control the behavior of carbon black so that SBR with better properties could be designed. Shelton and Wickham (2) employed three types of carbon blacks for their investigations. It can be seen that complications could arise due to the number of carbon blacks and curing systems. Attempting to isolate variables within such a complicated system makes life for the theoretical rubber chemist difficult indeed. A special article concerning the effect carbon black has on tire aging was written by Williams (4). An investigation made of carcass type compounds containing furnace type blacks varying in specific area from 16 to 134 square meters per gram showed that the finer blacks gave lower rebound and higher temperature resistance without improvement in hot tear strength. The inclusion of zinc oxide lowered the hot tear strength. FEF (Fast Extending Furnace) black was adequate for passenger cars and small truck tires.

Amine Antiaging Additives

Aiken (1) mentions the use of an amine sequestering agent, ethylenediamine tetracetic acid. The mechanism behind the success of the additive could be the combination of the additive with free metal. It has been shown that heavy metals accelerate the oxygen attack of the double bond.

Amines have been classified as staining type additives. Naphthylamines were found to be effective; in particular decahydronaphthylamine (2). A series of naphthylamines were found to be excellent antiaging additives (3).

A more complicated naphthylamine, O - Benzoyl - N - Phenyl - N - B (naphthyl) hydroxylamine was effective in combatting ultraviolet, heat or sunlight. (4)

A comparative study of various amines was made by Novikova (5).

The following materials were rated: (1) Naphthalene, (2) B - naphthal, (3) 2 - naphthal, (4) aldolpaphthylamine, (5) 2 - hydroxylpropyl aldehyde - 1 - naphthylamine, (6) 1 - naphthylamine, (7) naphthylamine, (8) nitronaphthylamine. In the presence of iron the ratings were: 2,4, 3, 5, 6, 7, 1, 8 respectively.

N - substituted ureas of the type:

$$RN\ HC(:X)\ N\ (R^{1})\ (R^{111})$$

can be included in SBR recipes (6).

N - hydrocarbon substituted ureas are particularly effective as cracking inhibitors (7). (General Formula: $RR^{1}NCXNR^{11}R^{111}$).

Test results showed that 20 - 30 ppm ozone for 56 hours produced only slight cracking, while the control showed severe cracking.

A variation of the amines previously discussed involves the inclusion of a sulfur group. These antioxidants in some instances also serve as accelerators for vulcanization. One type symthesized by Chemah (8). B - alkylpropionamides. Another general type has the following general structure (9):

$$R\ S(:O)\ N(R)(R^{11})$$

A combination of a mercaptogroup and a phenol could be used as accelerators or antioxidants. (10)

Higher aliphatic amines (11) are for less complicated structurally. A variety of triethanolamine products have been evaluated (12). Certain amines have a synergistic effect as SBR stabilizer. (13 and 15). A combination of two or more amines could be more effective than one by itself. DePree used a combination of aliphatic and

arylamines (14), ----$RR'(N(CH_2)_4(CHR)_yN(R'')(R''')$---
other amines contain alkyphenyl groups. (arylamines)

Diarylamines contain two alkylphenylgroups. Phenylamines contain no alkyl groups. In the presence of copper and manganese the use of a combination of mercaptobenzimiazoles and di substituted p - phenylenediamines were found to be effective antioxidants (17).

The effectiveness of an amine antioxidant could be increased by the use of the following combination, diarylamine cyclohexylamine (18).

Beil (19) employed N-N- Bis (hydroxydialkybenzyl) alkyamines.

Phenyl 2-naphthylamine containing two types of aromatic groups were employed as antiaging additives by Davis (20). Diphenylamine can also be used (21).

The replacement of all the hydrogen atoms attached to the amino nitrogen by alkyl groups enables N-N*-N*-N- tetra alkyl- p - phenylenediamine to be used as anticracking additives for SBR (22).

Thompson utilized aromatic amines to stabilize SBR latex (23). Included in the series he evaluated 2 and 2,4 bis (dodecylamino) 1,8 methylene naphthalene and alkoxyaminonaphthalenes. SBR vulcanizates formulated with 3,4,5 triethoxyaniline and N - cyclohexylaniline were investigated by Thompson (24). Substituted thiocarbonyl-p-phenylene diamine could be used as antioxidants in conjunction with either bis hydroxyphenyl methane and/or hyroquinone (25).

Merrifield used an interesting combination of additives, N-nitroso0 N-N' dialiphatic arylene diamine (26).

Tucker employed aminoalkyl benzenes as antiaging additives (27).

Roussel found that 1,3 diene-containing- vulcanizates were stabilized by using 0.25% - 0.5% by weight of a diarylamine (28). This is similar to the additive patented by Schneider (29). ($R'C_6H_4NHC_6H_4R$).

Phenyl-B-naphthylamine has been studied as an antiaging additive for SBR (30) (31). Day condensed a diphenylamine and an aliphatic ketone. (32)

An exotic amine salt synthesized by D'Amico and Herman has limited use (33). (assigned name: Di (loweralkyl) cyclohexylamine salts of 2,5 dimethyl - 4 - piperazine dicarbothiocacid).

To improve the age resistance of SBR, Harris employed 3-aminocarbazole (34). Coulter found that a morpholine derrivative served as an excellent scorch resistor during vulcanization (35). Specifically, the compounds were of the type N-N mono or dithiomorpholine.

Phenols and Phenoxy Derivatives

The nonstaining type of antiaging additives consist mainly of phenol and/or phenoxy derivatives.

Webb (1) investigated several phenol derivatives as nondiscoloring age resistors. Many of these chemicals have been included in the recipes of butadiene containing rubbers (2). Lambert and Sullivan synthesized some alkyl phenols for use as antioxidants (3). Composite antioxidants consisting of bis-hydroxydimethylphenyl derivatives of butane and methane were evaluated by Pelfreeman (4).

Quinones can be used in conjunction with mercaptans (5). Many types of alkyl groups can be attached to the phenol ring. (6) In fact, Chenick employed phenols with three alkyl substituents (7).

The following complicated ether has been incorporated into SBR recipes: (8) 3,5 (di tert-butyl-4-hydroxyphenyl-isobutyl) dodecyl ether. A simpler ether type, equally effective, contains trialkoxy phenols (9). The alkoxy group (-OR) para to the -OH group (e.g. 4-alkoxy phenol) was studied by the team of Davey, Lambert, and Williams (10).

A complicated phenol was synthesized and evaluated by Sullivan and Davis: (11) (2,6 bis (2-hydroxy-3-tert-butyl-5-alkylbenzyl) 4-methyl phenol.

Williams used a series of 2-alkyl-4-alkoxy phenols (12). The alkyl group evaluated included methyl, ethyl, isopropyl, butyl, and

3,4,4 trimethyl hexyl and dodecyl.

Phenyl phenols of the type 1,2,4,6 $(oH)(R)R'C_6H_{11}CH_2$ were used (13).

Some antioxidants contain two phenyl groups. Morris evaluated the following elaborate propyl derivative: (14) 1,2 bis (2-Hydroxyl 4,5-dimethylphenyl) propane. Bankert investigated a methane derivative 2-2 methylenebis- 5 isopropyl phenol (15). Some phenols are mixtures of several products such as results from the reaction of 2,6 bis (hydroxyl-methyl) 4- phenyl phenol and alkyl phenols (16). Foreman used the following series of alkyl phenols (17): $(OHR_x(C_6H_4CHRC_6H_4)$. (R = H or 1 - 10 C atoms).

Lambert employed a complicated cycloalkyl type: 3 a- (alkyl-cycloalkyl) - 5-methylphenyl methane (18).

By formulating with a sterically hindered phenol at a level of o.4 - 1.25%; SBR can be effectively stabilized (19). Davis and Sullivan selected 2-2 methylene bis (4,6- dialkyl) phenol for this purpose.

A group headed by Young used a series of biphenyl compounds. (No phenols here.) (20) Synergistic antioxidants employing phenylphenols were studied by Spacht (21). Possible candidates as candidates for SBR are phthalidylalkyl phenols (22). Bis (hydroxyphenyl) alkanes were studied by Forma (23).

Metal compounds combining aluminum, barium, calcium, magnesium, strontium, and zinc with phenols can be effective as SBR antioxidants (24).

Derivatives of bisphenol ethane at the level of 0.25 - 2% can be utilized in SBR vulcanizates (25).

The alkylated bisphenols discussed by Jansen contain structures previously listed (26).

Various halogens can be inserted into the phenol ring (27) (28). Bromine and chlorine would be more useful in these compounds than fluorine and iodine.

Various condensation products with undetermined configurations (perhaps polymerization is involved) have been applied to the SBR aging problem (29,30,31,32).

Various phenolic resins consisting of repeating monomers as presented in this section have been used as both antioxidants and antiozonants. (33,34,35,36)

Sulfated alkylphenols can serve as antioxidants, antiozonants, and vulcanizing accelerators. (37) (38)

Similarly, styrenated phenol can be incorporated into SBR for antioxidant protection. (39)

Andonol derivatives having an exotic structure have been used: (40)

$$R^{1}(OH)\ C_6H_3\ (\underline{C(R^{1^1})(CH_2)\ R\ (OHCH_3R''CH_3)})$$

Quinoline Derivatives

Although quinoline derivatives have not been used in commercial applications; much laboratory evaluation has been done. At levels of 1.5 - 3.0 parts by weight (on 100 pbw SBR polymer); Harns evaluated 1,2,3,4 tetrahydroalkyl quinoline substitutes (1). Perrolti and Castefranchi (2) used bi and polycyclic 1,4 hydroquinoline compounds as potential new stabilizers for synthetic elastomers. Wilde (3) employed another variation, 2,2,4 trimethyldecahydroquinoline.

Webb oxidized 2,2,4 trialkyl - 6 - substituted trialkyldihydroquinolines and found the resulting combination of products useful as rubber antioxidants (4) (5).

Harns and Turry (6) employed substituted amino 1,2,3,4 tetrahydroquinoline as a GRS antiozonant.

Thompson utilized a combination of quinoline derivatives, wax and other antioxidants (7). A GRS carbon - black - filled - stock was impregnated with these materials by swelling. (immersion in a solution of 6 - isopropylamino quinoline). Vulcanizates showed no cracks when exposed to 50 ppm ozone at a level of additive of 2.6%.

Esso engineering (8) evaluated I - phenylsulfonyl 8 - hydroquinoline chloride as a rubber antioxidant.

Hand and Tamolin protected vulcanizates against ozonation by using 6 - alkoxy - 1 - nitrosodihydroquinoline (9).

Dibbo tested a combination of 6 - alkoxy - 2,2,4 trimethyldihydroquinoline and p - phenylenediamine substitutes (10). He found that in most cases two additives gave better protection than one.

Miscellaneous Additives

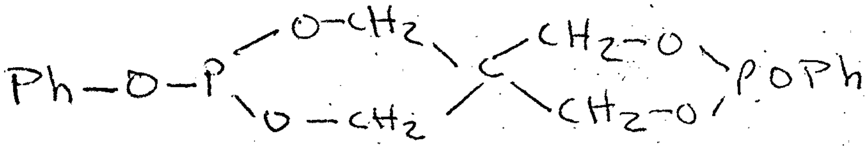
Various metals (mostly heavy) can be used in combination with standard organic groups.

One type consists of metal napthenates (1). Antimony compounds were evaluated by Hunter (2). Rarysden (3) evaluated some tin derivatives of tris (mercapto) borate esters. Various tin esters of the general formula $R_nSn(Sn(COOR")X)_{4-n}$ were found to nonstaining, nondiscoloring antioxidants for rubber (4). Weinberg and Tomka studied partial esters containing tin fatty acids (5). (example tin rinoleate) Weinberg and Ramsden studied the stabilization of SBR with hydrocarbon tin mercaptoalcohol esters (6). Manganese and copper salts were evaluated by Novikova (7).

Thompson tested 3,6 dihexyl tropolene as metal deactivators (8).

Chlorosulfonated polyethylene was incorporated into butyl containing rubber (9).

An interesting pentaerythratol derivatives was synthesized and tested by Lanou (10).



This compound has potential as an SBR antioxidant.

Other phosphates; of the type dialkyl - throphosphoric acid were used to combat ozone (11).

Esser found that 2,3 camphenediol at the level of 5% (by weight of rubber) had potential for antioxidant potential (12).

Use of a wax such as Sunoco anticheck can be effective as an antiozone agent (13).

Agents consisting of paraffin wax, alkyl phenols, polyethane and polyisobutylene can be used for this purpose (14).

Review of Mechanisms

Rubber - aging - mechanisms, although widely investigated, are still not understood completely. Since butadiene is one of the key building blocks in the SBR molecule, a study of the reaction of ozone with polybutadiene - containing rubbers is of great interest (1) (3). The kinectics of ozone, and its interaction with rubber has been studied by a Russian team (2). Since the unvulcanized double bond is most vulnerable to attack, the conversion of double bonds into crosslinks becomes important. Another Russian team performed a study of the conversion of sulfur bonds (as reacted with unsaturated sites) by thermal effects (4).

The possibilities of various chemical interactions stagger the imagination. Monta studied the reactions for systems containing mercaptobenzothiazole heated in air (5). He found that the free sulfur content decreased under heat aging conditions. Ossefert studied the influence of accelerator residues on age resistance of elastomeric vulcanizates (6).

A group of Russians studied the reactivity of free radicals and the role of the polar factor (7). LeBras and Dagjard proposed mechanisms for the deactivator effect (8). They proposed a different mechanism for compounds which prevent the deterioration of rubber aside from those connected with antioxidants. A compound such as zinc mercaptobenzimidazole retards deterioration by forming bonds which are able to repair damage caused by breaking of linkages. (The vulcanized rubber forms a three dimensional network).

Infrared spectroscopy was utilized by Salimov and coworkers (9). Key bands studied included: N-H @ 3450 and 860cm^{-1} and free radicals @ 2400cm^{-1}- 3200cm^{-1}.

N.F. Emolenko (10) postulated the following: the theory of rubber oxidation has two viewpoints. One theory is that oxidation occurs at double bonds; another at a - methylene groups. In either case the antioxidants are absorbed by polymer chains.

The induction period observed in oxidation is the time required for antioxidant desorption and liberation of active groups in the chain. Antioxidants prevent scission of chains.

Angert and Kuzminskii studied the kinectic of amine inhibitor (11). Below 70°C the inhibitor concentration has a direct effect on the rate of oxidation, conjugation assists the effect of the inhibitor.

The deuterium isotope effect of inhibited oxidation of SBR was studied by Shelton and McDaniel (12). It was concluded that the controlling step in the mechanism of autooxidation is the abstraction of hydrogen by peroxy radicals.

The studies and ideas proposed for the aging of rubber have been summarized by Delattre and LaBras (13) (14).

Chemical Reactions Involved In the Degradation of SBR

AH = antioxidant

RH = polymer molecule

R. = polymer free radical

RO. = polymer alkoxy free radical

ROO. = polymer peroxy radical

ROOH. = polymer peroxide

A. = antioxidant radical

ROOH---> RO. + RO_2. OH.

RH + O_2---> R. + HOO.

AH. + O_2 ---> A. + HOO.

RH--->high energy- R. + H.

R. + O_2----->ROO,

ROO. + RH ---> ROOH + R.

ROO. + AH---> ROOH + A.

