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PHENOTHIAZINE-TYPE ANTIOXIDANTS AND THEIR MODE OF ACTION

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ABSTRACT

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AUTHORIZATION

WPI Problems C02-002 and C02-112
WA 300-004 and WA 402-110

ABSTRACT

The oxidation inhibition action of phenothiazine-type compounds on lubricating oils has been investigated in a dynamic system over the temperature range 100° to 175° C in the presence of metal catalysts. Many of the compounds indicated activity at the higher temperatures. Resonance-stabilized free radicals, capable of reducing peroxides, were postulated to be the actual inhibiting configurations. It was demonstrated that the inhibitors were of the regenerative rather than the sacrificial class.

A comparable degree of effectiveness was found to exist in many of the oxygenated derivatives of phenothiazine; this was correlated with their ability to exist as resonance-stabilized free radicals. The ease of bond rupture to form free radicals at the heterocyclic nitrogen is discussed in relation to bond energies. The decreasing effectiveness of phenoselenazine and phenoxazine as compared to phenothiazine was ascribed to the lower oxidation potentials. Improvement of the antioxidant action of phenothiazine by appropriate changes in its molecular configuration is discussed.

Some high-molecular-weight derivatives of phenothiazine with lesser tendency to volatilize were shown to be of the same order of effectiveness as the parent compound. This is of practical importance in such high-temperature applications as lubricants for turbo-jet and gas-turbine engines and greases for silicone-clad motors and generators.

PROBLEM STATUS

This is an interim report; work is continuing.

AUTHORIZATION

NRL Problems C02-06D and C02-11R
NA 350-064 and NR 402-110

PHENOTHIAZINE-TYPE ANTIOXIDANTS AND THEIR MODE OF ACTION

INTRODUCTION

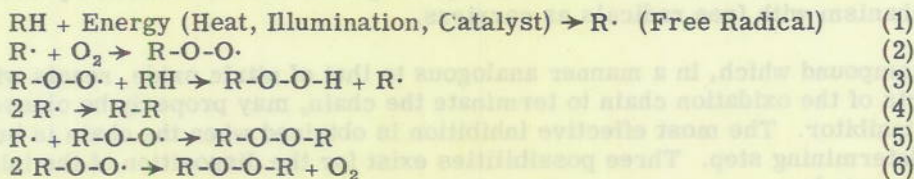
The use of phenothiazine for preventing oxidative changes in polyethylene oils has been reported (11,17). In a recent investigation at this laboratory (10) on antioxidants for turbo-jet lubricants, phenothiazine exhibited promise for use at temperatures up to 163° C. It was demonstrated that a pure reference fluid, di(2-ethylhexyl) sebacate, which has been utilized as a turbo-jet lubricant, could be stabilized with respect to viscosity changes and acid production by the presence of a comparatively low concentration of phenothiazine (0.02 to 0.50 weight percent, depending upon the temperature employed). At the upper temperatures, however, there was deposition of lacquer on the oxidation cell wall and on the metal catalyst strips, and there was also some indication of excessive volatility of the additive.

There are numerous applications for high-temperature antioxidants, such as additives to greases for silicone-clad motors and generators and as lubricants for gas turbines and the aforementioned turbo-jet engines. The inhibition activity of phenothiazine was of such high order as to warrant further investigation. Of particular interest were the determination of the practical upper temperature limit of inhibition, the elucidation of the possible mechanisms involved in the inhibition process, the effect of structure on inhibition activity, and the development of inhibitors less volatile than phenothiazine but with the latter's desirable features.

THEORETICAL CONSIDERATIONS

The Oxidation Phenomenon

It has been generally accepted that the majority of organic oxidation reactions proceed by a chain mechanism with the formation of a hydroperoxide as the rate-determining step, although other mechanisms have also been postulated (13,16). The available evidence concerning the auto-oxidation of such compounds as tetralin (14) indicates that decomposition of the hydroperoxide leads to new active molecules which may reinitiate other chains. The over-all process may be demonstrated in the following general fashion:



Reactions 1 to 3 represent the initiation and subsequent continuation of oxidation by means of the generated free radical $R\cdot$. Reactions 4 to 6 represent different methods of terminating the reaction chain. The presence of aldehydes and acids in the oxidation products may be accounted for by the decomposition of the hydroperoxide $R-O-O-H$:

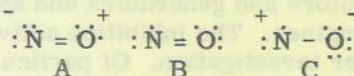


Oil-insoluble oxidation products such as lacquer and sludge are generally attributed to polymerization, as exemplified by reactions 4 to 6, and to esterification. Recent work on the chemical composition of oxidized mineral oils (6) indicates, however, that these insolubles are oxygenated products whose molecular weights are of the same magnitude as that of the original oil.

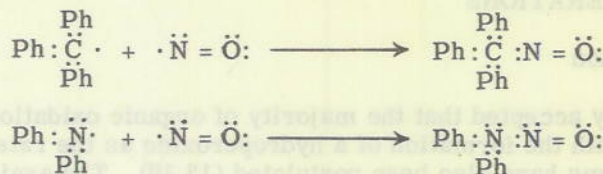
The Inhibition Phenomenon

There are several mechanisms by which the action of an oxidation inhibitor can be explained. According to one postulated mechanism, no oxidation of the bulk oil can occur until the inhibitor has been entirely depleted by preferential oxidation. This type of inhibition is undesirable in a lubrication system, because the antioxidant is rapidly consumed and the effective lubricant life is thereby shortened.

A more useful inhibitor type functions by breaking an oxidation chain reaction. Any reaction which proceeds with the generation of free radicals may be terminated readily by the addition of a relatively low concentration of an inhibitor or chain stopper. A classic example of the latter is nitric oxide whose electronic configuration may be written in three forms:



The neutral form B is rendered stable, despite its odd electron, because of the existence of the resonating configurations A and C. It will, however, react readily with free radicals such as those derived from triphenyl methane and phenyl nitrogen to form compounds with the stable electronic octet around the oxide nitrogen:



Should the nitric oxide molecule react with a free radical derived from a chain reaction, then the chain would be terminated. In fact, the retardation of a reaction after the addition of nitric oxide generally is considered proof per se that the reaction proceeded by a chain mechanism with free radicals as carriers.

Any compound which, in a manner analogous to that of nitric oxide, reacts with one of the products of the oxidation chain to terminate the chain, may properly be classed as an oxidation inhibitor. The most effective inhibition is obtained when the chain is broken at the rate-determining step. Three possibilities exist for the disposition of the inhibitor after it has reacted:

- (1) The inhibitor is oxidized to a compound which is incapable of further antioxidant action.
- (2) The inhibitor is oxidized to a compound which still exhibits antioxidant action, but generally to a reduced extent. Further oxidation may result in the formation of an inactive compound.
- (3) The inhibitor is capable of regeneration. This type of inhibitor is the most desirable, provided the rate of regeneration is high. The total period of effective inhibition would be a function of the efficiency of inhibitor regeneration.

EXPERIMENTAL PROCEDURE

As in the previous work (10), di(2-ethylhexyl) sebacate was employed as the reference oil. This fluid recommends itself for several reasons: it is representative of the higher boiling diesters which indicate promise as bearing lubricants for turbo-jet engines; it is readily available in a high degree of purity; and it is susceptible to the same types of oxidation inhibitors applicable to many petroleum oils. The additives were for the most part synthesized in this Laboratory (15) although several were obtained from commercial sources. All oxidation stability tests were conducted in the previously described dynamic-type apparatus (1,2) at temperatures ranging from 100° to 175° C for 168 hours.

