Inhibition of Polyglycol Autoxidation

W. G. LLOYD, Polymer Research Laboratory, The Dow Chemical Co., Midland, Mich.

POLYGLYCOLS have been known for over 100 years (*26*), but have become of industrial interest only within the past three decades. A wide variety of these synthetic polymers of the general structure $HO(-CH_2-CHR-O-)_nH$ is now available, principally as polyethylene glycols (R = H) and polypropylene glycols (R = CH_3). Newer polymers, such as those obtained from butylene oxides and styrene oxide, are becoming available; and a number of mixed-oxide polyglycols have long been produced in bulk to meet specific needs—e.g., Polyglycol 15-200, obtained by copolymerization of ethylene oxide and propylene oxide using glycerol as a starter (*14, 19*). In recent years polyglycols have come into their own as major synthetic polymers; consumption of unmodified polyethylene glycols has increased from about 2 million pounds to about 25 million pounds annually in the past decade.

This rapid expansion is due to the wide range of combinations of properties available in these synthetic polymers; they are well summarized by Curme and Johnston (*13*). Excluding a number of uses wherein polyglycols serve as chemical intermediates, the principal direct applications are as lubricants and plasticizers, solvents and mutual solvents, and hydraulic fluid components. Special applications include use as cutting and buffing agents, softening and antiblooming agents, emulsifying agents, and cosmetic bases. Polyglycols have found use as corrosion inhibitors in both acidic (*7*) and alkaline (*25*) aqueous systems.

Where polyglycols have displaced natural products, there have been good functional reasons—e.g., they have been found to be better lubricants than petroleum lubricants (*11, 35*). However, like the natural products they displace, polyglycols are inherently vulnerable to autoxidative degradation, owing to recurring ether groups in the chain structures. Unlike many natural products, however, polyglycols are of consistent and reproducible quality and are chemically homogeneous. Consequently, their susceptibility to autoxidation and their amenability to stabilization by suitable antioxidants can be studied with some precision. Several specific stabilizers are known, for protection of polyglycols against thermal (*5, 32, 33*) and oxidative (*17, 24, 28, 34, 36*) degradation. The purpose of the present work is to extend the general study of glycol oxidation (*22*) by employing an intensive empirical approach to the problem of antioxidant stabilization of polyglycols.

EXPERIMENTAL

Flash point determinations are made by the A.S.T.M. open-cup method (*1*). The standard deviation of 14 control determinations was found to be 4.9° F. (95% confidence limit ±10.5° F.)

Autoxidations and induction period determinations are carried out using an oxygen consumption apparatus described earlier (*22*), with the following modifications. Except for the stirrer-dependency tests (Table I), stirring is accomplished by a constant-speed 300-r.p.m. motor (Bodine) driving a primary magnet, which spins a 1⅛ × 5/16 inch Teflon-clad stirrer (Alnico) inside the flask. An inhibited polyglycol replaces water as the heat-transfer medium in the bath. Temperature control is maintained by thermostats (H-B Type 7910-A) through a relay (Lumenite Model LER 1281-Al). This system gives standard temperature deviations consistently below 0.1° C. Changes in oxygen pressure are recorded through an absolute mercury manometer by means of a sensitive inductance tuning circuit. The recording assembly is set for the range 519.0 to 774.5 mm. Hg, and gives a linear response, with a slope of 10.210 mm. per scale unit and a standard deviation of 0.0130 mm. per scale unit. Except where otherwise noted, all autoxidations are carried out under pure oxygen at 1-atm. pressure.

Table I. Effect of Stirrer Rate on Oxygen Consumption Rate[a]

Polyglycol	Stirrer, R.P.M.	Rate of Oxygen Pressure Drop[b]
Diethylene glycol	105	13
	300	47
	400	72
	500	96
Polyglycol 15-200[c]	None	82
	200	85
	300	102
	400	100
Polyglycol E-400[d]	None	130
	150	125
	250	130
	300	120
	350	130
	400	120

[a] At 126.1° C. under 1 atm. of oxygen. [b] Mm. Hg/hour, measured from 750 to 700 mm. [c] Copolymer of ethylene and propylene oxides, molecular weight about 2600. [d] Polyoxyethylenediol, molecular weight 400.

