

## Mechanism of Antioxidant Action in the Stabilization of Hydrocarbon Systems\*

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### INTRODUCTION

The stabilization of polymeric hydrocarbon systems involves protection against a number of factors which are encountered in processing and in use. One of the most important of these factors is oxidative degradation.<sup>1</sup> Heat and light are also important factors, but a major portion of their deteriorating action results from the accelerating effect of these agents upon the oxidation process.

### ANTIOXIDANT TYPES

Many substances are known which impart some degree of protection to hydrocarbon systems by retarding the oxidation reaction. These inhibitors of oxidation apparently do not all function by the same mechanism. Four types are indicated, based on differences in the method by which they exert their effect: (1) light absorbers, (2) metal deactivators, (3) peroxide decomposers, and (4) chain stoppers.

Light absorbers may either increase or decrease the rate of oxidation depending upon what ultimately happens to the energy absorbed. Many inhibitors for thermal oxidation actually promote photooxidation. Such a catalytic effect has been observed repeatedly with compounds of the secondary aryl amine type.<sup>2</sup> The use of small amounts of carbon black in polyethylene to protect it from outdoor weathering is a good illustration of this method of protection.

Deactivation of metal catalysts of oxidation is very important, since it is well known that many metal ions, such as iron and copper, when present as impurities in polymers will accelerate the oxidation process and bring about a rapid deterioration of the material. Organic compounds capable of forming

coordination complexes in which the metal is held in an inactive form will thus retard the oxidation process. These compounds usually have more than one coordination center, so that cyclic structures are formed which effectively enclose the metal ion in a cage. For this reason they are frequently referred to as chelating agents and as sequestering agents. Ethylenediaminetetraacetic acid is a well-known example of this type of compound.

Peroxide decomposers include those materials which promote the decomposition of peroxides to stable products rather than to free radicals. This type of antioxidant thus inhibits oxidation by reducing the rate of peroxide initiation of the free-radical oxidation mechanism. Kennerly and Patterson<sup>3</sup> have demonstrated that phenols, mercaptans, and a number of other organic sulfur compounds may function in this way as antioxidants for petroleum hydrocarbons. Some new thermal antioxidants for polyethylene recently reported from the Bell Laboratories<sup>4</sup> include similar thio compounds (e.g., phenyl benzyl sulfide) which are particularly effective in the presence of carbon black. These materials may also be functioning as peroxide decomposers. The mechanism by which peroxide decomposers act has not been established, but it is likely that a polar mechanism of decomposition is involved.

A similar explanation has been proposed<sup>5</sup> to account for the protective action of salts of the *N,N'*-disubstituted dithiocarbamates in the oxidative aging of natural rubber vulcanizates. It is known that zinc dimethyldithiocarbamate is formed in the vulcanization of rubber with tetramethylthiuram disulfide in the presence of zinc salts, and that the salt is extractable with acetone.<sup>6</sup> Since the superior aging resistance of these vulcanizates is destroyed by acetone extraction, it has been suggested<sup>7</sup> that this salt is responsible for the original good aging resistance.

\* Presented, by invitation, at the Symposium on Stabilization of Polyolefins, Division of Paints, Plastics, and Printing Ink Chemistry, 135th Meeting, American Chemical Society, Boston, April 1959.

## CHAIN STOPPING ACTION

The mechanism of antioxidant action with which we will be primarily concerned in this review is the fourth type, in which the inhibitor functions as a chain stopper for the free-radical chain mechanism of oxidation. The hindered phenols and secondary aryl amines are familiar examples of this type. The manner in which these compounds function is in dispute at the present time. Four different reactions have been proposed for the initial step of the chain-stopping action, and each is supported by some experimental evidence. Each of the reactions provides for interruption of the free-radical chain mechanism by interaction of a propagating radical with the antioxidant. The four mechanisms that have been proposed are: (1) hydrogen donation to  $RO_2\cdot$  by the antioxidant, (2) electron donation to  $RO_2\cdot$  by the antioxidant, (3) addition of  $RO_2\cdot$  to the aromatic ring of the antioxidant, and (4) formation of a  $\pi$ -complex between  $RO_2\cdot$  and the aromatic ring of the antioxidant.