Briefly, the apparatus consists of a pyrex glass oxidation cell, containing 25 gm of the reference fluid and additive, through which is bubbled clean, dry, CO₂-free air at the rate of 20 ml per minute. The effluent gases pass through a known volume of standard KOH solution. Daily titration of this solution with standard H₂SO₄ solution determines the amount of volatile acids generated by the sample. The milligrams of KOH required to neutralize the volatile acids, divided by the total sample weight, provides a value known as the volatile acid neutralization number. To accelerate oxidation and simulate service conditions, metal strips of cold-rolled steel, copper, and duralumin were placed in the sample so as to form a triangular prism. Among the criteria used to denote the efficacy of the inhibitors were changes in viscosity, color, acid numbers, metal catalyst weight and appearance, and the formation of sludge and lacquer.

The daily volatile acid neutralization number was utilized to follow the course of the oxidation and to define the induction period, the time interval under the given test conditions during which no appreciable oxidation of the oil occurs. Previous work at this Laboratory had indicated that the commencement of formation of volatile acids from the oxidation of diesters approximated very closely the end of the induction period (1). In the absence of antioxidants there is no difficulty in determining this period since the "break" in the curve of volatile acid vs. time is well defined. In the presence of some antioxidants the increase in the rate of formation of volatile acids during oxidation is very gradual, probably being a function of the inhibitor concentration. In such cases, the end of the induction period has been arbitrarily chosen, for the purpose of this investigation, as the time at which the rate of formation of volatile acids was equivalent to a neutralization number increase of 0.05 for a one-hour period. This was obtained from the curve of volatile acid neutralization number vs. time. When the concentration of the antioxidant falls below some limiting value, its inhibition activity is negligible, and thereafter the volatile acids are formed at a highly accelerated rate.

The concentration of the inhibitors is expressed both in molality and weight percent. Molality, which is defined as the number of moles of solute per 1000 gm solvent, was employed as being a true measure of the concentration of the inhibitor. Thus a direct

comparison of the efficiencies of different inhibitors can be made. Since the molal concentrations of the antioxidants used in this investigation were small decimal fractions varying from approximately 0.001 to 0.05, it was considered advisable to express their concentrations as millimolal (MM), or 10^{-3} moles per 1000 gm of solvent. The weight percent concentrations of the inhibitors are included since they are of economic interest and indicate whether the concentrations were so large as to affect the physical properties of the base fluid. In general, all additives were employed in the same molal concentrations as was phenothiazine at the various temperature levels employed.

DISCUSSION OF RESULTS

Efficacy of Antioxidants Studied

The behavior of the reference fluid, di-(2-ethylhexyl) sebacate under the test conditions with no additive present is shown in Table 1. At 100°C, although there was an induction period of 72 hours, serious oxidative changes were apparent after 168 hours. As the oxidation temperature was raised, deterioration of the fluid was increasingly rapid and more marked, until at 163°C gelation of the oil had taken place at the completion of the test period. The pure fluid was therefore sufficiently oxidation-sensitive, so that any improvement imparted by an additive could be readily discerned.

The antioxidant action of the compounds studied are shown in Tables 2 through 7. These compounds have been arranged according to types to facilitate their discussion. In Table 2 are the results obtained with phenothiazine and those analogues in which changes were introduced in the heterocyclic ring. The relative effectiveness of phenothiazine as an antioxidant through the entire temperature range is apparent. Acid production and viscosity changes were negligible from 100° to 150°C; above 150°C these oxidative manifestations were present to a slight extent. At 175°C a small amount of colored material in the water condenser indicated that some volatilization had taken place. Although no analysis of this material was made in this Laboratory, on the basis of other work which indicated the relatively high vapor pressure of the additive it was assumed the volatile matter was an oxidation product of phenothiazine. The deposition of lacquer on the metal catalysts and on the walls of the oxidation cell commenced at 150°C and thereafter became more pronounced as the test temperature was elevated. It should be noted that the concentration of phenothiazine required for inhibition increased with the test temperature. Equivalent concentrations were used for the additives included in this investigation.

The slightly soluble phenothiazine dimer, 10,10'-diphenothiazine, followed the same general antioxidant pattern as did the parent compound at 150° and 163°C, though there was somewhat less lacquer formation. At 175°C comparatively little inhibition was obtained, a possible consequence of the incomplete solubility of the compound. Neither phenoselenazine nor phenoxazine were as effective as was phenothiazine, the oxazine being the poorer. Both phenazine and thianthrene, with two nitrogen and two sulfur atoms respectively in the heterocyclic ring were markedly inferior inhibitors even at 150°C. No improvement over phenazine was offered by the partially hydrogenated derivative, 1,2,3,4-tetrahydrophenazine.

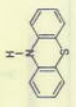
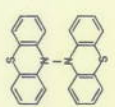
The results obtained with the oxygenated derivatives of phenothiazine are shown in Table 3. In the case of phenothiazone-3 with a quinoidal oxygen on one ring, antioxidant activity was comparable to that of phenothiazine despite somewhat less solubility. The more completely oxygenated compound, 7-hydroxyphenothiazone-3 (thionol) was not as effective as was phenothiazone-3 at 175°C. The induction period was only 150 hours and there was a noticeable increase in viscosity. However, since the purity of the thionol is

TABLE 1
Dynamic Oxidation of Di(2-Ethylhexyl) Sebacate, No Inhibitor Added*

Antioxidant	Temperature, °C	Induction Period, Hours	Molality x 10 ³	Weight Percent	Percent Increase in Viscosity at 100° F	Volatile Acid Neut. No.	Nonvolatile Acid Neut. No.	Metals						Sample Appearance		
								Weight Change Mg/Cm ²		Appearance		C.R.S.	Cu		Dural	Sample Appearance
								C.R.S.	Cu	C.R.S.	Cu					
None	100	72	---	---	14.	5.5	5.3	<0.1	-0.1	-0.1	Discolored.	Oxidized appearance.	No change.	No change.		
	125	12	---	---	375.	67.	58.	+0.1	-3.5	+0.3	Med. lacquer.	Etched.	Med. lacquer.	Opaque lacquer on wall.		
	150	12	---	---	1000.	83.	22.	<0.1	-4.2	+0.1	Dull deposit.	Bright etched.	No change.	Opaque, Black.		
	163	12	---	---	---	95.	---	<0.1	-67.	+0.1	Discolored.	Etched.	Lt. peacock colors.	Gelled.		

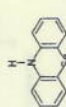
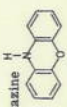
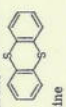
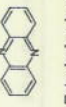
* Duration of test 168 hours.