A. + RH ---> AH + R.

2ROO. ----> stable products

2A. ----> stable products

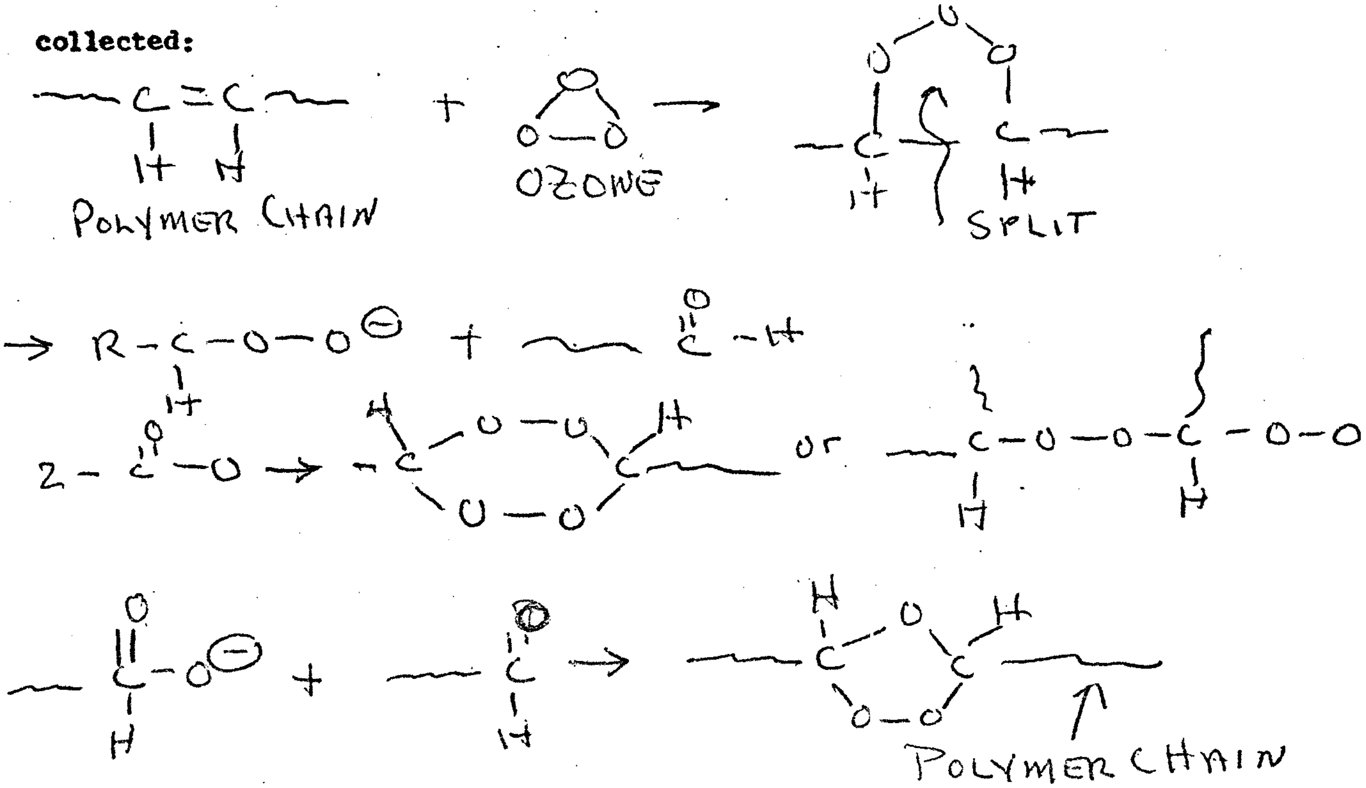
A. + ROO. ----> stable products

ROOH--->AH--> stable products

Reactions of Ozone With SBR

Ozone concentrations of low levels (50 ppm and less) have a devastating effect on SBR, which has vulnerable unreacted double bonds.

From the survey of mechanisms some key reactions have been collected:



Miscellaneous Reference Concerning The Testing of SBR Under Various Conditions

Ozone (O_3) is an important factor in failure of SBR vulcanizates. Two key ASTM articles (1,2) related the chemical structure of antiozonants, the factors affecting their applications, along with a general survey of the ozone resistance of various vulcanizates. Another ASTM publication (3) reveals the results of an interlaboratory ozone testing program. The mean crack length of the specimen was determined at various time intervals. An ozone concentration of 50 parts per hundred million at 120°F was used. Much variance was noted in the concentration of ozone as measured in the chamber, but overall agreement was found to be good. Some additional aging studies were conducted by Pollack and Matsuda who found the energy of activation for ozone cracking of vulcanize rubber to be 2-3 K.Cal./mole (4).

The oxidative degradation of polydiene vulcanizates was studied by Tobolsky and Mercurio (5). Similar work was also performed by Baumen and Maron (6). Techniques included swelling, intrinsic viscosity and infrared spectroscopy. (A wide variety of elastomer was reviewed by Shelton (7). In fact his article can be found listed in the reference section of this work).

The protective action by (absorption of inhibition) in oxadized vulcanizates was investigated by Novikova and Ermolenko (8).

The vulcanization of rubber in conjunction with oxidation was studied by another Russian team (9). The reaction of phenols with SO_2 produced no free sulfur; as the free sulfur reacts with accelerators. (These are similar to oxidation - reduction systems).

Besides the deterioration of SBR in the presence of oxygen and ozone, heat aging has been studied extensively to isolate the effect temperature plays in the aging of SBR.

Yamada and Kono (10) investigated the deterioration of rubber vulcanizates in heated air and their tensile strength changes. Plots of tensile strength vs. aging time and retention stress vs. aging time, correlate well in their trends. Energy loss can be derived from permanent set and retention of stress. The area of energy loss vs. aging time can serve as a criterion for rubber aging.

Konkle, McIntyre and Fenner studied the effect of high temperature on the properties of organic and silicone rubber (11). It appears unfair to compare the heat of aging properties of SBR to silicone rubber for the latter is known for its superior temperature resistance.

Juve and Schoch (12) concluded that the pattern of aging was found to be independent of temperature. The shelf age of most rubber products ranges from 8 - 12 years. Caution must be exercised when results are extrapolated.

The properties of GRS as affected by antioxidants were studied by Taft, Prem and Hernsen. The processing techniques vary the heat aging properties of the rubber. Vulcanizates were processed by (1) heat treatment; (2) open mill mastication; (3) Banbury milling.

Ionizing radiation does its share of damage to SBR vulcanizate as described by Smith (15). The French Rubber Institute studied methods of protecting rubber against atmospheric conditions (16). Certain amines coated on the surface of the specimen showed improved resistance to cracking and fissuring.

Cold cured rubber (17) was exposed to the following conditions: 1) dark room at room temperature 2) sun 3) heat.

Correlation of Antiozonant Protection and Chemical Structure *

With a vast complex of chemical and physical interactions among the various components of a SBR recipe; it would appear that it would be difficult to correlate the chemical structure of an additive with antiozonant performance. An important breakthrough was made by Kilbourne, Wilder, Van Verth, Hans and Tung *. By a systematic evaluation of many compounds it was found that mesomeric and steric effects contributed greatly. The following general rules can serve as a guide: (see also tables 3 and 8 in the appendix).

1. Basicity plays an important role; practically all the candidates listed contain nitrogen. (amino groups predominate).
2. For quinoline derivatives; the more basic the compounds; the more potent is the antiozonant.
3. Resonance plays an important part: reduced resonance inhibits the antiozonant protection for the phenylene - amino systems.
4. The substitution of electronegative groups on the benzene ring reduces the potency of the antiozonant.

It must be remembered that these rules serve for antiozonants in the protection of SBR vulcanizate. Applied to other systems, these rules may become invalid.

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* Rubber Chem. and Technology, 1135 - 63 31, (1958).

Aging of the SBR Crosslink

The properties of the SBR vulcanizate before and after aging can be derived from the following factors:

1. Type of SBR raw polymer used
2. Fillers used
3. Vulcanization system
4. Antiaging additives
5. Cure (Time and Temperature).

These variables determine in particular; the strength of the vulcanizate through its crosslinking network.

The efficiency of the curing system determines the quantity of initial crosslinks. An adequate crosslink density will produce a vulcanizate possessing adequate physical properties. If the system is undercured, the vulcanizate becomes weak. Overvulcanization makes the SBR vulcanizate brittle and eventually could render the article useless for any practical application.

It is the nature of SBR to increase in modulus while being aged.

The only apparent conclusion is that the number of crosslinks is being increased. Some chains (should break) during the aging process; but more chains appear to be formed then are being broken.

The effect of crosslink density on physical properties can be summerized as follows:

normal crosslink density	adequate - high strength vulcanizate
High crosslink density	strong tensile strength but tendency to become brittle.
Low crosslink density	weak rubber

Despite all the work performed by many rubber chemists, it is difficult to separate the variables that affect crosslink density.

Using an inefficient crosslink system has the following effects on the SBR vulcanizate:

A. Many crosslinking sites remain isolated.

B. Longer cure times at higher temperature can change the physical properties of the vulcanizate significantly.

C. Aging characteristics - double bonds of SBR are vulnerable to attack; particularly from oxygen and ozone. It would appear that undercured systems would be particularly vulnerable.

We must be able to isolate these factors which affect crosslinks and those which affect other portions of the vulcanizate.

By aging, the following changes can occur in the structure:

A. Crosslinks are destroyed

B. New crosslinks are formed at sites attached to sulfur residues

C. New crosslinks are formed at double bonds; not previously attached by vulcanization.

Destruction of Rubber Through Aging Not Involving the Crosslink Site

In the previous section only the crosslink was considered as being involved in the aging process. It is also possible for chain scission to occur, particularly at the double bonds. The resulting physical properties of the aging vulcanizate could then be the consolidation of the following effects.

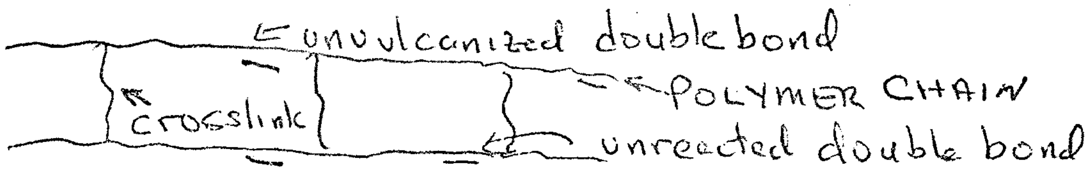
A. Formation of new crosslinks (result - increased tensile strength; may lead to brittleness).

B. Breaking of existing crosslinks (net effect - weaker rubber).

C. Breaking of polymer chain at double bond sites (net effect - weaker rubber).

See diagram:

Stage A



Oxygen attack: (aging)

Stage B

New crosslink formed: but possible peroxide formation; and scission:

Stage C

fractured segments

It appears that stage C, in aging, does not predominate; since as previously mentioned the SBR vulcanizate increases in tensile strength when aged. It would be inferred that the oxidation would stop at stage B in most cases.

Function of the Various Constituents Found in Most SBR Recipes

Component	Function	Disadvantage
SBR Polymer	The heart of the recipe; gives all the basic properties.	requires protection against aging
Zinc Oxide	Catalyst for the vulcanization process	promotes aging via oxidation.
Stearic Acid	solubilizes zinc oxide.	
Sulfur	vulcanizing agent	proper crosslink density important
Carbon Black	Gives strength	
Accelerator	Assists in vulcanization process	Efficiency of crosslinking important.
Antiaging additive	retards the aging process	May affect vulcanization rate.

Interactions Among the Various Components of the SBR Recipe

	1	2	3	4	5	6	7
1) SBR Polymer	-	+	+	+	+	+	++
2) Carbon Black	++	-	-	-	-	-	-
3) Sulfur	+	-	-	+	+	+	-
4) Accelerator	+	-	+	-	+	+	-
5) Stearic Acid	+	-	+	+	-	+	-
6) Zinc Oxide	✓	-	+	+	+	-	✓
7) Antiaging Additives	+	-	-	-	-	-	-

- Not an important interaction.

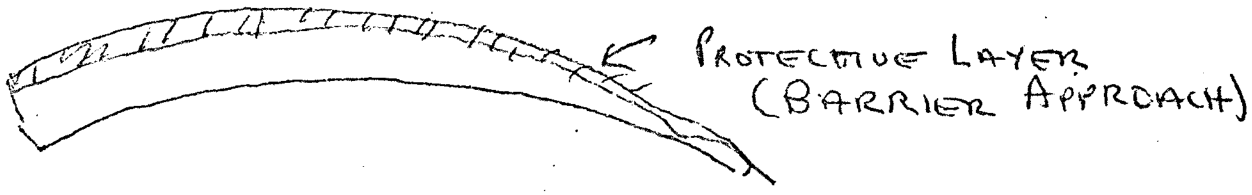
+ important - makes contribution

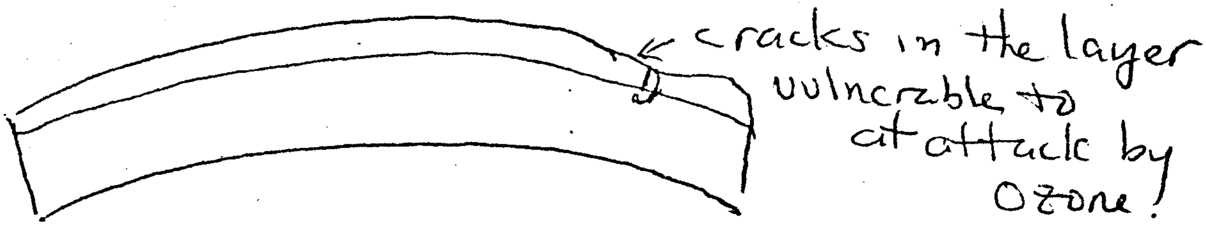
✓ makes negative contribution.

Simplified Mechanisms For Antiaging Additives

Some elaborate antiaging mechanism have been proposed by various workers. Complicated interactions among the various ingredients of the SBR would be difficult to explain. It would be ideal if a simplified mechanism could be proposed here.

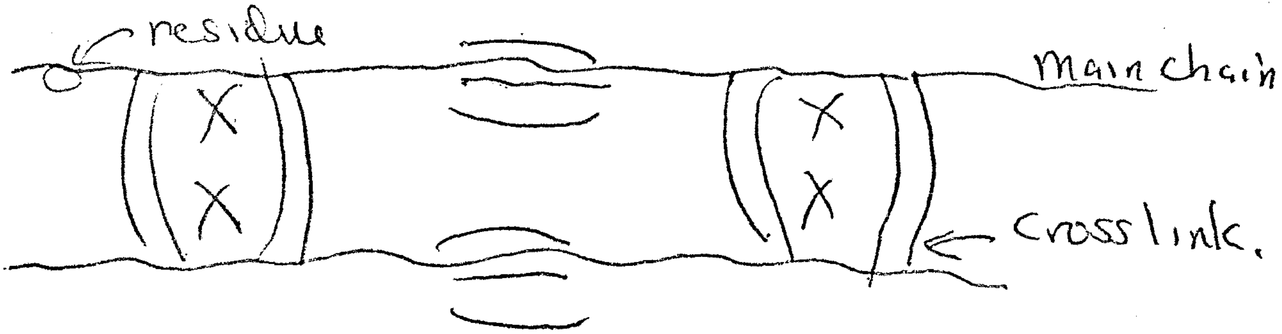
It has been shown that waxes protect vulcanizates from attack by ozone by blooming to the surface as illustrated here:





such a barrier can also prevent oxidation.

In a similar way antiaging additives can protect the SBR vulcanizate from attack by oxygen by forming a barrier. There is one major difference: these agents are homogeneously dispersed throughout the vulcanizate. Surface only protection does not occur. Antiaging additives can form protective barriers at the focal points as illustrated here:



A Numerical Rating System for Antioxidants

The relative effectiveness of the various antioxidant classification is given in Table 6. A numerical system has been devised by the writer. Assign the following values for each score: (E=excellent - 4, G=good -3, F=fair -2, P=poor - 1). The total value for all six ratings would approximate the versatility of any chemical classification.

Conclusions

1. Styrene - butadiene rubber is very susceptible to degradation unless a stabilizer is incorporated into the raw polymer during manufacturing.

2. During the compounding step SBR must be protected against environmental factors, (oxygen, ozone, heat, cold, light, and radiation) by the incorporation of an antiaging additive (carbon black gives some protection).

3. One must exercise care in the selection of an antioxidant package. Synerigistic action of two or more additives complicates the picture.

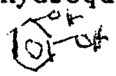
4. The best all around protection for SBR vulcanizates is given by the additives in the phenylenediamine category. (This group has the single disadvantage of producing stains in the SBR vulcanizate).