RESULTS

Autoxidation Susceptibility. Diethylene glycol is not readily autoxidized at storage temperatures (*22*). However, higher polyethylene glycols, possibly because of their "meandering" configurations (*13*), are considerably more susceptible to low temperature oxidation. Thus, polyethylene glycol of average molecular weight 600, at 35° C. under 1 atm. of oxygen and with initiation (by adding a small amount of oxidized polyglycol containing hydroperoxide), forms peroxides at a net rate of 2 meq. per liter per hour and acids at a rate of 5 meq. per liter per hour in this apparatus. On the other hand, mixed-oxide polyglycols more nearly resemble diethylene glycol in their high resistance to storage temperature autoxidation, even under forcing conditions. Thus, Polyglycol 15-200 (a mixed-oxide polyglycol of molecular weight about 2600) produces less than 0.2 meq. per liter per hour of peroxides at 35° C., and its acid formation rate is immeasurably slow.

At higher temperatures, however, polyglycols, like most organic compounds, are susceptible to autoxidation. Figure 1 illustrates typical oxygen consumption curves at 126.1° C. in the absence of added initiator, with lard oil as reference compound. Polyglycol autoxidation is readily inhibited by small quantities of antioxidant, as shown by the addition of 0.080% of hydroquinone (bottom curve, Figure 1).

Flash Point Elevation. The standard open-cup flash point determination (*1*) is widely employed for lower molecular weight materials, and in the usual case, the flash point is a function of vapor pressure and vapor flammability. High molecular weight materials possess only negligible vapor pressures at accessible temperatures. Yet, they too yield

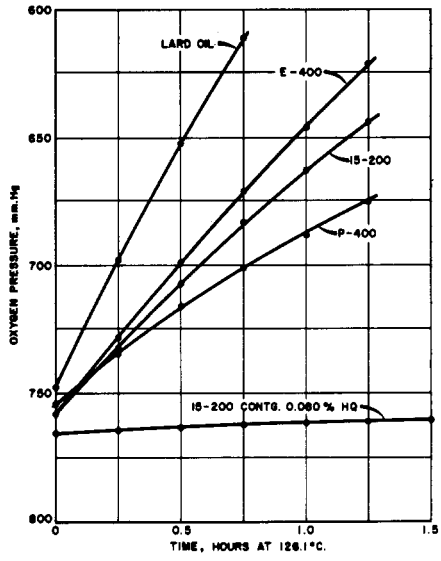

Figure 1. Oxygen consumption of polyglycols and of lard oil

Pressure drop of 1 mm. indicates uptake of 0.779 mmole of oxygen/liter of substrate

characteristic flash points, which are determined by a complex of factors, including notably the thermal and thermal-oxidative decomposition processes. This change in the controlling factors with increasing molecular weight is illustrated by the plateau obtained in a plot of open-cup flash points *vs.* molecular weight for the homologous polyethylene glycol series (Figure 2). These data indicate that for polyglycols of molecular weight above 1000, flash point is substantially independent of molecular weight, and is essentially a function of susceptibility to decomposition.

The addition of an effective antioxidant very markedly raises the flash point of a higher polyglycol. This may be seen by comparing flash points of three aliquots of Polyglycol 15-200, one with no additive, one with 0.500% of the radical-source initiator, azobisisobutyronitrile, and one with 0.500% of the antioxidant phenothiazine (N.F. purified). The aliquots were coded, randomized, and run in triplicate