TABLE 2
Oxidation-Inhibition Imparted to Di(2-Ethylhexyl) Sebacate by Phenothiazine and Analogous*

Antioxidant	Temperature, °C	Induction Period, Hours	Molality x 10 ³	Weight Percent	Percent Increase in Viscosity at 100° F	Volatile Acid Neut. No.	Nonvolatile Acid Neut. No.	Metals						Sample Appearance		
								Weight Change Mg/Cm ²		Appearance		C.R.S.	Cu		Dural	Sample Appearance
								C.R.S.	Cu	C.R.S.	Cu					
Phenothiazine 	100	>168	23.4	0.47	1.0	0.09	0.34	---	---	---	Dull.	Lt. lacquer. Lt. peacock colors.	No change.	No change.		
	125	>168	1.1	0.02	<1.0	0.17	0.12	<-0.1	<-0.1	<-0.1	Darkened.	Brassy appearance.	No change.	Clear, Dark brown.		
	150	>168	4.3	0.09	<1.0	0.56	<0.01	<+0.1	<+0.1	<+0.1	Lt. lacquer. Lt. peacock colors.	Lt. lacquer. Lt. peacock colors.	Lt. lacquer. Lt. peacock colors.	Clear, Light lacquer on wall.		
	163	>168	23.4	0.47	<1.0	0.28	1.0	+0.3	0.2	0.2	Heavy lacquer.	Heavy lacquer.	Heavy lacquer.	Clear, Light lacquer on wall.		
10,10'-Diphenothiazine 	175	>168	46.8	0.94	3.8	3.3	2.2	+0.4	0.4	0.5	Nonadherent deposit. Heavy lacquer.	Nonadherent deposit. Heavy lacquer.	Nonadherent deposit. Heavy lacquer.	Very dark red. Cloudy. Partially adherent deposit on wall. Small amount of volatile materials in upper coil.		
	150	>168	11.7	0.46	0.8	0.32	0.08	<+0.1	<+0.1	<+0.1	Heavy peacock colors.	Discolored.	Lt. peacock colors.	Compound insoluble in oil. Final clear red. Insoluble compound on bottom.		
	163	>168	23.4	0.93	1.6	0.95	0.52	<+0.1	+0.1	+0.1	Heavy peacock colors.	Med. lacquer.	Med. lacquer.	Clear, dark red. Sludge (probably undissolved anti-oxidant). Medium lacquer on wall.		
	175	120	46.8	1.85	36.	23.	91.	+0.2	<-0.1	-0.2	Nonadherent deposit. Heavy lacquer.	Etched. Adherent deposit.	Nonadherent deposit. Heavy lacquer.	Opaque, Black sludge. Medium lacquer on wall.		

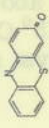



* Duration of test 168 hours.

TABLE 2 (Cont.)
 Oxidation-Inhibition Imparted to Di(2-Ethylhexyl) Sebacate by Phenothiazine and Analogues*

Antioxidant	Temperature, °C	Induction Period, Hours	Molality x 10 ²	Weight Percent	Percent Increase in Viscosity at 100° F	Volatile Acid Neut. No.	Nonvolatile Acid Neut. No.	Weight Change Mg/Cm ²			Metals			Sample Appearance	
								Cu		Dural		Appearance			
								C.R.S.	Cu	C.R.S.	Dural	C.R.S.	Cu		Dural
Phenothiazine 	150	> 168	11.7	0.29	< 1.0	3.8	0.88	< -0.1	-0.1	< -0.1	Med. lacquer.	Med. peacock colors.	Clear. Dark amber. Light lacquer on wall.		
	163	144	23.4	0.57	3.2	6.2	2.4	< +0.1	+0.4	+0.2	Etched. Some adherent deposit.	Nonadherent deposit. Lt. lacquer.	Clear. Very dark red. Sludge. Heavy lacquer on wall. Condensed volatiles in upper cell.		
Phenoxazine 	175	36	46.8	1.14	23.	26.	12.	+0.9	-0.1	+1.1	Nonadherent deposit. Heavy black lacquer.	Nonadherent deposit. Heavy black lacquer.	Opaque. Black. Very heavy lacquer on wall.		
	150	132	11.7	0.19	75.	18.	39.	< +0.1	+0.2	± 0.1	Med. lacquer.	Lt. peacock colors.	Cloudy. Brown. Light lacquer on wall.		
Thianthrene 	150	12	11.7	0.25	360.	56.	76.	< +0.1	-14.	± 0.1	Dull deposit. Peacock colors.	Lt. peacock colors.	Opaque. Brown. Bright lacquer on wall. Some sludge.		
	150	72	4.3	0.09	175.	22.	26.	< -0.1	-42.	± 0.1	Etched. Heavy oxide coat.	Etched. Heavy oxide colors.	Opaque. Brown.		
Phenazine 	150	72	11.7	0.21	407.	47.	43.	< +0.1	-44.	± 0.1	Etched.	Slightly discolored.	Opaque. Black.		
	150	72	11.7	0.21	466.	74.	64.	< +0.1	-13.	+0.1	Etched. Lt. peacock colors.	Lt. lacquer.	Opaque. Black.		

* Duration of test 168 hours.

TABLE 3
Oxidation-Inhibition Impacted to Di(2-Ethylhexyl) Sebacate by Oxygenated Derivatives of Phenothiazine*

Antioxidant	Temperature, °C	Induction Period, Hours	Molality x 10 ⁴	Weight Percent	Percent Increase in Viscosity at 100° F	Volatile Acid Neut. No.	Nonvolatile Acid Neut. No.	Metals						Sample Appearance			
								Weight Change Mg/Cm ²		C.R.S.		Appearance			Dural	Cu	Dural
								C.R.S.	Cu	Dural	Cu	C.R.S.	Cu				
Phenothiazine-3 	150	>168	4.3	0.09	<1.0	2.0	1.2	<+0.1	<+0.1	<+0.1	Discolored.	Discolored.	Discolored.	Clear. Red. Some sludge.			
	163	>168	23.4	0.50	1.3	1.0	0.80	<+0.1	<-0.1	<-0.1	Heavy peacock colors.	Med. peacock colors.	Med. peacock colors.	Clear. Red. Medium lacquer on wall. Condensed material in upper condenser.			
	175	>168	46.8	1.01	3.2	3.7	1.3	<+0.1	<-0.1	+0.8	Nonadherent deposit. Peacock colors.	Nonadherent deposit. Med. lacquer.	Nonadherent deposit. Med. lacquer.	Clear. Very dark red. Heavy lacquer on wall. Condensed material in upper condenser.			
7-Hydroxyphenothiazine-3 	150	>168	11.7	0.27	<1.0	2.7	0.23	<+0.1	<+0.1	<+0.1	Lacquer, peacock colors.	Lacquer, peacock colors.	Lacquer, peacock colors.	Clear. Dark red. Heavy lacquer on wall.			
	163	>168	23.4	0.54	3.0	2.0	0.80	+0.2	+0.1	+0.1	Heavy black lacquer.	Heavy black lacquer.	Spots of brown lacquer.	Clear. Dark red. Heavy lacquer on wall.			
	175	156	46.8	1.08	13.	6.8	6.8	+0.3	+0.2	+0.2	Nonadherent deposit. Heavy black lacquer.	Nonadherent deposit. Heavy black lacquer.	Nonadherent deposit. Heavy black lacquer.	Cloudy. Red. Sludge. Very heavy lacquer on wall.			
Phenothiazine-5-Oxide 	150	>168	11.7	0.25	<1.0	1.9	0.89	<+0.1	<+0.1	<+0.1	Heavy peacock colors.	Oxide coat.	Med. peacock colors.	Clear. Dark red. Heavy lacquer on wall.			
	163	>168	23.4	0.51	5.7	1.9	1.2	+0.1	<+0.1	+0.2	Heavy black lacquer.	Med. black lacquer.	Heavy black lacquer.	Clear. Dark red. Lacquer on wall. Sludge.			
	175	>168	46.8	1.01	6.5	2.5	1.7	+0.2	+0.3	+0.3	Nonadherent deposit. Heavy lacquer.	Nonadherent deposit. Heavy lacquer.	Nonadherent deposit. Heavy lacquer.	Cloudy. Red. Sludge. Heavy lacquer on wall. Condensed material in upper condenser.			
Phenothiazine-5-Dioxide 	150	12	11.7	0.27	643.	49.	60.	<+0.1	+19.	<+0.1	Med. peacock colors.	Nonadherent green deposit. Etched.	No change.	Opaque. Black.			
	163	12	23.4	0.54	757.	50.	51.	+0.2	+2.4	+0.2	Light lacquer.	Etched.	Light lacquer.	Opaque. Black. Medium lacquer on wall. Sludge. Condensed material in upper condenser.			
	175	12	46.8	1.08	71000.	49.	70.	+0.9	+1.4	+0.4	Heavy lacquer.	Heavy lacquer.	Heavy lacquer.	Opaque. Black. Heavy lacquer on wall. Sludge.			