The first reaction listed above in which the antioxidant donates a labile hydrogen to a peroxy radical to form a hydroperoxide has generally been considered to be the most probable reaction in the case of phenols and amines (other than tertiary). The extensive studies of Bickel and Kooyma<sup>8</sup> in which they measured the kinetics of the competition of  $RO_2\cdot$  for the hydrogen of the antioxidant,  $AH$ , and a reactive hydrocarbon,  $RH$ , are consistent with this mechanism. Products isolated from the reaction could be accounted for on the basis of removal of hydrogen by one radical and combination of the residue with another peroxy radical. The same products could be formed ultimately, however, starting with any of the other initial reactions.

Angert and Kuzminskii<sup>9</sup> have recently summarized chemical evidences from their extensive studies of antioxidant action which also support the view, that in phenyl-2-naphthylamine and its derivatives, cleavage of the  $N-H$  bond is primarily responsible for chain termination. Replacement of the hydrogen of  $N-H$  by an alkyl group decreased the effectiveness of the inhibitor. Infrared studies showed that  $N-H$  absorption decreased as inhibited oxidation progressed, and that  $C-N$  and  $N-N$  absorption increased. Substitution of electron-releasing groups in the phenyl group of phenyl-2-naphthylamine increased its effectiveness as an inhibitor, while electron-attracting substituents

decreased its effectiveness in rubber oxidation. Thus, a higher electron availability appears to favor the homolytic cleavage of the  $N-H$  bond. The increased electron density would also favor the alternative mechanism of electron donation by the antioxidant. Thus, while their work supports the hydrogen donation mechanism, it does not exclude the other possibilities.

## INHIBITED OXIDATION

The mechanism of inhibited oxidation differs from uninhibited oxidation in several important respects. Reactions involving the antioxidant must be included, and the relative importance of some of the reactions in the oxidation mechanism is altered. The rate of uninhibited oxidation is independent of oxygen concentration<sup>10</sup> (except at very low concentrations), but the rate of inhibited oxidation is affected by changes in the oxygen concentration.<sup>11</sup>

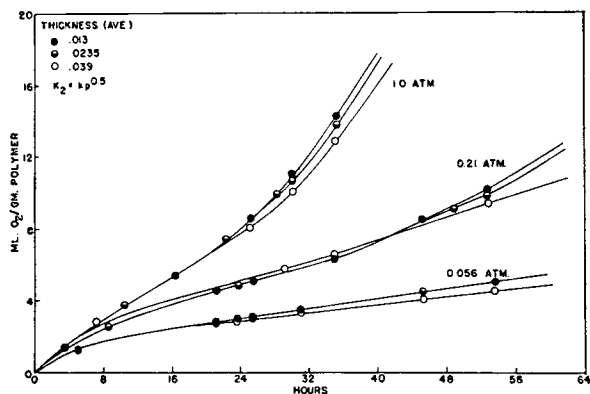


Fig. 1. Oxygen absorption (ml.  $O_2$ /g. polymer,  $25^\circ C.$ , 760 mm.) of inhibited Hevea black stock at  $100^\circ C.$  and various partial pressures of oxygen (total pressure 1 atm.)

Figure 1 illustrates a case in the oxidation of a natural rubber vulcanizate in which the rate in the constant-rate portion of the oxygen-absorption curve varies with the square root of the oxygen concentration. This constant-rate period is controlled by the antioxidant in that the slope and duration of the linear portion of the curve depend upon the nature and concentration of the antioxidant. This stage is usually not observed in uninhibited oxidation. Variations in the concentration of antioxidant and other changes in the compounding of the rubber resulted in some deviation from the simple square-root dependence on the partial pressure of oxygen in the aging atmosphere.