Appendix

TABLE I

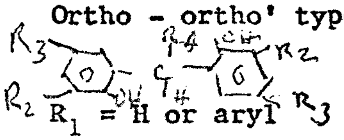
SBR STABILIZERS

Chemical Name	Class
I. B- conidenral	nondiscoloring
2,5 di(tertamyl) hydroquinone	"
2,5 di-t-butyl hydroquinone	"
Polycyclic hydroquinones	discoloring



2. hindered - bisphenols

Ortho - ortho' type



R_1 = H or aryl

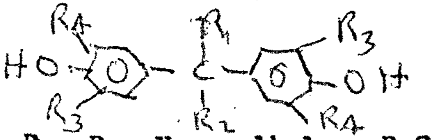
R_2 = tert - butyl, a-methyl, cyclohexyl or H or naphthyl

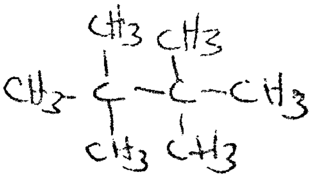
R_3 = methyl, ethyl

R_4 = CH may be replaced by S

Chemical Name	Class
1-1 Benzylidene bis (6-tert butyl-2-napthol)	D.C.
1-1' Benzylidene bis (6-tert-octyl - 2-napthol)	"
2-2' Methylene bis (6- tert-butyl -4-methyl phenol)	"
2-2'- Methylenebis - 6-tert butyl - p - cresol	"
2-2' Methylene bis (6-tert-butyl-4-ethyl phenol)	"
2-2' Methylene bis(6-methyl cyclohexyl-4-methyl phenol)	"
1-1'- Thiobis (6-tert-butyl-2-napthol)	sl. d.c.

B. Para - Para' Type





t,t-octyl)

R_1, R_2= H or alkyl or R,CR_2 may be S or may be absent

R_3 = tert-butyl, tertamyl or TT-octyl

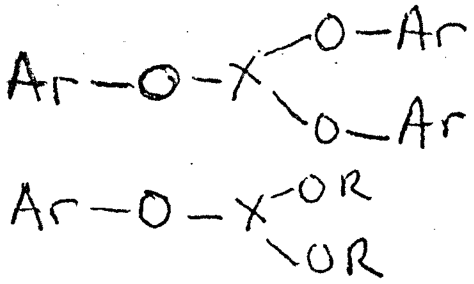
R_4 = H, methyl, tert-butyl or methyl may be at 5 and 5'

Chemical Name	Class
Alkylated bisphenol	Discoloring
4-4'- Bis (2,6 - ditert-butyl phenol)	Discoloring
Polybutylated Bisphenol	
4-4 Butylidnene bis (6- tert butyl-3-methyl phenol)	Non d.c.
4-4'- Butylidene bis (6-tert-butyl -3-mcresol)	
4-4'- Methylenebis (2,6 di-tert butyl phenol)	sl. d. c.
4-4' Methylene bis (6-tert-butyl-2-methyl phenol)	Sl. D.C.
4-4' Methylene bis (6-tert-butyl-o-cresol)	
4-4'- Thiobis (6-tert butyl - 3-methyl-phenol)	Non d. c.
4-4' - Thio bis (6-tert-butyl-m-cresol)	
4-4' Thio bis(6-tert-butyl-2-methyl-p-phenol)	sl.d.c.
4-4'-Thio bis(6-tert-butyl-o-cresol)	
4-4'-Thio bis (disec-amyl phenol)	Non d.c.

III Metal Complexes of Phenols

A. Catechol derivatives	
Antimony catecholate	Non d.c.
Antimony alkylcatecholates	"
Antimony phenylcatecholates	"
Stannous Catecholate	"
Stannous alkylcatecholate	"
Stannous phenylcatecholate	"
B. Monohydric Phenol derivatives	"
Antimony oxide-thio bisphenols	"
Antimony oxide hindered phenols	"
Stannous oxide - phenols	"
Stannous phenol sulfoxide	"

IV Compounds of Trivalent Group V Elements

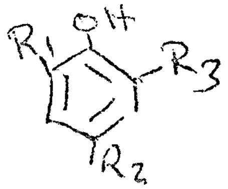


X = P or As

Chemical Name	Class
Triphenylarsenite	Nondiscoloring
Mono-nonylphenylphosphite	"
Tri (mixed-mono and dinonyl)phenyl phosphate	"
Dialkyl (mono-nonyl)phenyl phosphate	"

V. Hindered monohydrisphenols.

Alkylated Phenols:



R_1= Pref-tert butyl or tt-octyl or a-phenylether.

R_2= H or methyl or substituted methyl

R_3= H or alkyl

Aralkylated phenol (styrenated or a-phenylethylated)	Nondiscoloring
2,6 ditert-butyl-4-methyl-phenol 2,6 ditert-butyl-p-cresol)	Nondiscoloring
2,6 ditert butyl-a-dimethylamino-4-methyl-phenol (2,6 ditert butyl a-dimethylamine-p-cresol)	Nondiscoloring
2,6 Ditert-butyl-a-methoxy-4-methylphenol (2,6 ditert butyl-a-methoxy-p-cresol)	Nondiscoloring

Chemical Name	Class
secondary arylamines	
N-N^{-} diaryl-p-phenylenediamines	Discoloring
Diphenylamine Acetone condensation product	Discoloring
N-sec-Butyl-N^{1}-phenyl-p-phenylenediamine	"
Octylated diphenylamine	Semidiscoloring
Nonylated diphenylamine	"
N-phenyl-2-naphthylamine	Discoloring
Phenothiazine	"
Sulfur compounds	
Diphenylarsine sulfide	
Diphenystilbine sulfide	
N-allylthiourea	
N-phenylthiourea	

TABLE 2

VULCANIZATE ANTIOXIDANTS

I. Secondary diarylamines

A. Phenyl napthylamines

N-Phenyl-1-napthylamine

N-Phenyl - 3-napthylamine

B. Substituted diphenylamines

Nonylated diphenylamines	Semistaining

Octylated diphenylamine

4-4'-Dimethoxydiphenylamine

Isoproxy-diphenylamine

C. Para-Phenylenediamines

R_1= alkyl or aryl

R_2= alkyl or aryl

N-N' Bis (1,4 dimethylpentyl) - p-phenylenediamine

N-N'-Bis(1-ethyl-3-methyl pentyl) -p-phenylenediamine

N-N' Diaryl-p-phenylenediamine

N-N' Dinapthyl-p-phenylenediamine

N-N' - Diphenyl-p- phenylenediamine

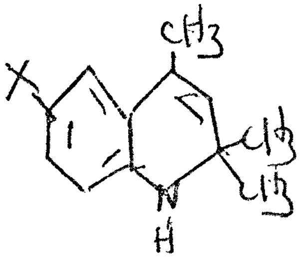
N-Cyclohexyl-N-phenyl-p-phenylenediamine

N(1-methylpropyl)-N-phenyl-p-phenylenediamine

N-Isopropyl-N-phenyl-p-phenylenediamine

II. Ketone amine Condensates

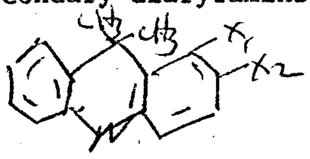
A. Dihydroquinolines, primary arylamine reaction products



X = H, alkyl, alkoxy

Polymerized, 1,2 dihydro 2,2,4 - trimethyl quinoline, 6-Dodecyl-1,2 dihydro-2,2,4 trimethylquinoline, 6-Ethoxy 1,2 dihydro 2,2,4 trimethylquinoline.

B. Secondary diarylamine reaction products



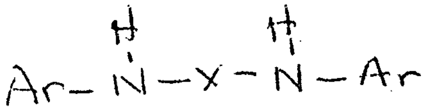
X_1, X_2 = H or Phenyl
Diphenylamine - acetone
N-phenyl-2-naphthylamine-acetone

III. Aldehyde-Amine Condensates

Aldol-1-napthylamine

Butyraldehyde-aniline

IV. Aryl-Aryl secondary amines


$$\mathrm{Ar-\overset{H}{N}-X-\overset{H}{N}-Ar}$$

N-N'-Diphenyl-ethylenediamine

N-N'- Diphenyl-propylenediamine

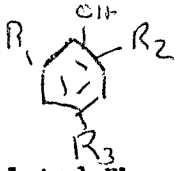
N-N'- Di-o-tolyl ethylenediamine

V. Primary- arylene diamines

NH_2-X-NH_2

X = m-tolylene or 4-4'-methylenediphenol

VI. Hindered Phenols



R_1 = tert alkyl or α-phenyl ether
R_2 = Methyl, substituted, methyl or tert alkyl
R_3 = alkyl or H

Alkylated Phenol

2,6- Ditert-butyl-4-methyl phenol

2,6- Ditert-butyl-a-dimethylamino-4-methyl phenol

2,6-Di-tert -butyl-a-methoxy -4-methyl-phenol

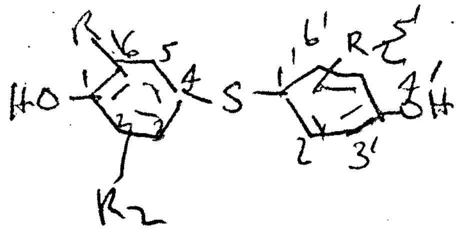
Mixed Tert Butyl Phenols

Mixed Tert-Butyl and tt-oxtyl phenols

styrenated (a-phenyl ethylated, phenol

VII. Hindered-thio-bisphenols

Non d.c to d.c.



R_1 = tert butyl or sec amyl

R_2 = methyl in 3 or 2

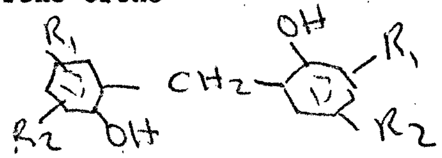
4-4- thio bis (6-tert-butyl-2-methylphenol)

4-4'-thio bis (6-tert-butyl-3-methyl phenol)

Thio-bis(di-sec-amyl phenol).

VIII Hindered bis phenols - Nondiscoloring to discoloring

A. Ortho-Ortho'



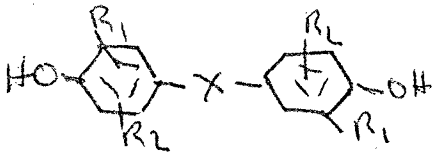
R, = tert butyl or a-methylcyclohexyl

R_2 = methyl or ethyl

2-2'- Methylene bis (6-tert-butyl-4-ethylphenol)

2-2'-Methylene-bis(6- tert-butyl-4-methyl phenol)

2-2' Methylene bis(6a-methylcyclohexyl-5-methyl-phenol)



X= alkylidne or may be absent

R_1 = tertbutyl

R_2 = methyl or tert butyl

4-4'-Bis (2,6-di-tert-butylphenol)	Discoloring
4-4'-Methylene bis (6-tert-butyl-2-methylphenol)	Sl. D.C.
4-4'-**Butylidene** bis (6-tert-butyl-3-methylphenol)	"
4-4' Methylene bis (2,6-di tert- butylphenol)	D.C.

Polybutylated-p-isopropylidene phenol

C. Unclassified polymeric phenols.

- 6-Alkyl-2-methylphenol-ketone condensate
- Butyrated butylidene-bisphenol
- Butylidene bis(dimethylphenol)
- Methylene bis(dismethylphenol)
- Methylene bis(3-isopropyl phenol)
- Trimeric alyl phenol - formaldehyde condensate

IX. Polyhydroxy phenols - formaldehydes (condensates)

- Butyrated hydroxy anisole
- 2,5 - di tert butyl hydroquinone
- Hydroquinone-mono benzyl ether

X. Sulfur compounds

- 2-mercaptobenzimidiazole

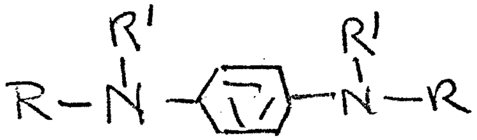
TABLE 3

CHEMICAL ANTIOZONANTS

(Listed in Approximate Order of Decreasing Activity)

I. p-phenylene diamine antiozonants

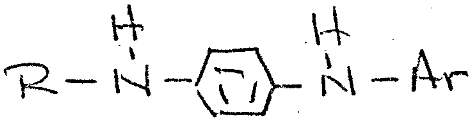
A.



R = sec alkyl or cycloalkyl

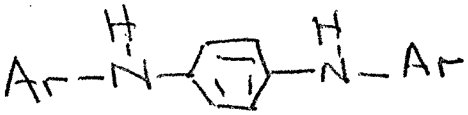
R' = H or Methyl

B.

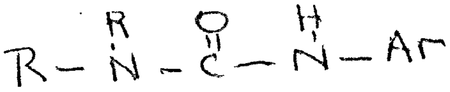


Ar = aryl

C.



	Activity
A. N-N- Bis(1,4-dimethylpentyl)-p-phenylenediamine	Highest
N-N'- Bis(1-methylheptyl)-p-phenylenediamine	
N-N-Bis(1-ethyl-3-methylpentyl)-p-phenylenediamine	
N-n'-Dimethyl-N-N'-bis(1-methylpropyl) p-phenylenediamine	"
B. N-isopropyl-N'- phenyl-p-phenylenediamine	High
N-(1-methylpropyl)-N'-phenyl-p-phenylenediamine	
N-N'- disecbutyl durenediamine	
nondiscoloring	
N-Substituted ureas and thioureas	
1,3-Dibutyl thiourea	Low
1-p-Ethoxyphenyl-3-phenyl thiourea	



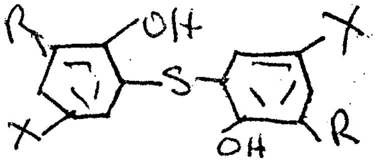
1-cycohexyl-3-a-napthylurea

1,1 Dicyclohexyl-3-phenylurea

1,2- Napthyl-3- phenylurea

4-4-p-Ethoxyphenyl-3-phenylurea

VIII Bisphenol Sulfides



R = C_4 and C_8 Slight

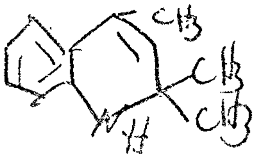
X = methyl, isopropyl, methoxy

2,2'- thiobis- (6-tt-octyl-4-methylphenol)

N-Cyclohexyl-N-phenyl0p-phenyleneidamine

C. Mixed - N-N- diaryl-p-phenylenediamine Intermediate

II <u>Dihydroquinoline</u> <u>antiozonants</u>



6-amino-2,2,4 trimethyl-1,2-dihydroquinoline

6-diethyleamino-2,24 trimethyl 1,2 dihydroquinoline

6-ethylamino-2,2,4 trimethyl 1,2 dihydroquinoline

6-ethoxy- 2,2,4 trimethyl-1,2- dihydroquinoline

III Organometallic compounds

Nickeldibutylthiocarbamate

Nickel-isopropyl xanthate

IV p-alkoxy N-alkylanilines

R = methyl,ethyl,decyl

R' = H, Hexyl, octyl, decyl

Diamino diurenes Low

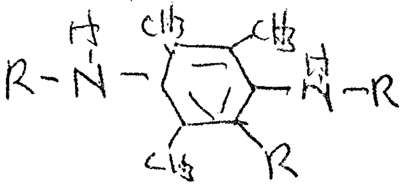


table 3 (concluded)

R = H, sec butyl, or 5-methyl-3-heptyl	Low
R' = methyl, ethyl, butyl or decyl	

TABLE 4

Commercial Antioxidants

Chemical Name	Trade Mark Name
Aldehyde- Amine type	
aldol-1-napthylamine	Age Rite Resin, Aceto AN
butyraldehyde-aniline product	Antox
acetaldehyde-aniline product	crylene
aldol - aniline product	Resistox
p-p'-diaminodiphenylmethane	Tonox
Ketone- Amine Type	
1,2 dihydro 2,2,4 trimethylquinoline resin	Agerite Resin D, Flectol II, Aceto POP
1,2 dihydro 2,2,4 trimethyl 6-ethoxy quinoline	Santoflex AW, Polyflex
1,2 dihydro 2,2,4 trimethyl -6-phenyl quinoline	Santoflex B
1,2 dihydro 2,2,4 trimethyl-6-dodecylquinoline	Santoflex DD
Diaryldiamine Type	
N-N'- diphenyl-p-phenylenediamine	Age Rite DPPD, JZF
N-N' di B-napthyl-p-phenylenediamine	Age Rite White, Aceto DIPN
N-N'- dialkyphenyl-p-phenylenediamine	Wingstay 100, Wingstay 300
Diarylamine Type	
phenyl -1- napthylamine	Neozone A, Aceto PAW
phenyl-2-napthylamine	Neozone D, special Agerite Powder; PBN, Aceto PBN
alkylated diphenylamine	Agerite Stalite, Octamine Pennox A, Wyton ADP, Polylite