* Duration of test 168 hours.

questionable (15) and since its solubility in the oil was exceeded, these results may not be a true indication of the effectiveness of the compound.

Oxidation of the heterocyclic ring of phenothiazine occurs at the sulfur atom and takes place in two stages. Phenothiazine-5-oxide is the first product of oxidation; its inhibition activity was generally comparable to that of phenothiazine, though solubility was incomplete at the higher concentrations. At 163° and 175° C, the increase in viscosity of the reference fluid at the end of the test period was only slightly greater than that observed with phenothiazine. The product of the second stage of oxidation is phenothiazine-5-dioxide whose solubility is less than that of the 5-oxide. However, it is a much inferior inhibitor, even at 150° C.

Aliphatic and aromatic substitutions on the heterocyclic ring of phenothiazine occur at the nitrogen atom. The inhibition effect of these compounds is shown in Table 4. Of the aliphatic derivatives, 10-ethylphenothiazine and 10-stearoylphenothiazine displayed no inhibition activity at 150° C when employed in the usual concentrations. Satisfactory inhibition with respect to prevention of acid generation and viscosity changes, but not in reference to precipitation of insolubles, was obtained with 10-octadecylphenothiazine up to 163° C. At 175° C the inhibition imparted by the compound was negligible, a possible consequence of the relatively low concentration employed. The behavior of 10-octadecylphenothiazine is somewhat anomalous in that it has inhibitory action, and the 10-ethyl and 10-stearoylphenothiazines, which are also aliphatic-substituted, display little inhibition. 10-Benzylphenothiazine acted similarly to the 10-octadecyl compound through 163° C. The generation of acids at 175° C was somewhat high although not sufficient to shorten the induction period, i.e., the volatile acid number did not rise more than 0.05 during any one-hour period. The only aromatic-substituted compound investigated was 10-phenylphenothiazine; it displayed no inhibition activity above 150° C.

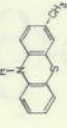

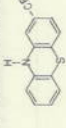



In Table 5 are the results obtained with benzenoid ring-substituted phenothiazines. With 3-methylphenothiazine some sludge was formed in the reference fluid at 150° and 163° C but inhibition was otherwise satisfactory. At 175°, the antioxidant action of this compound was poor. The behavior of 3,7-dimethylphenothiazine was analogous to that of the 3-methyl derivative; it was not, however, completely soluble in the concentrations employed at 163° and 175° C.

The trifluoromethyl derivatives of phenothiazine offered no improvement over the methyl analogues as regards antioxidant action and promoted the attack of the copper catalysts even when acid generation was not particularly excessive. This attack was probably a consequence of halogen acid derived from hydrolysis or an impurity. Etching was evident at 163° C with the 2-trifluoromethylphenothiazine and at 150° C with 2-trifluoromethyl-8-methylphenothiazine. Both 3-isopropoxyphenothiazine and 7-benzo [c] phenothiazine, although incapable of preventing the formation of insolubles, were otherwise satisfactory antioxidants.

The role of nitrogen in the high antioxidant activity of phenothiazine-type compounds was investigated by studying some aromatic-substituted amines (Table 6). None, with the exception of phenyl- α -naphthylamine, provided inhibition above 150° C. In high concentration, this compound was satisfactory at 163° but not at 175° C. It will be noted that the trifluoromethyl-substituted amine attacked the copper catalyst as did the trifluoromethyl-substituted phenothiazine.

In Table 7 are the results obtained with some miscellaneous additives. To study the contribution of sulfur to the inhibition activity of phenothiazine compounds, diphenylsulfide was investigated. It was found that no appreciable inhibition was obtained with the sulfide

TABLE 5
 Oxidation-Inhibition Imparted to Di(2-Ethylhexyl) Sebacate by Ring-Substituted Derivatives of Phenothiazine*