Three variations in the dependence of rate  $K_2$  were encountered experimentally:

$$K_2 = kP^{1/2} \text{ (strongly inhibited)} \quad (1)$$

$$K_2 = k(P + a)^{1/2} \text{ (weakly inhibited)} \quad (2)$$

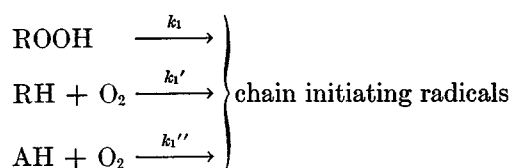
$$K_2 = k(P + a)^{1/2} + \gamma P \text{ (different accelerator)} \quad (3)$$

The observed dependence of rate on oxygen concentration indicated that some initiation of oxidation resulted from direct attack of  $O_2$  on the hydrocarbon, on the antioxidant, or both, in addition to the usual initiation by peroxide decomposition. The latter is the only important initiation reaction in uninhibited oxidation.

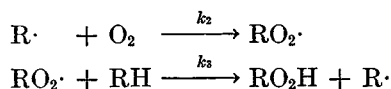
There is good evidence that radicals derived from the antioxidant by removal of the active hydrogen can, in some instances, participate in a continuation of the oxidation mechanism. The catalytic effect of certain amine-type antioxidants in photooxidation has already been mentioned. In thermal oxidation, an optimum antioxidant concentration is usually observed such that larger amounts lead to a more rapid rate of oxygen uptake by the hydrocarbon.

A mechanism for inhibited oxidation which includes all of the ways in which the antioxidant appears to function<sup>11</sup> is presented in the following sequence of reactions. Participation of the antioxidant in initiation and in propagation (by chain transfer) is included, as well as in termination. The chain transfer process may actually involve reaction of  $A\cdot$  with  $O_2$  to form  $AO_2\cdot$ , and this radical then attacks  $RH$  as has been proposed by Angert and Kuzminskii.<sup>9</sup> The initial step in the chain stopping action is represented as involving the abstraction of a hydrogen atom from the antioxidant by a peroxy radical to leave a more stable antioxidant radical which subsequently combines with another free radical.

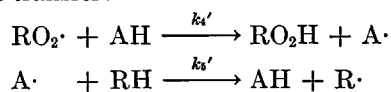
Initiation:



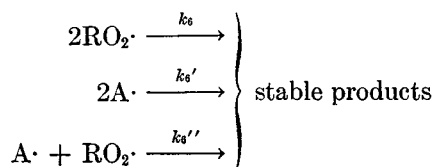
Propagation:



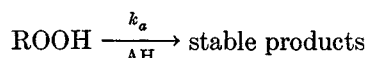
Chain transfer:



Termination:



Peroxide destruction:



An equation for the rate of oxygen absorption  $K_2$  has been derived<sup>11</sup> on the basis of the postulated sequence of reactions using steady-state kinetics. The equation includes both square root and first-power terms involving oxygen concentration and thus can be converted to a form similar to the empirical equations previously given.

$$K_2 = b(P + cK_2)^{1/2} + a(P + dK_2) \quad (4)$$

Solving for  $K_2$  and making some simplifying substitutions we obtain a more convenient form for calculation of rates:

$$K_2 = \alpha[1 + (1 + \beta P)^{1/2}] + \gamma P \quad (5)$$

When the second term is negligible and when  $c$  in eq. (4) approaches zero, a simple square-root dependence on the partial pressure of oxygen is obtained. The experimentally observed rates at different oxygen concentrations can be correlated even better by use of these equations than was possible with the empirical relationships originally developed, eqs. (1)–(3). This results from the effect of the quantity  $cK_2$ , which changes with the rate of oxidation rather than being constant as indicated in the original approximation. The observed and calculated rates are compared in Table I for natural rubber vulcanizates over a range of oxygen concentrations with typical examples of amine and phenolic antioxidants. The agreement of the experimental results with the predictions of the mechanism shows that the reactions postulated for the antioxidant are reasonable.