Ketone - diarylamine type

Chemical Name	Trade Mark
diphenylamine - acetone, high temperature product	Age Rite; Superflex, BLE 25, Neozone L Cyanoflex 100
diphenylamine - acetone Low Temperature product	Aminox
phenyl 2-napthylamine - acetone low temperature product	Betanox Special
diphenylamine - acetone -aldehyde product	BXA

Substituted Phenol Type

2,6- di-t-butyl-4-methylphenol	CAO -1, DBPC, Tenamene 3, Inol Amoco 533, Dalpac 4, Deenax, Tenox BHT. CAO 3.
Butylated hydroxyanisole	Tenox BHA, Sustane BHA
2-a-methylcyclohexyl-4,6 dimethyl phenol	Nonox WSL
Styrenated phenol	Age Rite spar, Wingstay S Styphenol
hindered phenol	Wingstay T, Nevastain A, Cyanox LF, Santowhite 54
butylated styrenated m p cresol	Singstay V

Bisphenol Type

4-4' bis (2,6 t-butylphenol)	Ethyl 712
2-2' Methylene bis (4-methyl 6-t butylphenol)	Plastwax 2246 CAO 5

Chemical Name	Trade Mark
hindered bisphenol	Age Rite Superlite, Naugawhite, Pennox D
hindered polyphenol	Wingstay L
Hydroquinone Type	
benzyl ether of hydroquinone	Tecquinol
amyl hydroquinone	Santovar A
Amino Phenols	
p-aminophenols	Tenamene 1
2-octyl -4-paminophenol	Suconox 12
4- hydroxy-p-diphenylamine	Age Rite 150
Phosphite Type	
High molecular weight hindered tris non phenylphosphite	Age Rite, NC 1
benzyl phosphite	Polygard

TABLE 5

COMMERCIAL ANTIOZONANTS

Chemical Name	Trade Name or Commercialized Name
Symmetrical Diamines	
N-N'- disec-butyl-p-phenylenediamine	Estazone 2, HO 22
N-N'-dimethyl-N-N'-dimethylpropyl-p-phenylenediamine	Eastozone 31, UOP88, Antozite 2, Santoflex 17
p-phenylenediamine	
N-N' bis(1-methylheptyl)-pphenylenediamine	Eastozone 30, UOP 288, Santoflex 217, Antozite 1
phenylamine mixture	Wingstay 100, 200
N-N'- bis (1,4-dimethylpentyl)-phenylenediamine	Eastozone 33, Santoflex 77
Unsymmetrical Diamines	
N-isopropyl-N'-phenyl-p-phenylenediamine	Santoflex 36, Eastozone 34
N-phenyl-N'- cyclohexy-p-phenyl-phenylenediamine	Santoflex 66, A. O. 4010
N'-phenyl-N' Sec butyl-p-phenylenediamine	Flexzone 5-L
N-phenyl-N'- (13-dimethyl butyl)-p-phenylenediamine	UOP 588, Wingstay 300, Flexzone 7-L
N-phenyl-N8-sec-octyl-p-phenylenediamine	UOP 688
Other Types	
1,2 dihydro 2,2,4 trimethyl-6-ethoxy quinoline	Santoflex AU
Nickel dibutylthiocarbamate	NBC
nickelisopropylxanthate	KPNI

TABLE 6

EFFECTIVENESS OF ANTIOXIDANTS

	Oxygen Aging	Heat Aging	Flexing	Staining	Ozone Aging	Metal Inclusion
Aldehyde-Amine	F	G	P-F	P-F	P	P
Ketone-Amines	G	G	P	P	F-G	P
Ketone-diarylamines	G	G	E	P	F	F
Darylamines	G	G	G	P	F	F
Alkylateddi phenyl amines	G	G	F	F	P	P
phenylene diamines	G	G	G	P	E	G
phenolics	F	F	P	E	P	P
diphenolics	G	F	P	E	P	P
phenolic sulfides	G	F	P	G-E	P	P

TABLE 6A

Effectiveness of Antioxidants

	Total Value	Oxygen Aging	Heat Aging	Flexing	Staining	Ozone Aging	Metal Inclusion
Aldehyde Amine	10	2	3	1.5	1.5	1	1
Ketone-Amines	11.5	3	3	1	1	2.5	1
Ketone diaryl amines	15	3	3	4	1	2	2
Diaryl amines	14	3	3	3	1	2	2
Alkylated diphenyl amines	12	3	3	2	2	1	1
Phenylene diamines	17.5	3	3	3	1.5	4	3
phenolics	11	2	2	1	4	1	1
diphenolics	12	3	2	1	4	1	1
phenolic sulfides	11.5	3	2	1	3.5	1	1

TABLE 6B

Relative Ranking of Antioxidants

Ranking Number	Class of Antioxidant	Total Value
1	Phenylenediamine	17.5
2	Ketonediarylamine	15.0
3	Diarylamine	14.0
4 (t)	Diphenolics	12.0
4 (t)	Alkylateddiphenylamines	12.0
6	Ketone amines	11.5
6 (t)	Phenolic Sulfides	11.5
8	Phenolics	11.
9	Aldehyde-Amine	10.

Table 7

Comparison of Standard Antioxidant Types

Chemical	Relative Effectiveness of Antiozone
6-Ethoxy 1,2-dehydro-2,2,4 trimethylquinoline	25
6-4'-Thiobis (6-tert-butyl-m-cresol)	100
Ditert-octyldiphenylamine	25
2-2'-Methylene bis (4-methyl-6-tert-butylphenol)	25
5-Mercaptobenzionidazole	25
8-phenyl-2-naphthylamine	40
Diphenylamine/acetone condensate	50
Diphenylethenediamine	50
Polymenzed 1,2,dehydro 2,2,4 methyl quinoline	60
Wing Stay 100	100
N-N'-Disec-octyl-paraphenylenediamine	115
3-Cyclohexyl-N'-phenyl-p-phenylenediamine	115

TABLE 8

Anti-Ozone Effectiveness of Various 6-Substituted Derivatives

R	Relative Ozone Rating
H-	40
CH_3O-	85
CH_3CH_2O-	100
	95
$(CH_3)_2CH$-	65
$(CH_3)_3CCH_2$	70
$(CH_3)_3C$-	65
	50
$C_{12}H_{25}$	65
$CH_3(CH_2)_3CH_2$-	60

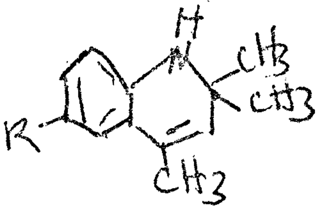
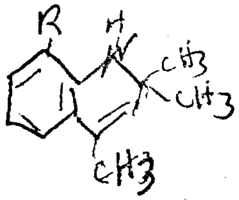


TABLE 9

8- Substituted Quinolines



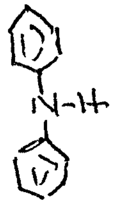
R	Ozone Rating
CH_3 -	50
CH_3O -	40
CH_3CH_2O-	50
$CH_3(CH_2)_3CH_2O$-	55
$CH_3(CH_2)_3CH_2$-	50

Reference: Kilbourne and Al, Rubber Chem. Technol. 31, 1155-65 (1955).

TABLE 10

STRUCTURES AND ANTIOZONANT ACTIVITY

40



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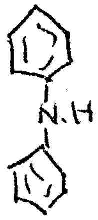
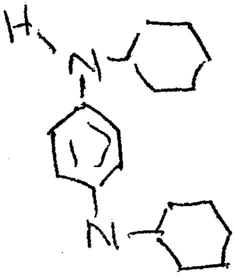
85



110

110

115



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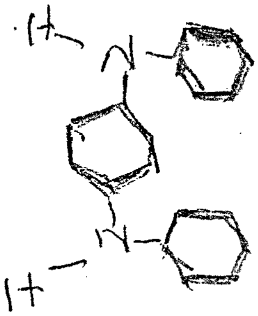

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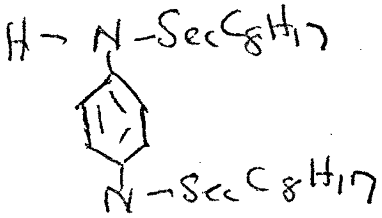

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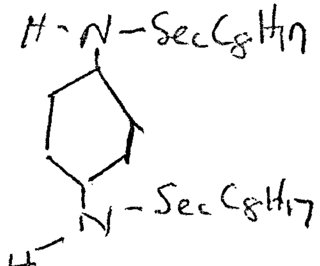

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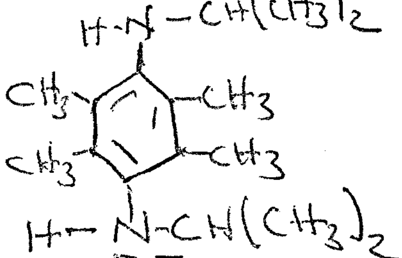

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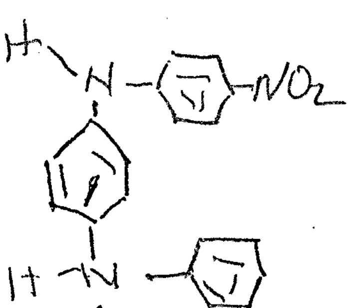

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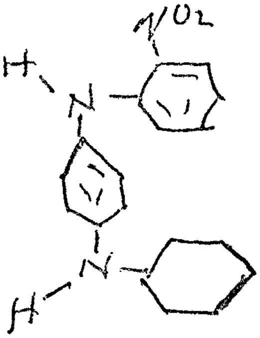


65

TABLE 10 A

FLEX CRACK INHIBITORS

N-N'- Diaryl-p-phenylenediamines

N-N- Di-2-napthyl-p-phenylenediamines

N-N'- Diphenyl-p-phenylenediamines

N- Sec-Butyl-N-phenyl-p-phenylenediamine

N- Cyclohexyl-N-phenyl-p-phenylenediamine

8-(1-methylheptyl)-N- phenyl-phenylenediamine

N- Isopropyl-N'- (methyl phenyl)-p-phenylenediamine

N-Isopropyl-N- pheny-p-phenylenediamine

N-N'-Bis(1-4-dimethylpentyl-p-phenylenediamine)

N-N- Bis (1-ethyl-3-methylpentyl-p-phenylenediamine)

N-N'= Bis (1-methylheptyl) -p-phenylenediamine

Aryl Amines

Phenyl-2-napthylamines

Dimethoxydiphenylamine

Diphenylamine-acetone products

Arylated diphenylamines

Isopropoxy diphenylamine

Phenyl-2-napthylamines acetone condensation product

Appendix B*

Key equation: $V-A=Be^{-a(+-x)}$

V= corrected dilute solution viscosity (DSV) at time (+).

A+B= corrected DSV of original polymer.

A= limiting or lowest DSV that is reached.

B= constant indicative of the extent of change in DSV.

a= constant associated with the rate of breakdown.

x= The induction period in days prior to the start of breakdown.

Antioxidant	ChemicalType	Use
PBNA	Phenyl-2-naphthylamine	Staining
BLE	Acetone-diphenylamine reaction product	Staining
B Conidendol	Phenolic	Nonstaining
Statite	Mixedalkyldiphenylamines	Nonstaining
Polygard	Trisnonylphenylphosphite	Nonstaining
Wingstay S	Mixed alkylated phenols	Nonstaining
Santovaro	2,5-ditertbutyl hydroquinone	Nonstaining
2246	2,2 methylene bis 4-methyl 6-tertbutyl phenol	Nonstaining

---

* W.K. Taft, J. Duke and D. Prem; Ind. and Eng. Chem., 49, 1293-96 (1957)

Parameters For Equation Base Polymer

	A	B	a	x
BC	3.10	0.46	0.05	9
Poly G	2.90	0.67	0.2	4
St.	3.00	0.50	0.2	2.5
BLE	3.00	0.53	0.15	4
PBNA	3.20	0.36	0.10	4
Wingstay S	1.60	1.93	0.7	1.5
2246	2.50	1.03	0.1	0.5
Santovaro	2.00	1.58	0.8	0.5
	Circosol 2xH*			
BC	2.80	0.90	0.08	6
PG	2.10	1.60	0.20	3.5
St.	2.39	1.27	0.3	1
BLE	3.05	0.65	0.15	1
PBNA	2.70	0.83	0.10	6
WS	1.28	2.41	0.4	0.9
2246	1.70	2.02	0.08	0
SAO	2.10	1.53	0.4	0

---

* At 37.5 parts per hundred polymer

Sundex 53*

	A	B	a	X
BC	2.20	1.52	0.07	6.5
PG	1.50	2.18	0.25	3.5
St	1.40	2.26	0.6	1
BLE	1.40	2.31	0.07	0
PBNA	1.70	1.84	0.1	1
Wing St	1.10	2.55	0.6	2.5
2246	1.40	2.23	0.08	0
Santovar O	1.30	2.33	0.3	0

Dutrex 20*

BC	1.10	2.58	0.35	3.0
PG	0.96	2.68	0.4	2.1
ST	1.18	2.56	1.4	0
BLE	1.16	2.30	0.5	0.5
PBNA	1.07	2.48	0.4	0.5
Wing S	1.08	2.66	0.8	0.9
2246	1.00	2.71	0.85	0
Sant O	0.96	2.75	0.35	0

---

* At 37.5 parts per hundred polymer

APPENDIX C

Carbon Black- Effect on Oxidation*

Recipe

Polymer	100
ZnO	3
Stearic Acid	2
N-Cyclohexyl-2-benzothiazolesulfenamide	1

Absorption of O_2/ gram polymer (25°C)

Fernex Black	C. Black Concentration PHR				
Hours @ 100°C	0	10	20	40	60
6.6	1.0	1.0	1.0	1.0	0.8
19.0	2.0	2.2	2.2	2.0	--
46.0	3.6	3.7	4.0	3.7	3.4
73.5	4.9	5.1	5.5	5.2	5.6
96.5	6.0	6.2	6.8	6.6	7.5
166.5	9.0	9.3	10.4	10.8	-
190.0	10.3	10.5	12.2	12.6	15.4
292.5	14.6	14.8	17.6	18.8	-
Cure at 307°F min	30	30	30	30	30

---

* J. Reid Shelton and W. T. Wickham, Ind. and Eng. Chem, 47, 1277-82(1956).