Antioxidant	Temperature, °C	Induction Period, Hours	Molality x 10 ³	Weight Percent	Percent Increase in Viscosity at 100° F	Volatile Acid Neut. No.	Nonvolatile Acid Neut. No.	Metals						Sample Appearance
								Weight Change Mg/Cm ²			Appearance			
								C.R.S.	Cu	Dural	C.R.S.	Cu	Dural	
3-Methylphenothiazine 	150	>168	4.3	0.09	<1.0	0.50	0.04	<+0.1	<+0.1	+0.3	Heavy peacock colors.	Discolored.	Med. peacock colors.	Clear. Amber. Lacquer on walls. Sludge.
	163	>168	23.4	0.40	1.6	1.0	0.59	<+0.1	<+0.1	<+0.1	Heavy peacock colors.	Heavy peacock colors.	Clear. Deep red. Medium lacquer on wall. Sludge.	
	175	120	46.8	0.99	315.	33.	40.	+0.2	-1.0	+0.1	Heavy lacquer.	Etched. Adherent deposit.	Lt. peacock colors. Lt. lacquer.	Opaque. Black. Medium lacquer on wall. Sludge.
3,7-Dimethylphenothiazine 	150	>168	11.7	0.51	1.0	0.44	0.30	<+0.1	<+0.1	<+0.1	Heavy peacock colors.	Heavy peacock colors.	Amber. Medium lacquer on wall.	
	163	>168	23.4	1.03	1.4	0.79	0.55	<+0.1	<+0.1	<+0.1	Heavy peacock colors.	Heavy peacock colors.	Amber. Some sludge. Heavy lacquer on wall.	
	175	72	46.8	1.05	>4000.	39.	47.	+0.2	-3.7	+0.2	Heavy peacock colors. Lt. lacquer.	Etched. Heavy lacquer.	Lt. peacock colors. Med. lacquer.	Opaque. Brown. Sludge. Heavy lacquer on wall. Condensed material in upper condenser.
2-Trifluoromethylphenothiazine 	150	>168	11.7	0.27	<1.0	2.5	0.79	<+0.1	<+0.1	<+0.1	Discolored.	Med. peacock colors.	No change.	Clear. Brown.
	163	>168	23.4	0.54	4.1	2.7	1.6	<+0.1	-0.4	<+0.1	Discolored.	Etched.	No change.	Clear. Very dark brown.
	175	24	46.8	1.08	8.9	11.	6.5	<+0.1	<+0.1	<+0.1	Discolored.	Slightly etched.	No change.	Opaque. Black. Medium lacquer on wall.
2-Trifluoromethyl-6-Methylphenothiazine 	150	>168	11.7	0.29	1.6	0.72	0.38	<+0.1	-2.3	<+0.1	Med. peacock colors.	Etched. Oxide coat.	No change.	Clear. Amber.
	163	>168	23.4	0.57	4.1	2.7	1.9	<+0.1	-2.3	<+0.1	Med. peacock colors.	Etched.	Very lt. peacock colors.	Clear. Deep red.
	175	24	46.8	1.14	29.	34.	20.	+0.2	-8.1	+0.2	Med. lacquer.	Etched. Med. adherent coat.	Med. lacquer.	Opaque. Black. Heavy lacquer on wall.
3-Isopropoxyphenothiazine 	150	>168	11.7	0.30	<1.0	1.9	1.4	<+0.1	<+0.1	<+0.1	Heavy peacock colors.	Heavy black lacquer.	Med. peacock colors.	Clear. Red. Heavy lacquer on wall.
	163	>168	23.4	0.60	4.0	3.2	1.3	+0.1	<+0.1	+0.2	Heavy black lacquer.	Heavy black lacquer. Nonadherent black deposit.	Heavy black lacquer.	Clear. Very dark red. Heavy lacquer on wall.
	175	36	46.8	1.20	5.6	6.0	2.3	+0.4	+0.1	+0.3	Heavy black lacquer. Nonadherent black deposit.	Heavy black lacquer. Nonadherent black deposit.	Heavy black lacquer. Nonadherent black deposit.	Clear. Very dark red. Heavy lacquer on wall. Condensed material in upper condenser.
7-Benzo[C]phenothiazine 	125	>168	4.3	0.11	<1.0	0.49	<0.01	<+0.1	+0.2	<+0.1	Med. peacock colors.	Heavy lacquer.	Med. peacock colors.	Clear. Amber.
	150	>168	11.7	0.29	<1.0	1.3	1.0	<+0.1	<+0.1	<+0.1	Nonadherent deposit. Heavy peacock colors.	Nonadherent deposit. Heavy lacquer.	Heavy black lacquer.	Clear. Brown. Heavy lacquer on wall.
	163	>168	23.4	0.58	3.2	1.4	1.2	+0.2	+0.3	+0.3	Heavy lacquer.	Heavy lacquer.	Heavy lacquer. Nonadherent deposit.	Clear. Very dark red. Sludge. Heavy lacquer on wall. Condensed material on upper cell wall.
175	>168	46.8	1.16	6.5	3.7	2.4	+0.4	+0.5	+0.5	Heavy lacquer. Nonadherent deposit.	Nonadherent deposit. Heavy lacquer.	Nonadherent deposit. Heavy lacquer.	Cloudy. Red. Sludge. Very heavy lacquer on wall.	



* Duration of test 168 hours.

TABLE 6
Oxidation-Inhibition Imparted to Di(2-Ethylhexyl) Sebacate by Amine Precursors of Phenothiazine*

Antioxidant	Temperature, °C	Induction Period, Hours	Molality x 10 ²	Weight Percent	Percent Increase in Viscosity at 100° F	Volatile Acid Neut. No.	Nonvolatile Acid Neut. No.	Metals						Sample Appearance
								Weight Change Mg./Cm ²		Appearance				
								C.R.S.	Cu	Dural	C.R.S.	Cu	Dural	
Diphenylamine 	100	>168	4.3	0.07	<1.0	0.97	0.19	<-0.1	<-0.1	<0.1	Slightly discolored.	Heavy peacock colors.	No change.	Clear.
	150	>168	23.4	0.36	53.	2.9	0.69	<+0.1	-0.1	<0.1	Heavy peacock colors.	Heavy peacock colors.	Med. peacock colors.	Clear. Deep red. Light lacquer on wall.
4-Isopropoxydiphenylamine 	100	>168	4.3	0.09	<1.0	0.30	0.20	<-0.1	<-0.1	<0.1	No change.	Pink coat.	No coat.	Clear. Light amber.
	125	>168	1.1	0.02	1.2	0.53	<0.01	<-0.1	<-0.1	<0.1	Discolored.	Discolored.	No change.	Clear.
	150	>168	46.8	0.50	1.6	2.1	0.84	<-0.1	<-0.1	<0.1	Adherent deposit.	Adherent deposit.	Lt. peacock colors.	Clear. Dark amber.
	163	156	23.4	0.25	52.	6.4	16.	<+0.1	-2.9	<0.1	Med. peacock colors.	Etched.	Lt. peacock colors.	Opaque. Brown. Sludge.
Triphenylamine 	150	72	11.7	0.29	362.	54.	41.	<-0.1	-25.	<0.1	Discolored.	Etched.	Discolored.	Opaque. Black.
Phenyl alpha naphthylamine 	100	>168	23.4	0.51	<1.0	0.32	0.03	<-0.1	<-0.1	<0.1	No change.	Lt. peacock colors.	No change.	Clear. Dark purple.
	125	>168	1.1	0.02	<1.0	0.03	<0.01	<-0.1	<-0.1	<0.1	Darkened.	Brassy appearance.	No change.	Clear. Amber.
	150	>168	11.7	0.26	<1.0	1.1	0.26	<-0.1	<-0.1	<0.1	Med. peacock colors.	Med. peacock colors.	Med. peacock colors.	Clear. Amber. Light lacquer on wall.
	163	156	23.4	0.51	728.	6.9	2.4	+0.1	-15.	+0.1	Lt. peacock colors.	Etched.	Lt. peacock colors.	Opaque. Black lacquer on wall.
	163	>168	46.8	1.00	6.4	1.6	0.56	<+0.1	<+0.1	<0.1	Heavy peacock colors.	Heavy peacock colors.	Heavy peacock colors.	Clear. Dark amber. Lacquer on wall.
	175	36	46.8	1.00	17.	43.	71.	+0.5	-5.5	+0.5	Heavy lacquer.	Etched. Heavy lacquer.	Heavy lacquer.	Opaque. Black. Heavy lacquer on wall.
	150	84	11.7	0.25	50.	25.	17.	<+0.1	-25.	<0.1	Discolored.	Etched.	Slightly discolored.	Opaque. Black. Green sludge above liquid level.
3-Trifluoromethyl-3'-methylidiphenylamine 	150	>168	11.7	0.23	1.7	1.6	0.65	<+0.1	<+0.1	<0.1	Heavy peacock colors.	Heavy oxide coat.	Lt. peacock colors.	Clear. Light amber. Fluorescent. Light lacquer on wall.
4,4'-Dimethyldiphenylamine 	163	84	23.4	0.45	112.	28.	30.	+0.2	-8.6	+0.1	Med. lacquer.	Etched.	Med. lacquer.	Opaque. Brown. Sludge. Medium lacquer on wall.

* Duration of test 168 hours.