The effect of initiation by direct oxygen attack is represented by the oxygen pressure term  $P$  in eq. (4), while the term  $cK_2$  reflects the effect of initiation by a process which is independent of oxygen concentration. This is presumed to be the usual initiation by peroxide decomposition. The fraction  $cK_2/(P + cK_2)$  should, therefore, indicate the proportion of the total initiation contributed by peroxide decomposition. Table II

shows how this fraction varies with antioxidant concentration in a natural rubber vulcanizate containing carbon black. The decrease of this term effectively to zero with the higher concentrations indicates that the antioxidant is functioning

TABLE I  
Comparison of Observed Rates of Oxidation with Calculated Values at Various Oxygen Concentrations

	O <sub>2</sub> pressure, atm.	Rate, K <sub>2</sub> , ml. O <sub>2</sub> 25°C./g. polymer/hr.	
		Observed	Calculated
Hevea black stock			
+ Phenyl-2-naphthyl-amine (2 phr) at 90°C.	1.00	0.100	0.100
	0.43	0.061	0.062
	0.21	0.042	0.420
	0.13	0.033	0.033
Hevea gum stock			
+ 2,6-Di- <i>tert</i> -butyl-4-methylphenol (3 phr) at 100°C.	1.00	0.110	0.110
	0.76	0.096	0.096
	0.41	0.072	0.072
	0.21	0.055	0.055

in part by reducing peroxide initiation. The most likely explanation is that in the presence of carbon black this antioxidant also functions as a peroxide decomposer. This is the experimental basis for including the final reaction, illustrating

TABLE II  
Evidence for Decreased Initiation by Peroxide in the Presence of Amine Antioxidants and Carbon Black

	Antiox. concn., (phr)	c	cK <sub>2</sub> /(P+cK <sub>2</sub> )	
			In O <sub>2</sub>	In air
Hevea black stocks at 90°C.				
Uninhibited	0	7.2	0.60	0.73
Phenyl-2-naphthyl-amine	1	2.8	0.27	0.46
	2	0.0	0.0	0.0
	3	0.0	0.0	0.0

peroxide destruction by conversion to stable products, as a part of the mechanism of inhibited oxidation. The effect was much smaller in the absence of carbon black, and a hindered phenol was less effective than the secondary aryl amine in reducing peroxide initiation. The chain stopping mechanism of antioxidant action would also reduce peroxide initiation by limiting peroxide formation, but the peroxide decomposer also destroys peroxide that is formed.

## KINETIC ISOTOPE EFFECT

If hydrogen abstraction is the initial step in the chain stopping mechanism of antioxidant action, it is reasonable to expect that replacement of the reactive hydrogen by deuterium should alter the rate of the reaction. The abstraction of deuterium by a peroxy radical would be expected to be slower and therefore the deuterated form of the antioxidant would be less effective. As a result, the rate of oxidation would be greater and a kinetic isotope effect would be observed for the oxidation reaction.

Hammond, Boozer, and co-workers<sup>12</sup> employed deuterated secondary aryl amines in a study of the oxidation of cumene and Tetralin. Their data showed no significant difference in the rate of oxidation when N—H was replaced by N—D in the antioxidant. They concluded from this work that chain termination by antioxidants did not involve hydrogen abstraction, and proposed instead that a  $\pi$ -complex was formed between the RO<sub>2</sub> radical and the aromatic ring. Reaction of a second radical with the complex would then give the observed products.

Pedersen<sup>13</sup> used deuterated *N,N'*-diphenyl-*p*-phenylenediamine in a study of the induction period in the oxidation of gasoline. No significant change in length of the induction period was observed when deuterium was present in place of hydrogen in the antioxidant. Pedersen, too, concluded that hydrogen abstraction was not the initial step in the chain stopping action at least for amine-type antioxidants. Electron donation by the antioxidant was proposed as an alternative which would also explain the known weak antioxidant activity of tertiary amines.

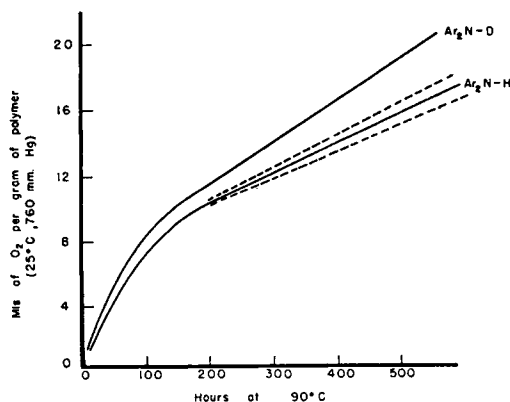


Fig. 2. Kinetic isotope effect in inhibited oxidation of butadiene-styrene polymer with 3 phr normal and deuterated *N*-phenyl-2-naphthylamine, 90°C., 1 atm. oxygen pressure.