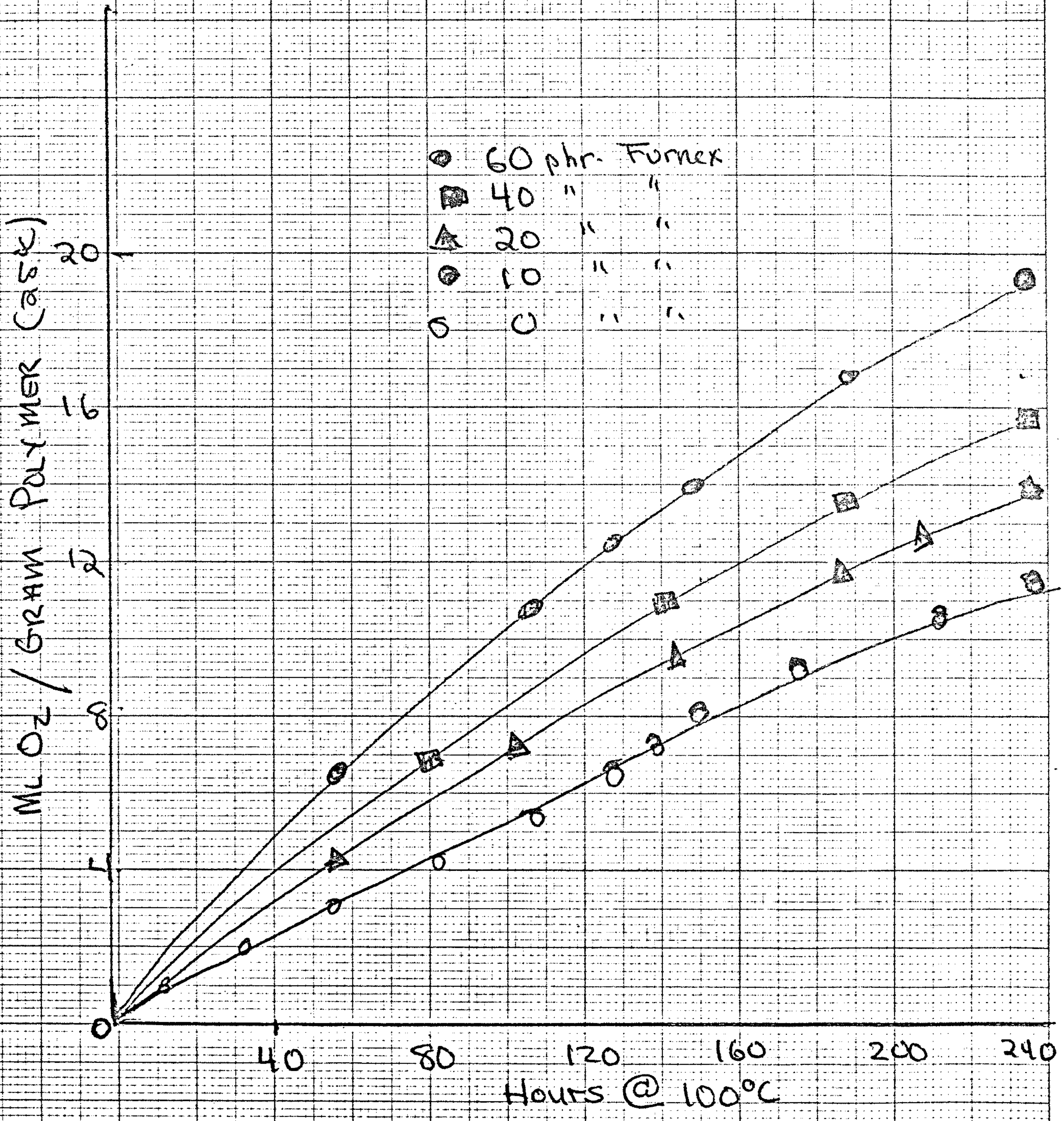
STATEX M

C Black Concentration PHR

Hours @ 100°C	mls. O_2/gr. (25°C)				
	0	10	20	40	60
6.6	0.9	1.0	1.0	--	--
22.0	---	2.4	2.3	2.4	2.4
46.0	3.6	3.8	3.6	3.7	4.2
96.5	6.0	6.8	6.7	7.5	8.7
138	8.0	9.3	9.3	---	---
155	---	---	---	12.3	14.2
217	---	13.7	14.2	16.8	19.9
261	---	16.0	16.0	19.8	23.4
Cure @ 307°F	30	30	30	30	30

STATEX B

	0	5	10	30	60
10.25	1.0	1.1	1.2	1.2	1.3
31.75	2.2	2.5	2.8	2.7	2.5
56.25	3.4	3.7	4.2	4.1	4.3
103.75	5.2	5.8	6.5	6.7	7.2
130.5	6.3	7.1	7.9	8.3	8.9
164.5	7.7	8.7	9.7	10.2	11.0
215.0	9.8	10.9	12.2	12.0	14.2
265.0	11.7	13.1	14.5	15.5	17.3



● 60 phr. Furnex
■ 40 " "
▲ 20 " "
● 10 " "
○ 0 " "
ML O2 / GRAM POLYMER (cast)
0
4
8
12
16
20
40
80
120
160
200
240
Hours @ 100°C

FIGURE 1

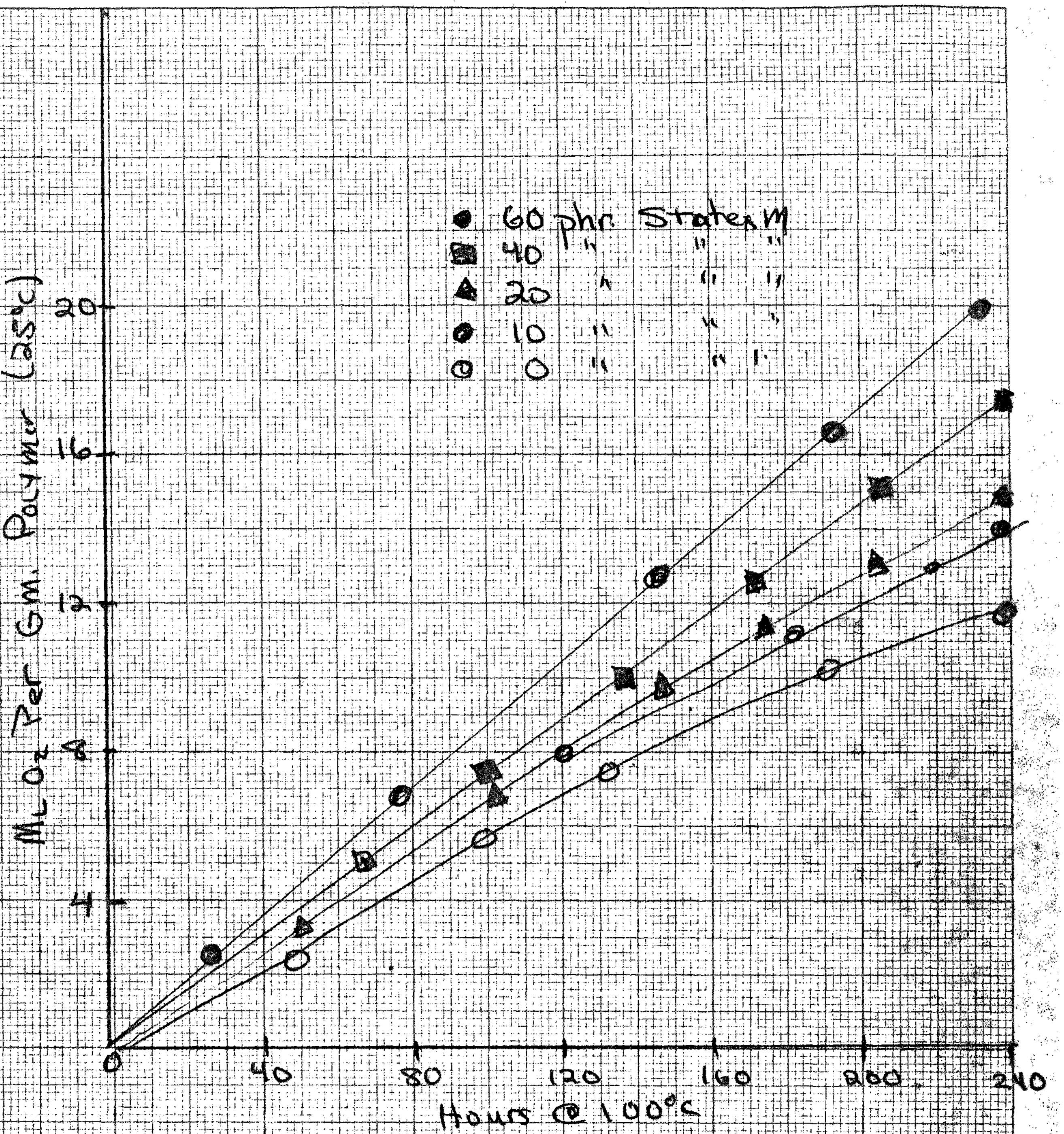
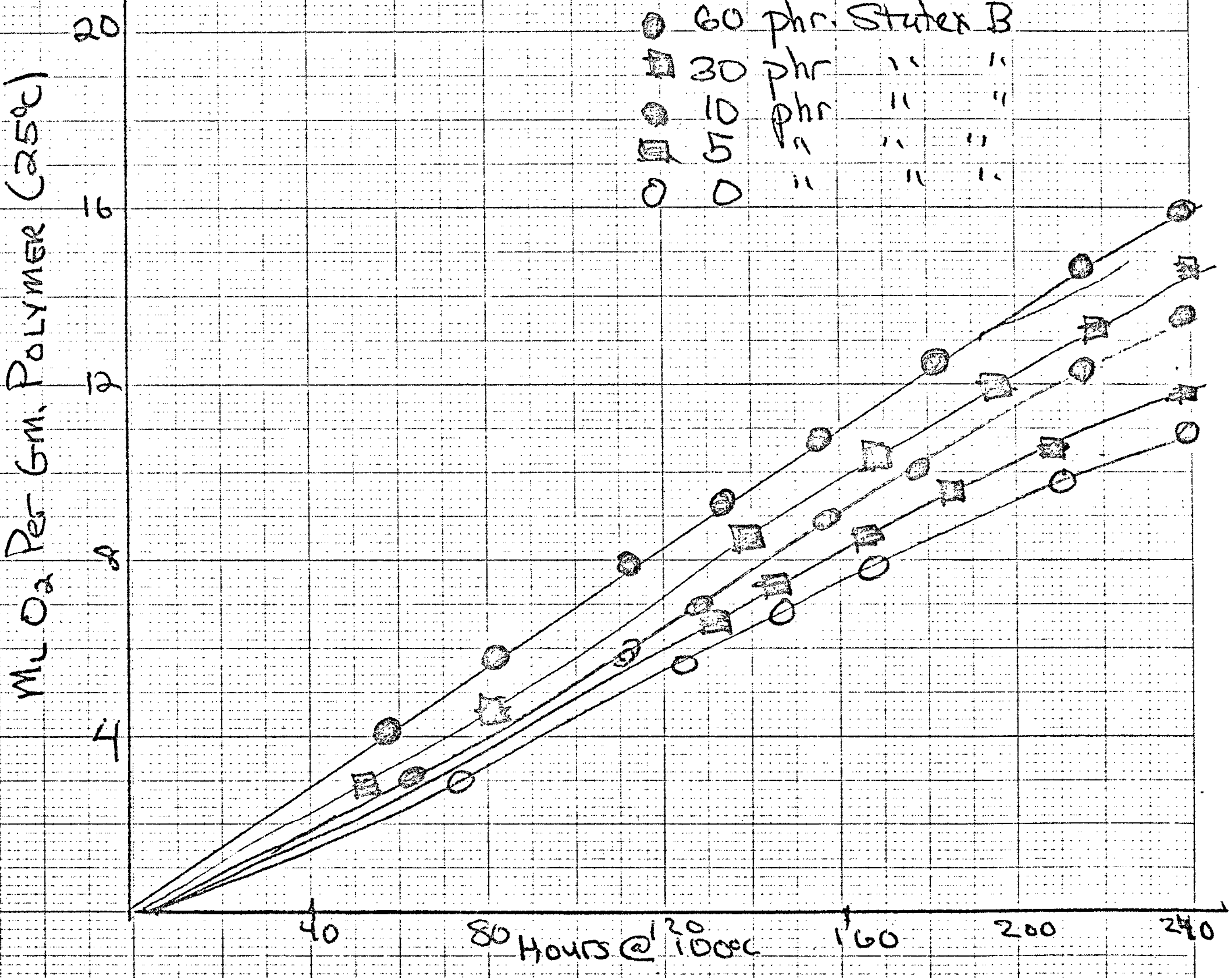

● 60 phr. Statex M
■ 40 " " "
▲ 20 " " "
● 10 " " "
○ 0 " " "
ML O2 Per GM. Polymer (25°C)
20
16
12
8
4
0
40
80
120
160
200
240
Hours @ 100°C

FIGURE 2



● 60 phr. Statex B
▨ 30 phr " "
● 10 phr " "
▨ 5 " " "
○ 0 " " "
ML O2 Per GM. POLYMER (25°C)
20
16
12
8
4
40
80
120
160
200
240
Hours @ 100°C