TABLE 7
Oxidation-Inhibition Imparted to DI(2-Ethylhexyl) Sebacate by Miscellaneous Compounds*

Antioxidant	Temperature, °C	Induction Period, Hours	Molality x 10 ²	Weight Percent	Percent Increase in Viscosity at 100° F	Volatile Acid Neut. No.	Nonvolatile Acid Neut. No.	Metals						Sample Appearance		
								Weight Change Mg./Cm ²			Appearance				Dural	Sample Appearance
								C.R.S.	Cu	Dural	C.R.S.	Cu	Dural			
Diphenylsulfide 	150	84	11.7	0.22	46.	17.	40	<+0.1	-37.	<+0.1	Discolored.	Etched.	Slightly discolored.	Opaque. Black.		
Diphenylsulfide and Diphenylamine Mixture	150	>168	11.7	{ 0.20 0.22	1.7	1.4	0.58	<+0.1	<-0.1	<+0.1	Heavy peacock colors.	Heavy peacock colors.	Lt. peacock colors.	Clear. Dark amber. Light lacquer on wall.		
3,6-Di-tert-butylcarbazole 	163	84	23.4	{ 0.40 0.54	88.	28.	16.	<+0.1	-28.	+0.1	Lt. lacquer, Lt. peacock colors.	Etched.	Lt. lacquer, Lt. peacock colors.	Opaque. Brown. Light lacquer.		
	150	72	11.7	0.33	323.	60.	58.	<+0.1	-8.4	+0.1	Lt. lacquer.	Etched.	Lt. lacquer.	Opaque. Black.		

* Duration of test 168 hours.

even at 150° C. A mixture of diphenylsulfide and diphenylamine, in the respective concentrations of sulfur and nitrogen with which inhibition was obtained with phenothiazine, was unsatisfactory at temperatures above 150° C.

The carbazoles represent a class of compounds which resemble the phenothiazines except for the absence of sulfur in the heterocyclic rings. There was no antioxidant activity evident at 150° C in a representative of this class, 3,6-di-tert-butylcarbazole.

It is apparent from the foregoing that none of the compounds investigated were more satisfactory than phenothiazine, which was effective as an antioxidant up to 163° C and had considerable activity at 175° C. Substituents on the benzenoid rings did not materially affect antioxidant action, but etching of the metal catalysts occurred in the presence of compounds containing fluorine. Departures from the thiazine structure of the heterocyclic ring tended to reduce antioxidant activity. All of the oxygenated derivatives except the 5-dioxide were practically as effective as was the parent compound. No general conclusions could be reached as to the effect of substitutions on the nitrogen atom.

Mechanism of Antioxidant Action

The experimental results indicate that the phenothiazine structure possesses an antioxidant action which is not dependent upon the nitrogen-phenyl or the sulfur-phenyl linkages. Thus phenazine, thianthrene, 3,6-di-tert-butylcarbazole, phenyl- α -naphthylamine, and diphenylsulfide or a combination of diphenylamine and diphenylsulfide impart substantially less inhibition to the reference fluid than do either phenothiazine or many of its analogues.

To ascertain whether the action of the phenothiazine-type inhibitors could be due to a regenerative process, the following experiment was performed. Di(2-ethylhexyl) sebacate, to which was added tetralin (5% by weight) was aerated for 24 hours at 115° C, in order to obtain a reasonably high concentration of peroxides. Periodic peroxide determinations by the potassium iodide-sodium thiosulfate method indicated that the reaction reached equilibrium when the concentration of active oxygen was 0.00250 gm per gm of solution. To aliquot portions of this fluid were added equimolar quantities (0.02 molar) of phenothiazine, phenothiazone-3, phenothiazine-5-oxide, and phenothiazine-5-dioxide, the latter two compounds not being completely soluble. These samples, together with a portion of the peroxidized oil containing no additive and serving as the blank, were maintained at 115° C for 16 hours and were analyzed at intervals for peroxide content. The results obtained, corrected for a slight diminution of peroxide concentration in the blank run, are shown in Figure 1.

The samples containing phenothiazine, phenothiazone-3, and phenothiazine-5-oxide showed a marked decrease in peroxide content to approximately 10 percent of the initial value after 16 hours, phenothiazine causing the most rapid decrease. In contrast, the peroxide content in the presence of phenothiazine-5-dioxide and in the blank run remained essentially unchanged. Since peroxide formation is the rate-determining step in oil oxidation, it is not too surprising that the relatively good antioxidants, as judged by the dynamic oxidation test, should destroy peroxides, in contrast to phenothiazine-5-dioxide which displayed poor inhibition activity.

The decrease in peroxide content in the presence of the first three compounds converged to a value approximating the consumption of 7 equivalents of peroxide oxygen per mole of additive. Since this value is far greater than could be accounted for by any plausible reaction between the additives and peroxide, it may be reasonably assumed that inhibitor regeneration takes place. There is no apparent theoretical significance to the convergence

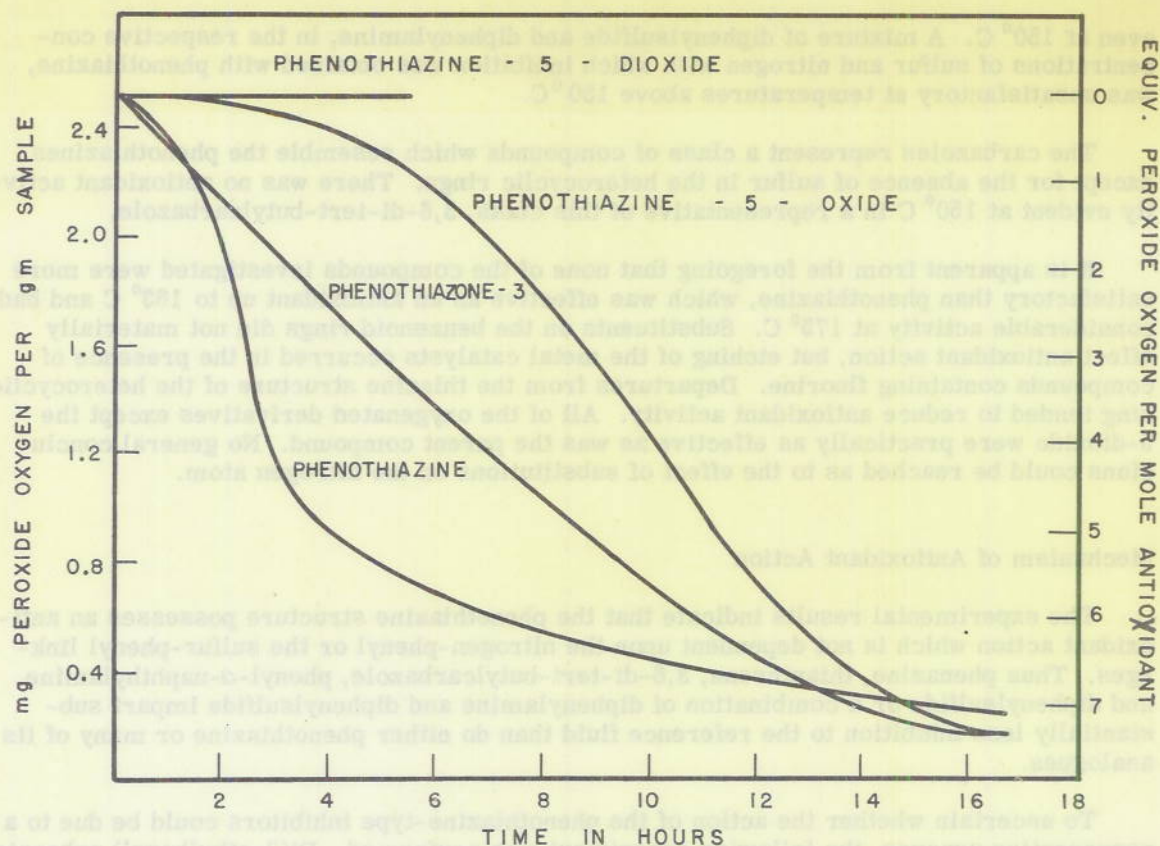
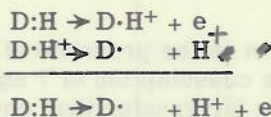