Bickel and Kooyman,<sup>14</sup> have commented on the work of Boozer and Hammond to the effect that the absence of an isotope effect is inconclusive if the activation energy is low since it would lead to a very small isotope effect. They studied the reaction of a less active radical (diphenylpicrylhydrazyl) which would have a correspondingly higher energy of activation. In this case they obtained a ratio,  $k_H/k_D$ , of 1.95 for the rates of reaction with normal and deuterated 2,6-di-*tert*-butyl-4-methylphenol.

We have used the deuterium isotope effect to study the mechanism of antioxidant action in the inhibited oxidation of butadiene-styrene rubber.<sup>15</sup> The volumetric oxygen absorption method<sup>16</sup> which we have used to study oxidation and antioxidant action in natural and synthetic rubber<sup>11</sup> provides a reproducible constant-rate stage which is a measure of the rate of inhibited oxidation. Both hindered phenols and secondary aryl amines have been studied and a definite isotope effect was observed with each type. Figure 2 illustrates the data obtained with phenyl-2-naphthylamine in SBR polymer, in which case the ratio of the slopes in the constant-rate stage,  $k_D/k_H$ , was 1.8 with a deuterium substitution on nitrogen of not less than 60%. The dashed lines show the calculated standard deviations of the data for the normal N-H form of the antioxidant. In the case of 2,6-di-*tert*-butyl-4-methylphenol, the observed ratio of oxidation rates was 1.3 with a deuterium substitution of not less than 77% on the phenolic oxygen. These results strongly support the hydrogen donation mechanism of antioxidant action in the inhibited oxidation of rubber.

Additional support for this mechanism is supplied by isotope effects observed in analogous studies involving the reaction of free radicals with phenolic antioxidants. Walling and co-workers<sup>17</sup> reacted acyl peroxides with phenols and observed a small but constant isotope effect ( $k_H/k_D = 1.3$ ) when O-H was replaced by O-D. The isotope effect obtained by Bickel and Kooyman<sup>14</sup> in the reaction of diphenylpicrylhydrazyl radical with a hindered phenol has already been cited above. Ingold<sup>18</sup> has reported an appreciable isotope effect in the oxidation of mineral oil in the presence of a phenolic inhibitor.

Recent studies<sup>19</sup> in our laboratory have included additional antioxidants in synthetic rubber polymer and some preliminary work has also been carried out with vulcanized rubber. In some of these cases no significant isotope effect could be measured.

Indeed, there was even a reversal of the isotope effect in a few cases. All of these variations can be accounted for on the basis of the combined effects of changes in temperature, concentration, and nature of the antioxidant employed. The negative results reported in the literature<sup>12,13</sup> might be accounted for similarly on the basis of a resultant effect too small to be measured by the particular experimental method involved, or by exchange reactions (resulting, for example, from exposure to small amounts of water in the atmosphere or formed by oxidation) which removed most of the deuterium before the effect could be measured.

### CONCLUSIONS

The present status of our understanding of the mechanism of antioxidant action in hydrocarbon systems indicates that more than one mechanism is involved. Different types of antioxidant and different conditions of oxidation give evidence of four different types of antioxidant action: (1) protection against photooxidation by light absorbers, (2) deactivation of metal catalysts of oxidation, (3) destruction of peroxides by decomposition to stable products, and (4) chain-stopping action by reaction with free radicals involved in the oxidation process.

The mechanism of the chain-stopping action is in itself complex in that more than one mode of action is possible. The reactions that have been proposed include donation of hydrogen or donation of an electron by the antioxidant to a free radical, or combination of a free radical with the aromatic ring of the antioxidant either by direct addition or by  $\pi$ -complex formation.