FIGURE 3

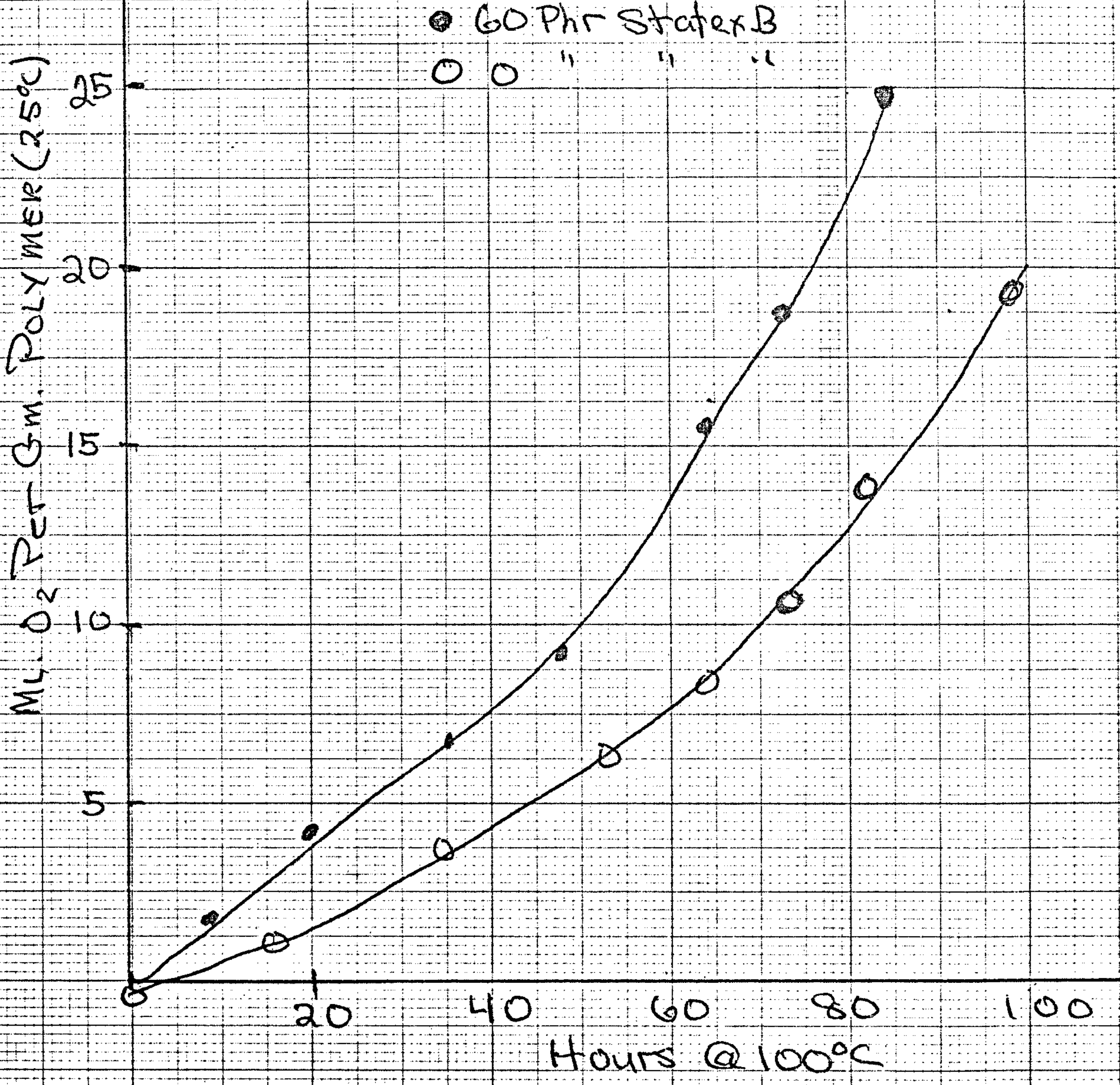
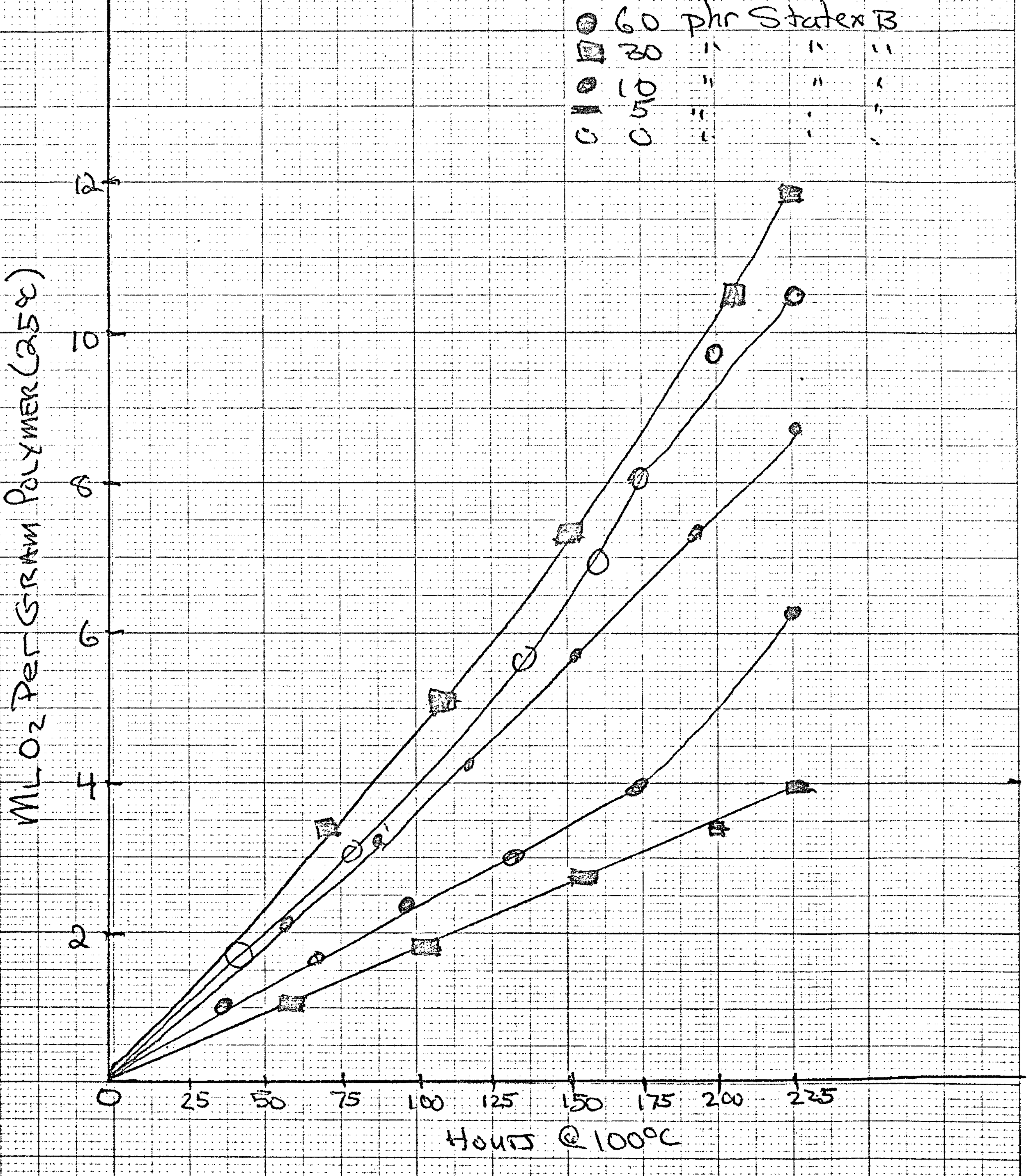
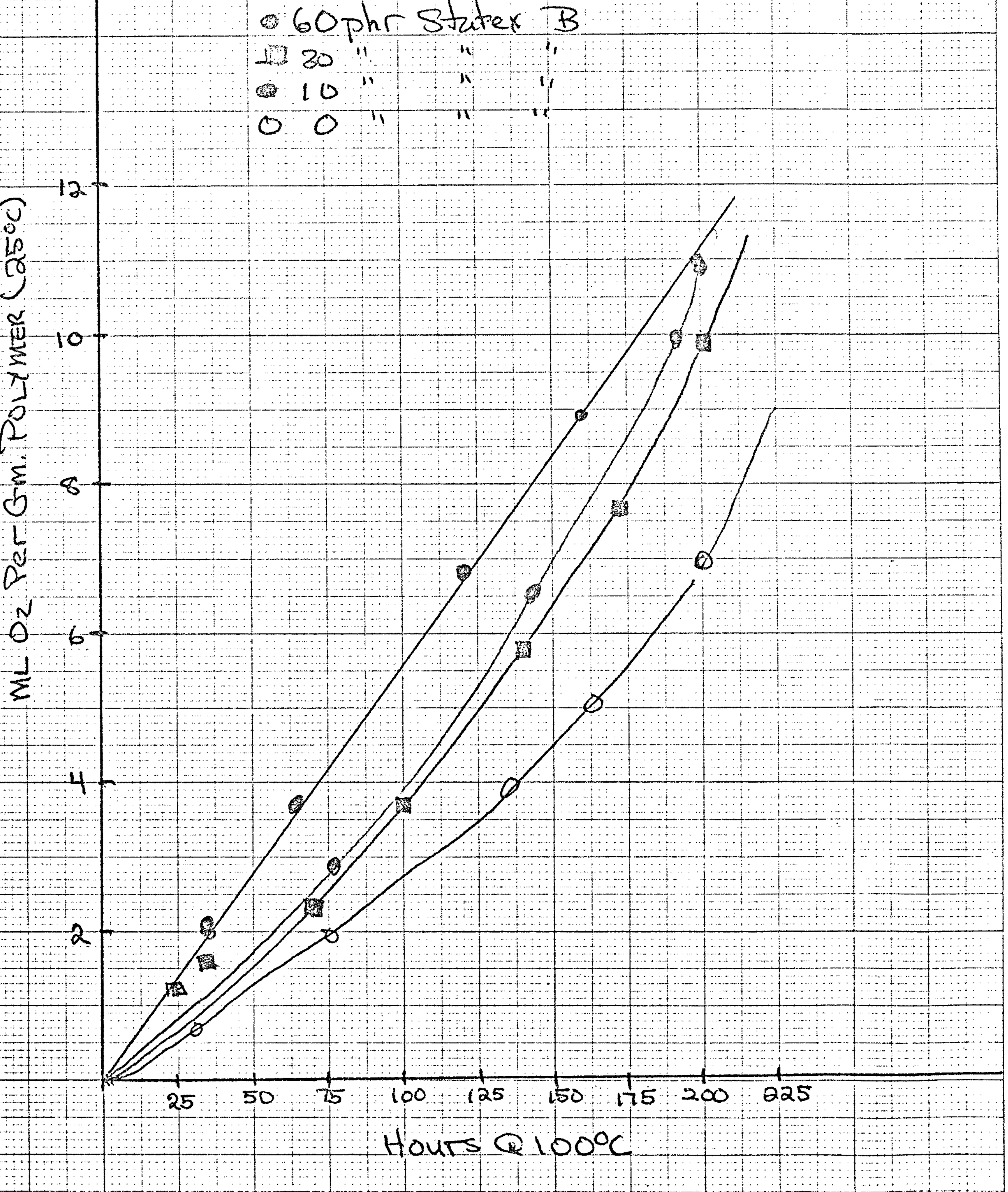

● 60 Phr Statex B
○ 0 " " "
ML. O2 Per Gm. POLYMER (25°C)
25
20
15
10
5
20
40
60
80
100
Hours @ 100°C

FIGURE 4



60 phr Statex B
30 " " "
10 " " "
5 " " "
0 " " "
ML O2 Per Gram Polymer (25°C)
12
10
8
6
4
2
0
25
50
75
100
125
150
175
200
225
Hours @100°C

FIGURE 5



● 60phr Statex B
■ 30 " " "
● 10 " " "
○ 0 " " "
ML O2 Per Gm. Polymer (25°C)
12
10
8
6
4
2
25
50
75
100
125
150
175
200
225
Hours @ 100°C

FIGURE 6

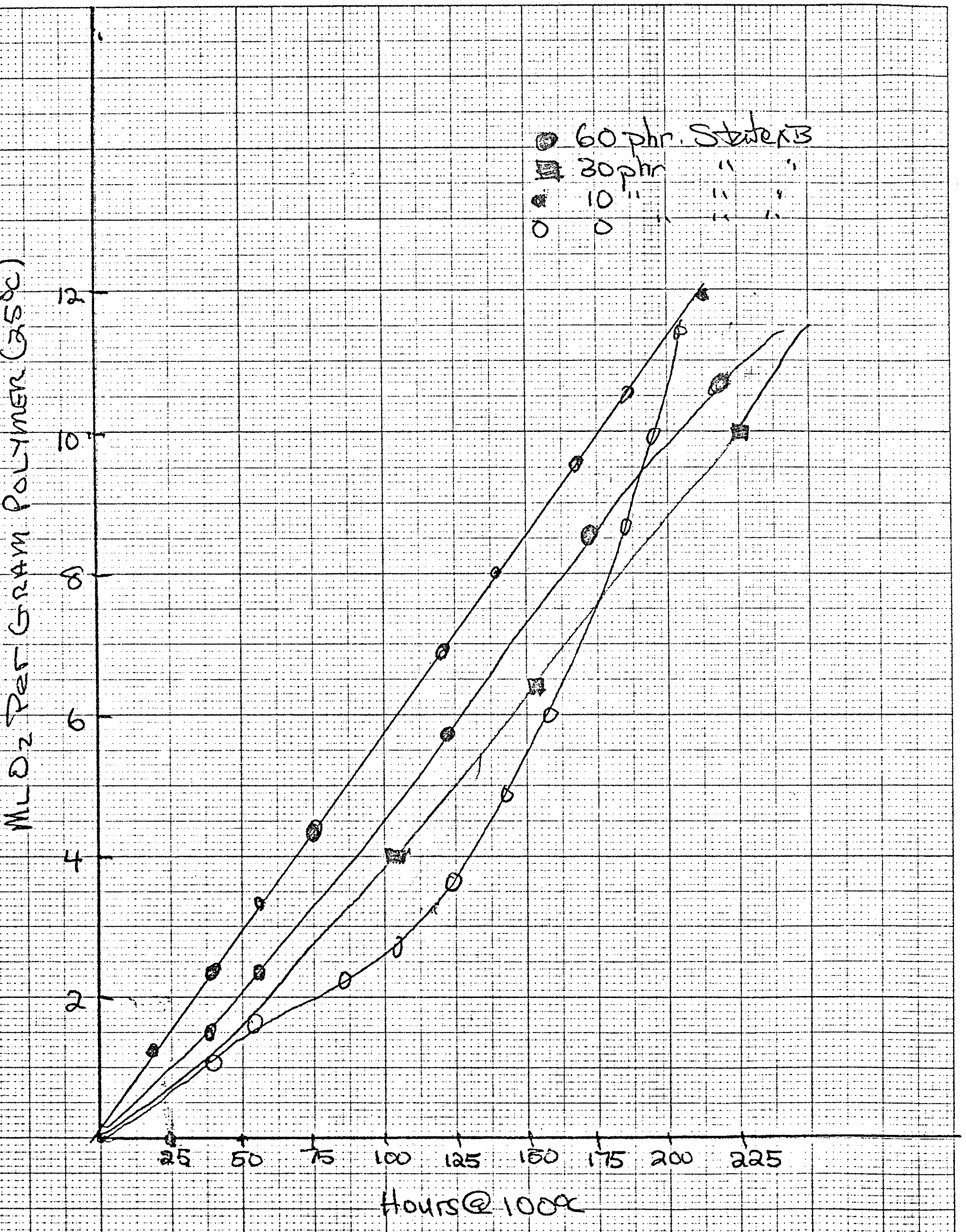

60 phr. Statex B
30 phr " "
10 " " "
0 0 " " "
ML O2 Per Gram Polymer (25°C)
2
4
6
8
10
12
25
50
75
100
125
150
175
200
225
Hours @ 100°C

FIGURE 7

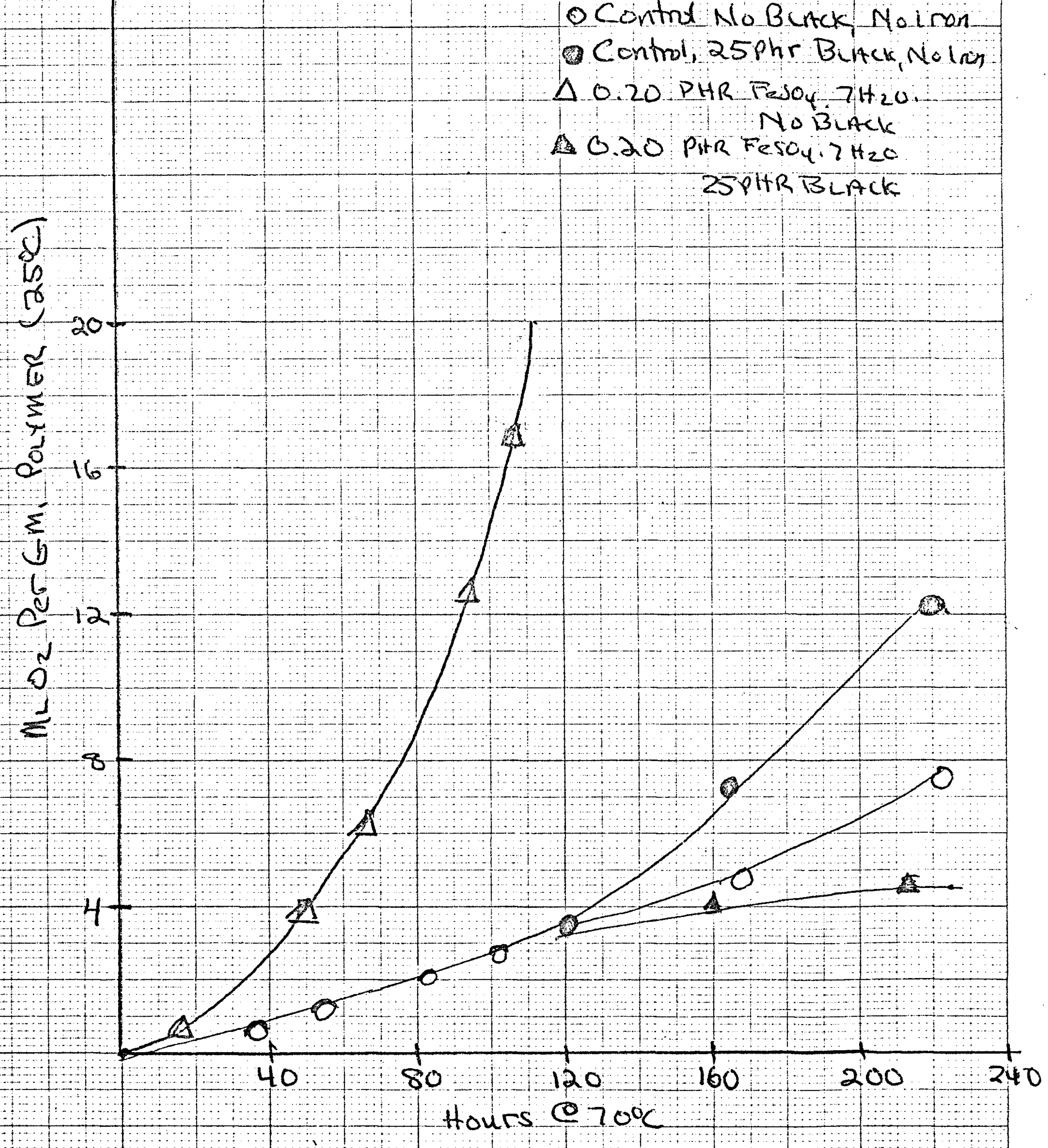

○ Control No Black, No Iron
● Control, 25 Phr Black, No Iron
△ 0.20 PHR $FeSO_4 \cdot 7H_2O$. No Black
▲ 0.20 PHR $FeSO_4 \cdot 7H_2O$ 25 PHR BLACK
ML O_2 Per GM. Polymer (25°C)
20
16
12
8
4
40
80
120
160
200
240
Hours @ 70°C