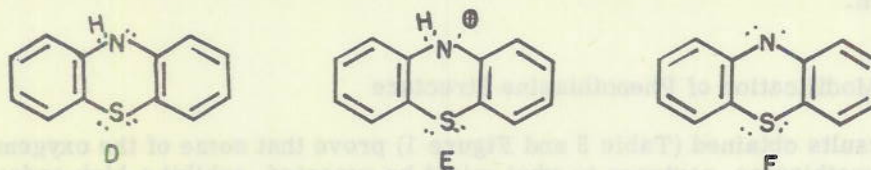
Figure 1 - Reaction of antioxidants with peroxides at 115° C

towards the value of 7 equivalents of peroxide oxygen per mole of additive; it is merely a measure of the efficiency of inhibitor regeneration under the particular experimental conditions.

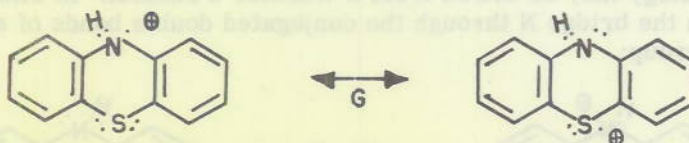
A plausible mechanism for the unique inhibition activity of the phenothiazine nucleus may be deduced from its behavior under excitation conditions. The photochemical reactions associated with phenothiazine and some related compounds have been studied in detail (7,8). To facilitate the discussion, conventional symbolism is adopted, where D:H represents the phenothiazine molecule or an analogue in which sulfur is replaced by selenium or oxygen, H represents the hydrogen attached to the heterocyclic nitrogen, and D represents the remainder of the molecule. When D:H type compounds are illuminated in a rigid solvent at low temperatures, two semiquinone radicals result. The first is produced as a result of the emission of an electron, and the second upon standing grows from the first by the loss of a proton:



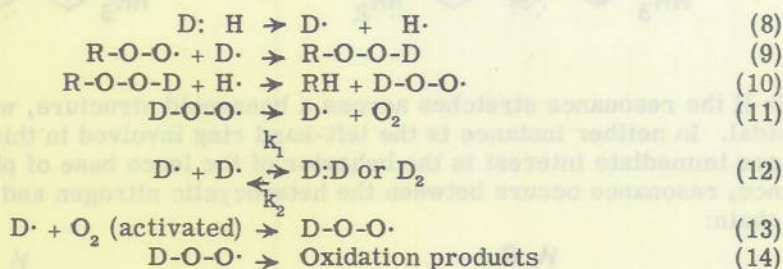
The parent compound D:H and the semiquinone free radicals D·H⁺ and D· are represented thus:



Michaelis and his colleagues have shown (9) that radicals of the types E and F are probably resonance-stabilized:



The spectral region in which the free radical D· exhibits maximum light absorption corresponds, as a first approximation, to an activation energy of 30 kcal per mole; it is therefore reasonable to assume free radical formation at the usual chemical reaction temperatures. Provided the life of D· were of sufficient duration, we may speculate that the inhibition activity of phenothiazine may be accounted for by the following mechanism:



Reactions 8 through 11 demonstrate a mechanism whereby oxygen at a high energy level (O-O·) can be subsequently released at a lower energy level (O₂). If this process were reasonably efficient, the chain oxidation of the oil and its deterioration (reactions 2 through 7) would be drastically curtailed.

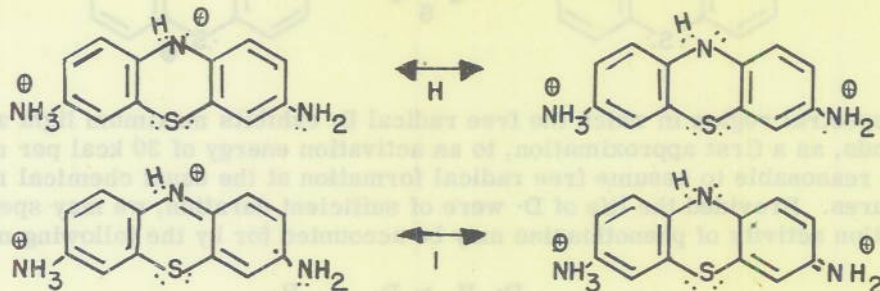
The regeneration of inhibitor may be explained in part by reaction 11. If no factors which reduced the concentration of D· were operative, the inhibitor would be completely regenerated. A lowering of concentration of D·, however, would ensue if k₁ (reaction 12) were to predominate at the expense of k₂. However, if k₂ occurred to an extent just sufficient to meter out D· to serve as a source for reaction 9, then the regenerative process would be aided. Reaction 14 does not necessarily imply that antioxidant activity is lost, since, as has been demonstrated, partial oxidation of phenothiazine results in compounds which are fairly effective inhibitors and which are also regenerative. It can be shown that these compounds are capable of forming stabilized free radicals.

The existence of R-O-O-D and D-O-O· is purely speculative. They have never been identified, perhaps because of their transitory nature. There is tangible evidence, however, for some of the other postulated reactions. Lewis and his associates (7) show that D₂, in addition to D·, is formed when D:H is activated. The fact that 10,10'-diphenothiazine (D₂) exhibits strong antioxidant activity (Table 3) indicates that k₂ in reaction 12 proceeds

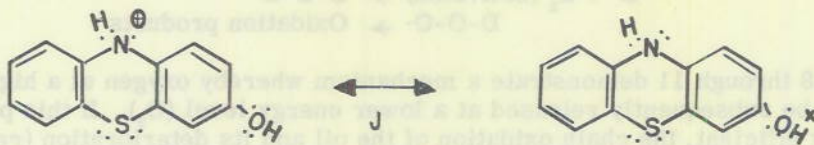
to a reasonable extent. Reactions similar to 11, in which a peroxidized compound undergoes thermal dissociation to regenerate the original compound and molecular oxygen (3), are common.

Effects of Modification of Phenothiazine Structure

The results obtained (Table 3 and Figure 1) prove that some of the oxygenated derivatives of phenothiazine, contrary to what might be expected, exhibit a high order of antioxidant action. This may best be explained by a free radical mechanism similar to the one postulated for phenothiazine but involving an alternate, or possibly an additional, type of resonance. An analogy may be drawn from a Wurster's radical. In this case there is resonance between the bridge N through the conjugated double bonds of a ring across to the substituent N group:

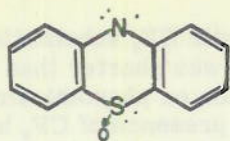


In H the resonance stretches across a benzenoid structure, whereas in I the ring is quinoidal. In neither instance is the left-hand ring involved in this type of resonance (9). Of more immediate interest is the behavior of the leuco base of phenothiazone-3. In this instance, resonance occurs between the heterocyclic nitrogen and the oxygen-containing side chain:

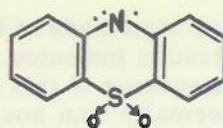


When oxidation of phenothiazine occurs at the 3 and 7 positions to form phenothiazone-3 and thionol, it is, therefore, not unreasonable to assume a resonance-stabilized semiquinone radical resulting from interaction within the molecule. As a matter of fact, the semiquinone radical derived from thionol has recently been postulated as a result of other considerations (4).