The demonstration of a deuterium isotope effect in the inhibited oxidation of synthetic rubber polymer with both amine and phenolic inhibitors indicates that the donation of a hydrogen atom by the antioxidant to a chain-propagating radical is the initial step in the usual mechanism by which these compounds serve as chain stoppers. Earlier failures to observe such an effect may be attributed either to limitations of the experimental methods and the particular systems studied or to possible exchange reactions which would displace the deuterium before the effect could be observed. This interpretation is supported by other examples of deuterium isotope effects reported in the literature for reactions involving free radicals and phenols.

It does not follow that hydrogen donation is the only mechanism by which chain stoppers act, since many compounds with no replaceable hydrogen exhibit some activity. Tertiary amines, for exam-

ple, may act by some other mechanism such as electron donation or combination of a peroxy radical with the aromatic ring. Nevertheless, the deuterium isotope effects that have been observed, together with supporting chemical and kinetic evidences, clearly establish hydrogen donation as one of the important mechanisms by which amine and phenolic antioxidants function as chain stoppers in the stabilization of hydrocarbon systems.

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### Synopsis

Four antioxidant classifications, based on differences in the method by which they exert their effect, are noted.

The mechanism of the chain-stopping action is discussed in terms of four different reactions which have been proposed. The participation of the antioxidant in the mechanism of inhibited thermal oxidation is reviewed. The hydrogen donation mechanism as the first step in the chain-stopping mechanism has been investigated by observing the effect of replacing the active hydrogen of the antioxidant by deuterium. Contrary to the findings of some prior workers, a kinetic isotope effect has been demonstrated with a secondary aryl amine antioxidant as well as with phenols. These results, together with other supporting evidences reported in the literature, indicate that abstraction of a hydrogen from the antioxidant is the initial step in the usual mechanism by which antioxidants serve as chain stoppers in the oxidation of hydrocarbon systems.

### Résumé

On présente ici quatre classifications d'antioxydant, basées sur les différences dans le processus par lequel ils exercent leurs effets. Le mécanisme d'action de l'arrêt de chaîne est discuté sur la base des quatre réactions différentes qui ont été proposées. La participation de l'antioxydant dans le mécanisme d'inhibition de l'oxydation thermique est également envisagé. Le mécanisme qui fait intervenir un transfert d'hydrogène dans le premier stade de la réaction de coupure de chaîne, a été contrôlé en observant l'effet du remplacement de l'hydrogène actif de l'antioxydant par du deutérium. A l'encontre de ce qui a été trouvé par quelques chercheurs précédents, un effet cinétique de l'isotope a été mis en évidence aussi bien avec une arylamine secondaire qu'avec les phénols. Ces résultats, joints, à d'autres preuves rapportées dans la littérature, indiquent que la capture de l'hydrogène actif de l'antioxydant est le stade initial dans le mécanisme habituel par lequel les antioxydants agissent comme stoppeurs de chaîne dans l'oxydation des systèmes hydrocarbonés.

### Zusammenfassung

Es werden vier Klassifizierungen für Antioxydantien angegeben, die sich auf Unterschiede in der Art und Weise gründen, in der diese ihren Einfluss ausüben. Der Mechanismus der Kettenabbruchswirkung wird an Hand von vier verschiedenen Reaktionen diskutiert, die bis jetzt vorgeschlagen wurden. Ein Überblick über die Teilnahme des Antioxydants am Mechanismus der inhibierten, thermischen Oxydation wird gegeben. Die Wasserstoffübertragung als der erste Schritt beim Kettenabbruchsmechanismus wurde untersucht, und zwar durch eine Beobachtung des Einflusses des Ersatzes des aktiven Wasserstoffs des Antioxydants durch Deuterium. Im Gegensatz zu den Befunden früherer Autoren wurde sowohl bei einem sekundären Arylamin als Antioxydants als auch bei Phenolen ein kinetischer Isotopeneffekt nachgewiesen. Diese Ergebnisse sowie die in der Literatur vorhandenen, in die gleiche Richtung weisenden Angaben, zeigen dass Übertragung eines Wasserstoffs vom Antioxydants der erste Schritt beim normalen Mechanismus der Kettenabbruchswirkung von Antioxydantien bei der Oxydation von Kohlenwasserstoffsystemen ist.

Received August 24, 1959