FIGURE 8

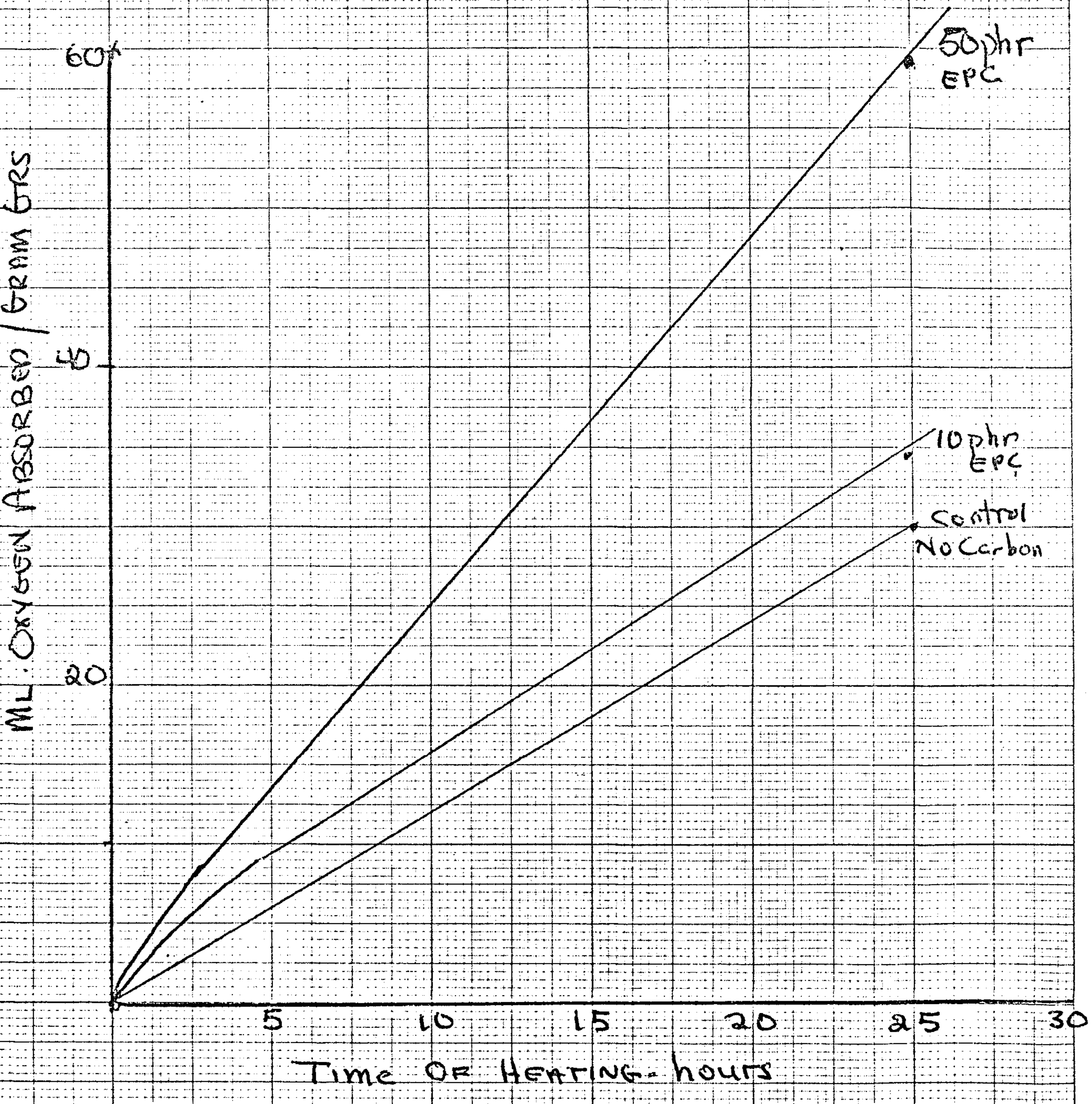

ML. OXYGEN ABSORBED / GRAM GRS
60
40
20
5
10
15
20
25
30
TIME OF HEATING - hours
50phr EPC
10phr EPC
control No Carbon

FIGURE 9

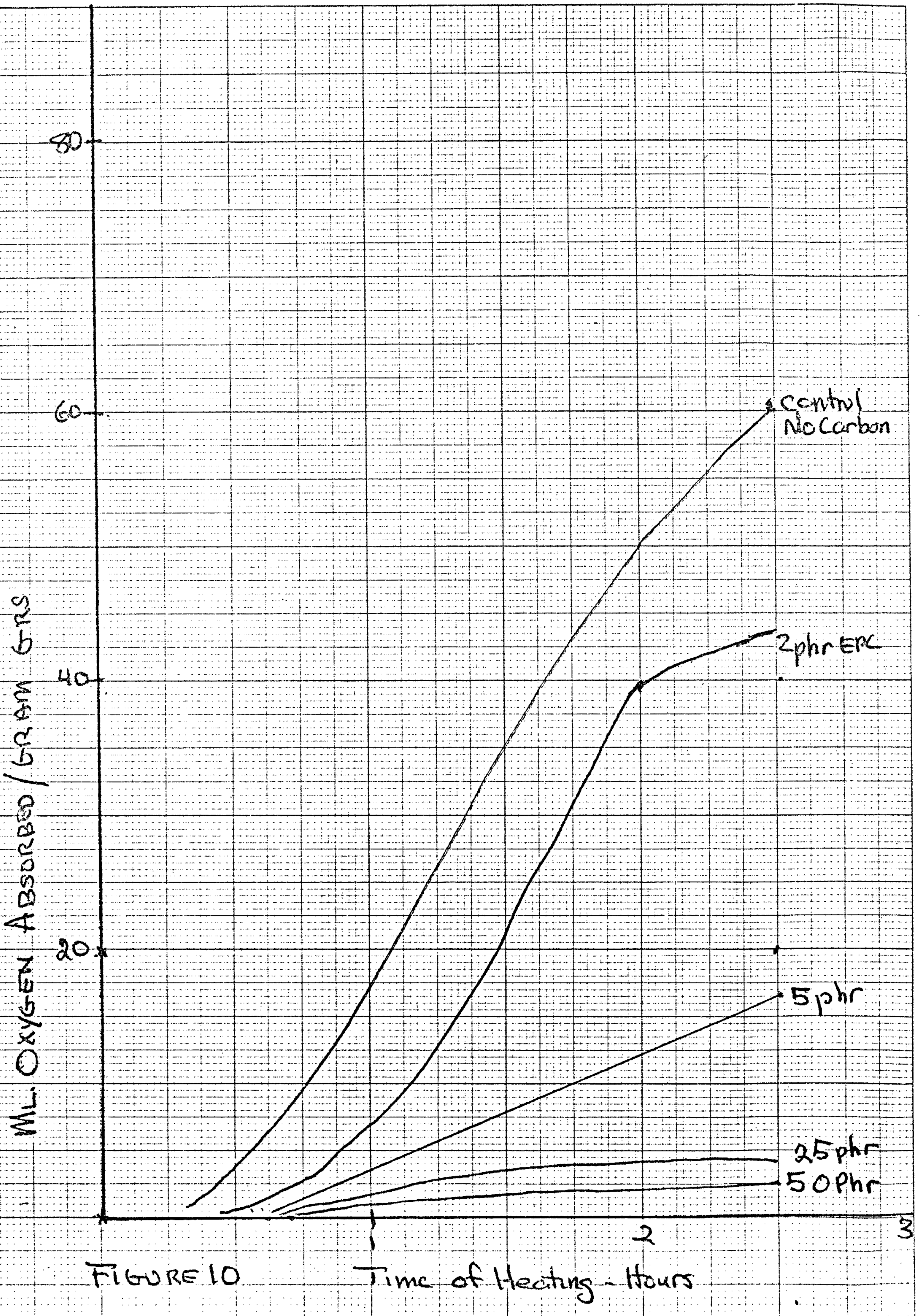
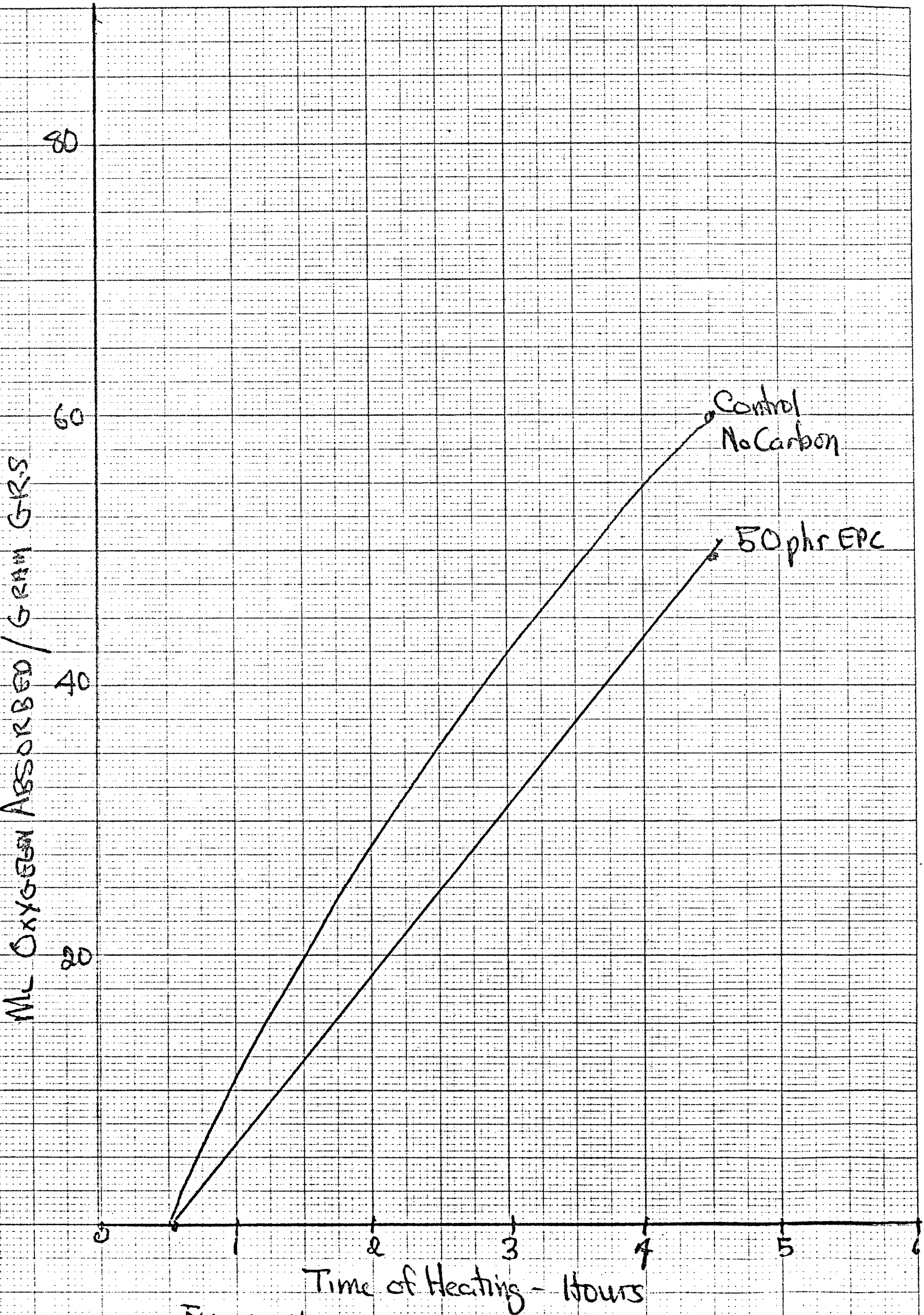

ML. OXYGEN ABSORBED / GRAM GRS
80
60
40
20
1
2
3
Time of Heating - Hours
Control
No Carbon
2phr EPC
5phr
25phr
50Phr

FIGURE 10



ML OXYGEN ABSORBED / GRAM GR-S
80
60
40
20
0
1
2
3
4
5
6
Time of Heating - Hours
Control
No Carbon
50 phr EPC

FIGURE 11

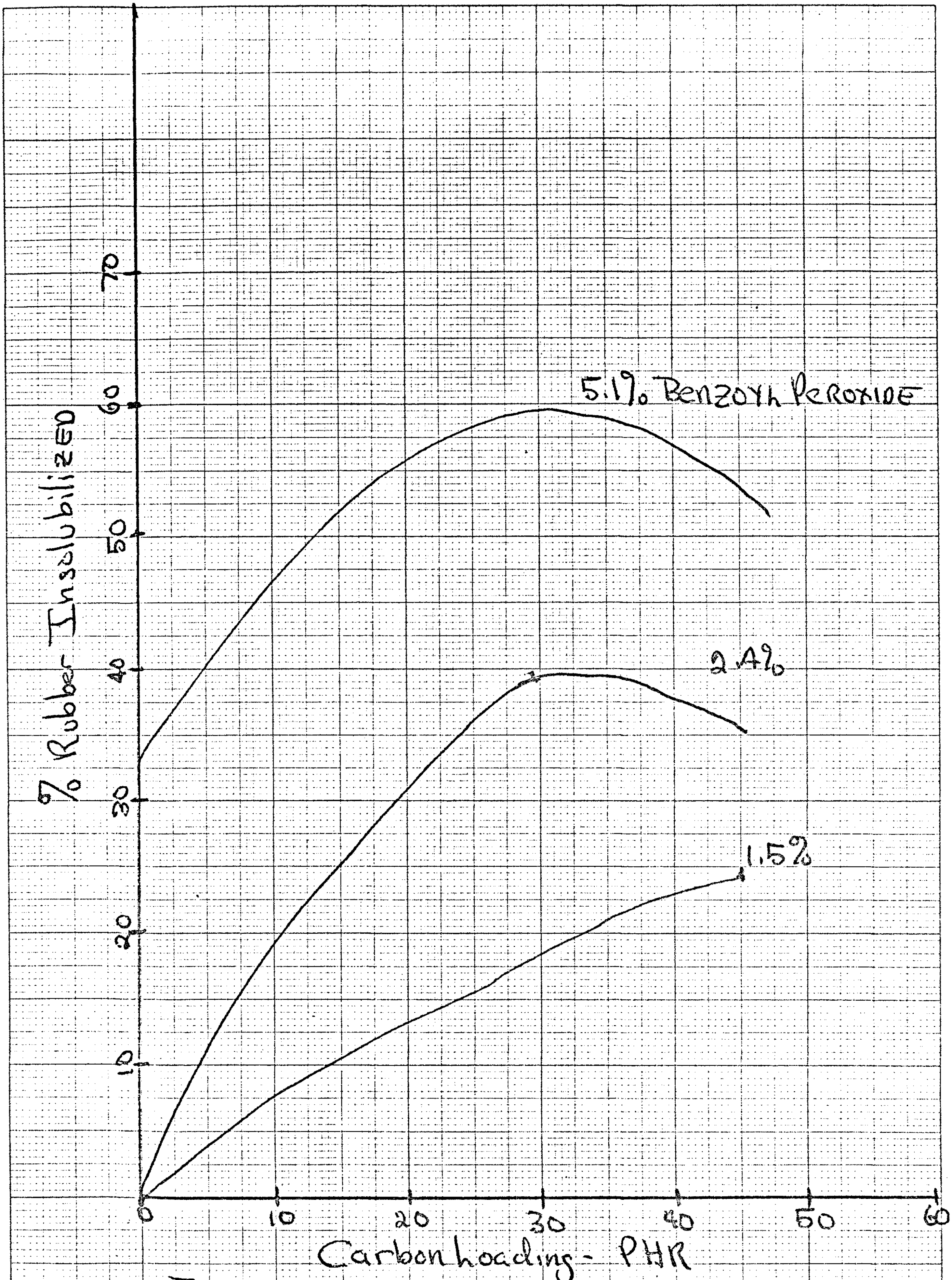

% Rubber Insolubilized
70
60
50
40
30
20
10
0
10
20
30
40
50
60
Carbon Loading - PHR
5.1% Benzoyl Peroxide
2.4%
1.5%