Should oxidation of phenothiazine occur at the 5 position, the oxide is first formed, resulting from coordination of sulfur with an oxygen atom (semi-ionic bond); if oxidation proceeds further, the dioxide is formed. The radical derived from the oxide should have somewhat less resonance energy than the parent compound, since only one pair of electrons is now available. The possibility of a stabilized radical from the dioxide is unlikely since no resonance-available electrons remain associated with the sulfur atom. Thus:



5-Oxide radical



5-Dioxide radical

Hence, the existence of stabilized free radical forms of phenothiazone-3, phenothiazine-5-oxide and thionol which can react with peroxides in a manner analogous to that of phenothiazine explains their antioxidant action. The high order of their effectiveness is primarily a result of the regeneration, as has been experimentally demonstrated.

Consideration of free radical formation at the heterocyclic nitrogen atom, assuming that the inhibition-producing free radical was derived from bond rupture and not merely electron emission, involves a study of the relative bond energies of N-H, N-C, and N-N. The average bond energies as calculated by Pauling (12) are 83.7, 48.6, and 20.0 kcal/mole respectively. Hence bond rupture, with subsequent free radical formation, should occur to a lesser degree in phenothiazine than in such compounds as 10-ethylphenothiazine and 10,10'-diphenothiazine, where an atom other than hydrogen is attached to the heterocyclic nitrogen. It is probable that for effective inhibition a slow rather than a rapid evolution of free radicals is desirable, since only that minimum concentration necessary to react with peroxides as they are formed need be available. Any higher concentration than this minimum could promote reactions 12-k, 13, and 14 in which free radicals are destroyed or so modified that they cannot react. If, therefore, bond rupture at N-C or N-N were to occur too readily, the formation of free radicals, and hence their ultimate destruction, would be promoted. There is no certainty that at the reaction temperatures employed in this investigation N-C or N-N bond ruptures occur to this excessive degree; however, at more elevated temperatures this factor may assume added importance.

The experimental results confirm this reasoning to some extent. Except for 10-benzylphenothiazine, none of those compounds with a carbon attached to the heterocyclic nitrogen atom exhibited inhibition activity of the order of phenothiazine at 175°C. Although 10-octadecylphenothiazine did not provide effective inhibition at 175°C in the low concentration employed (29.4 MM), it is not known whether increasing this concentration to the usual 46.8 MM would be of any value. The only N-N compound studied, 10,10-diphenothiazine, was not effective above 163°C, although as previously noted its limited solubility might in part account for this behavior. Substituent groups at points other than the heterocyclic nitrogen should have little bearing on the bond strength of the latter since the usual positions of ring substitution are sufficiently distant.

Michaelis and colleagues (8) have stated that a radical even more stable than that derived from phenothiazine would result if the reactive 3 and 7 hydrogen atoms were replaced by methyl groups to prevent oxidation. This stability, it is to be emphasized, refers only to the chemical variety, as for example oxidation to phenothiazone-3 or thionol. From a pyrolytic standpoint, a CH₃ substitution on the ring may be more labile than was the original hydrogen since the energy value of the C-C bond is 58.6 kcal/mole while that of the C-H bond is 87.3 kcal/mole. It should be noted that the energies required for the thermal rupture of C-H and C-C bonds involve relatively high temperatures. Nevertheless, some fission takes place at ordinary reaction temperatures, and at elevated temperatures the rupture of these groups from the ring may well be a dominant factor in the breakdown of the entire molecule. It seems probable that organic substitution on the benzenoid rings of phenothiazine would not materially affect its antioxidant action but might alter the physical properties in some respects.

Studies have been made of bond distances associated with CF_3 substitutions on aromatic rings. Results indicated that a $\text{C}-\text{CF}_3$ bond distance was shorter than was that of a $\text{C}-\text{CH}_3$. A consequence of this fact is that a CF_3 substitution on phenothiazine should be more stable thermally than would be a CH_3 . However, the presence of CF_3 has a negligible effect on the $\text{C}-\text{C}$ bond distances within the aromatic ring and should not contribute to any additional stability imparted to the latter. Experimentally, it was demonstrated that CF_3 substitutions on the aromatic rings offered no improvement in inhibitor stability over CH_3 .

Previous reference (7, 8) has been made to the fact that phenoxazine, phenoselenazine, and phenothiazine are all capable of resonance-stabilized free radical formation under similar conditions. It would therefore be expected that all would be comparable antioxidants. But, it has been shown that this is not the case and that the order of increasing antioxidant effectiveness of these compounds is phenoxazine, phenoselenazine, and phenothiazine. A possible explanation for this phenomenon may lie in their oxidation potentials, which, as measured by Granick, Michaelis, and Schubert (5), varied considerably. In aqueous media over a wide pH range, the phenoxazines had the lowest oxidation potentials and the phenothiazines the highest. To a first approximation, the relative order of these potentials would be unchanged in a nonaqueous system such as that employed in this investigation. It follows that phenothiazine is a stronger reducing agent than either phenoselenazine or phenoxazine and would therefore be the most likely to effect the reduction of the peroxides formed in oil oxidations (reactions 9, 10, and 11).

CONCLUSIONS AND RECOMMENDATIONS

Phenothiazine has been shown to be an effective antioxidant for use in a diester fluid through 163°C (325°F). However, above this temperature the deposition of lacquer is objectionable. Modifications thus far studied offered no improvement over the parent compound (except for somewhat lower volatility) and in many instances a less desirable inhibitor resulted.

Derivatives of phenothiazine with higher molecular weights and, presumably, lower vapor pressures than that of the parent compound have been shown to possess fairly good antioxidant properties at 163°C . These compounds (7-benzo [c] phenothiazine, 10-benzylphenothiazine, and 10-octadecylphenothiazine) may be useful in those high-temperature applications where the volatility of phenothiazine is objectionable, as in the turbo-jet engine.

The phenothiazine structure possesses an antioxidant action best explained by the formation of a regenerative free radical stabilized by resonance between the nitrogen and sulfur atoms, the odd electron being at the nitrogen atom. Resonance may also take place between the nitrogen atom and the meta-position oxidized side rings. A mechanism to explain this action has been postulated. The antioxidant action of the oxygenated derivatives of phenothiazine has been explained by a similar mechanism.

A positive correlation has been shown to exist between the antioxidant activities and the oxidation potentials of phenothiazine, phenoselenazine, and phenoxazine, although all are capable of stable free radical formation. All other factors being equal, proper modification of the phenothiazine structure to increase its oxidation potential would result in an even more effective inhibitor.

Proper modification of phenothiazine may result in a structure stabilized both chemically and thermally, thus raising its upper effective temperature limit. However, if the chemical stability should be increased to a degree where high energies are required to

actuate the molecule, then the pyrolytic stabilities of the additive and the bulk fluid would be the limiting factor as to the degree of inhibition obtained.

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