FIGURE 12

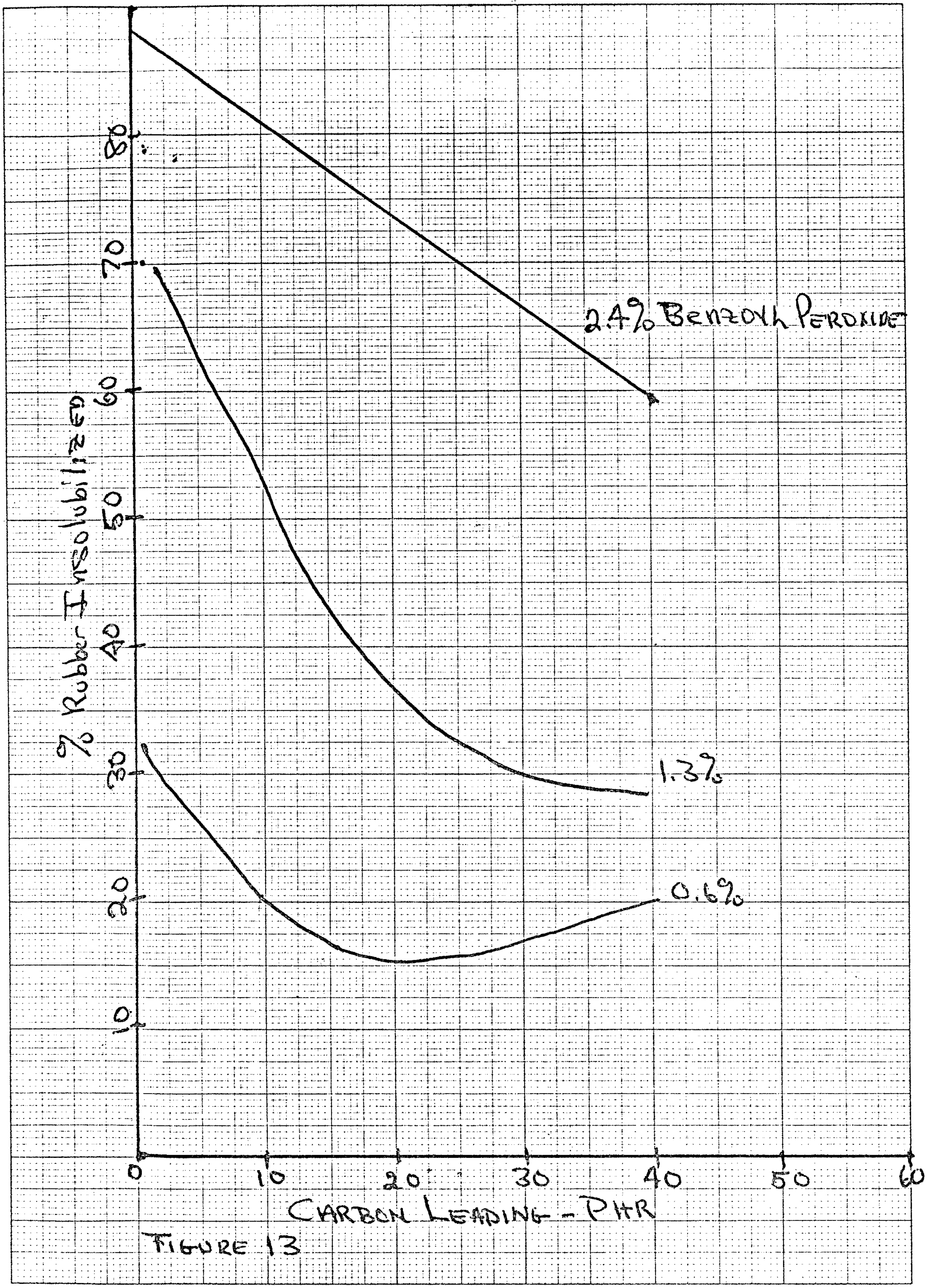

% Rubber Insolubilized
80
70
60
50
40
30
20
10
0
10
20
30
40
50
60
2.4% Benzoyl Peroxide
1.3%
0.6%
Carbon Loading - PHR

FIGURE 13

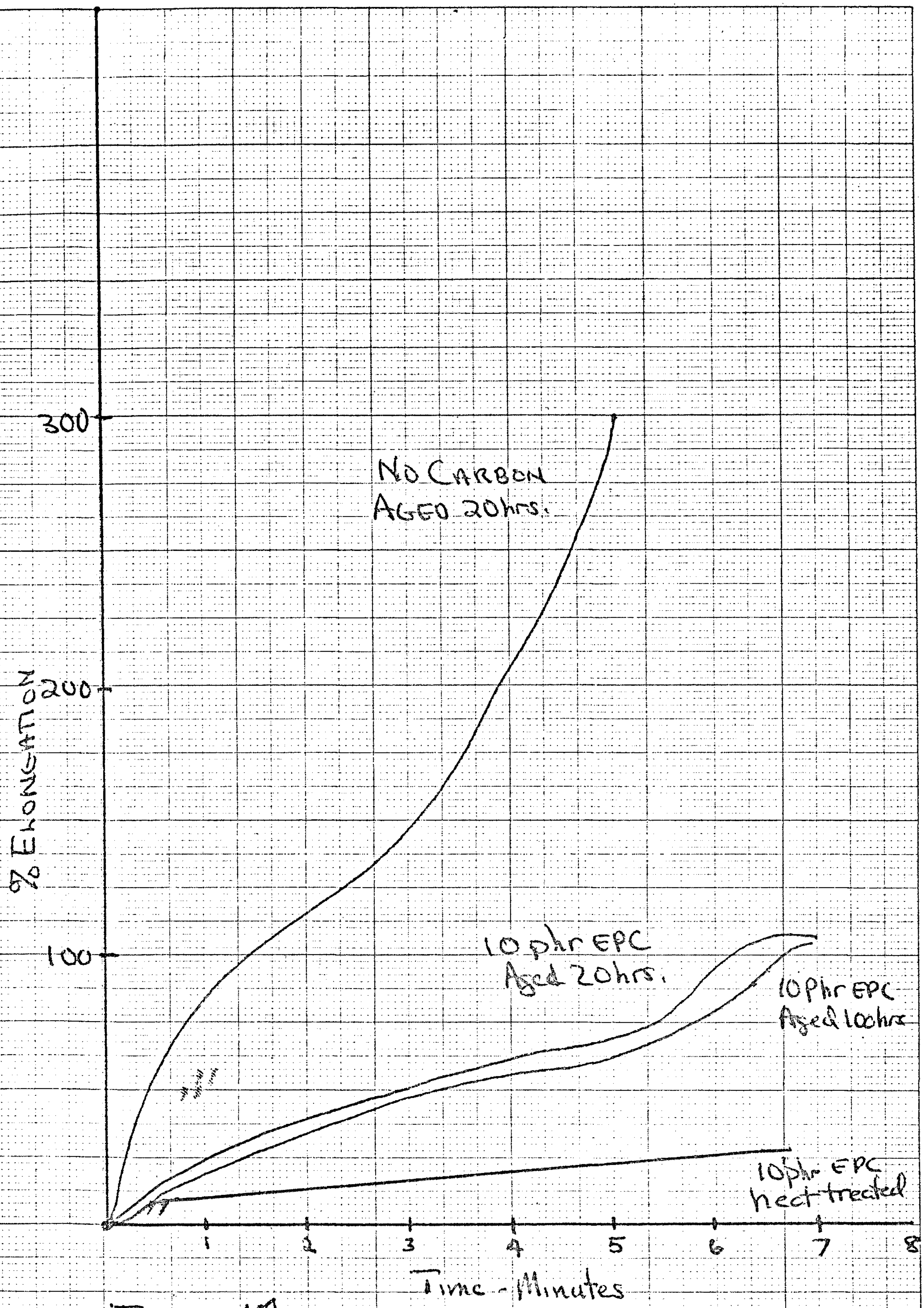
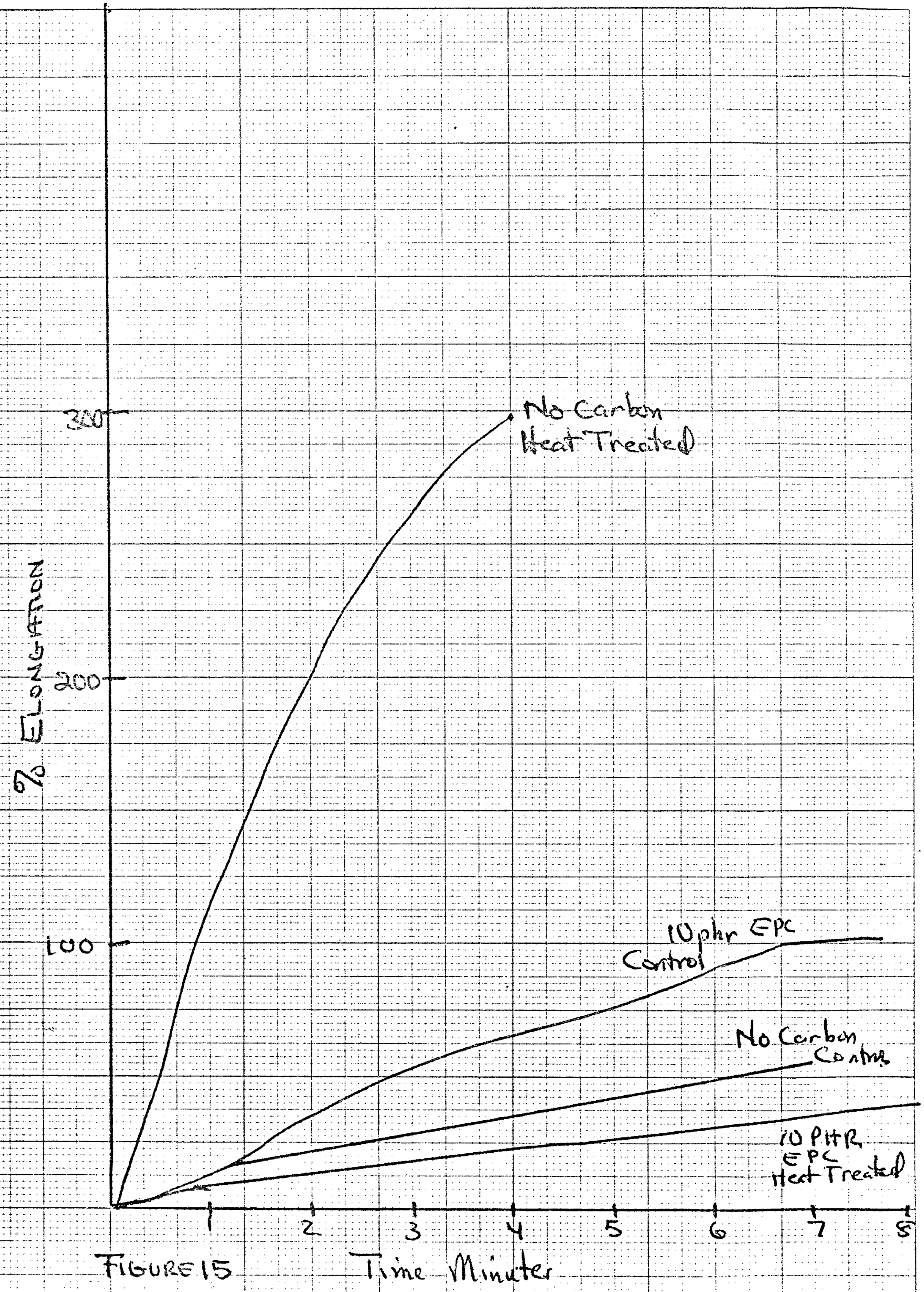

300
200
100
% ELONGATION
NO CARBON
AGED 20hrs.
10 phr EPC
Aged 20hrs.
10 phr EPC
Aged 100hrs
10 phr EPC
heat treated
1
2
3
4
5
6
7
8
Time - Minutes

FIGURE 14



300
200
100
% ELONGATION
No Carbon
Heat Treated
10 phr EPC
Control
No Carbon
Control
10 PHR
EPC
Heat Treated
1
2
3
4
5
6
7
8
Time Minutes

FIGURE 15

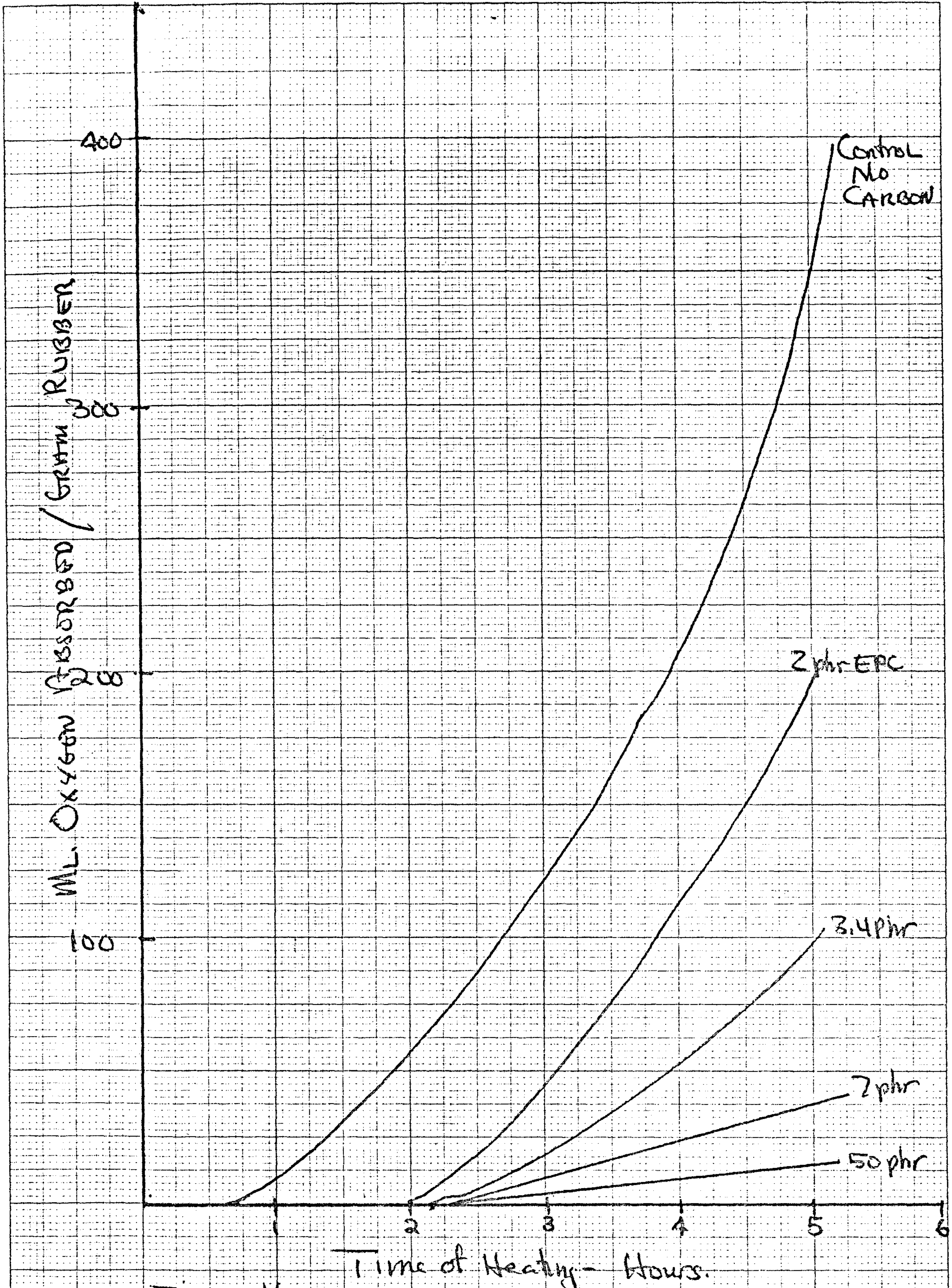

ML. OXYGEN ABSORBED / GRAM RUBBER
400
300
200
100
Control
No
Carbon
2 phr EPC
3.4 phr
7 phr
50 phr
1
2
3
4
5
6
Time of Heating - Hours.

FIGURE 16

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