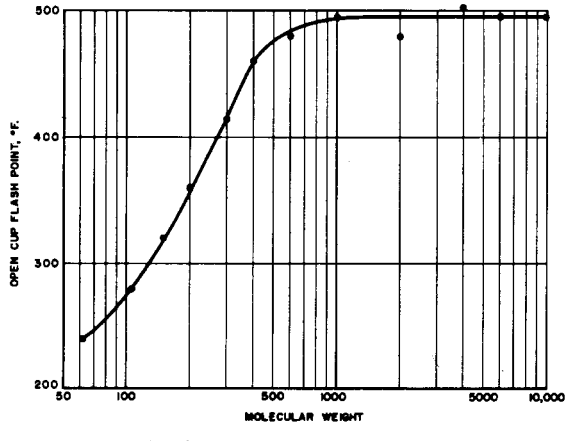

Figure 2. Flash points of polyethylene glycols

by different operators, following a simple Latin Square design (*38*). Results (Table II) indicate a slight depression of the flash point by the azo initiator (probability of significance exceeds 95%), and a very sizable elevation of the flash point by the antioxidant (probability of significance greatly exceeds 99%).

Table II. Open Cup Flash Points of Polyglycol 15–200

Sample	Operators JES	DFW	HDD	Av. Flash Point, ° F.
Control, no additive	485	475	475	478
+ 0.50% azo initiator	460	470	460	463
+ 0.50% phenothiazine	610	605	605	607

Std. dev. (6 DF); 5.0° F.

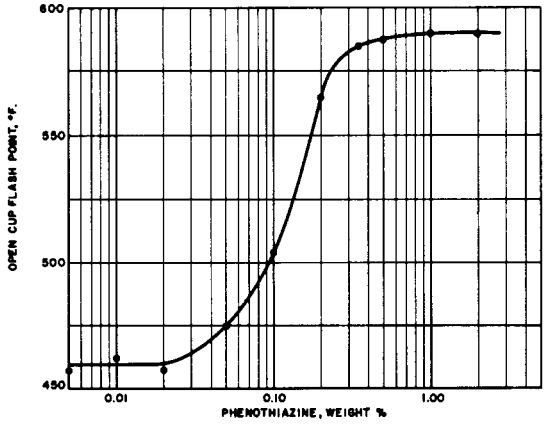

Figure 3. Flash points of Polyglycol 15-200 containing phenothiazine

The effect of antioxidant concentration upon flash point is illustrated for Polyglycol 15-200 with phenothiazine in Figure 3. The flash point of this uninhibited polyglycol is 460° F. (238° C.). The flash point rises smoothly with rising phenothiazine concentration in the range 0.02 to 0.3%, then levels off at about 590° F. (310° C.) and is substantially independent of further increases in phenothiazine concentration. On the basis of this curve, a concentration level of 0.50% is selected for comparing various antioxidants.

While obvious theoretical objections may be raised against the use of flash point elevation as a rigorous or theoretically significant procedure, the great simplicity, speed, and reproducibility of the flash point determination make it attractive to consider as a possible preliminary screening technique for high temperature antioxidants in polyglycol systems. Polyglycol autoxidation (Figure 1) can be effectively checked by addition of a good antioxidant. If a suitably small amount of antioxidant is employed, a brief period of substantially complete protection is obtained, followed by rapid autoxidation. This period of protection, or induction period, is illustrated in Figure 4, showing the oxygen consumption of Polyglycol 15-200 containing 0.0125% of phenothiazine, at 126° C. under 1 atm. of oxygen. The sharp definition of the induction period and its independence of such factors as secondary oxidation products and oxygen diffusion rates make it an ideal reference criterion in examining antioxidant protection of polyglycols. The validity of flash point elevation as an antioxidant screening technique may therefore be tested by comparison of flash point and induction period data for a number of aliquots of antioxidant-loaded polyglycols.

The results of such a comparison with 13 additives are shown in Table III. A good, rough correlation is immediately evident. Thus, the first six compounds listed, of varying antioxidant efficacy at lower temperatures, are all rather ineffective antioxidants under these conditions, and all yield only moderate flash point elevations. Mercaptobenzothiazole and bisphenol A have been recommended in industrial literature as good polyglycol antioxidants; how-

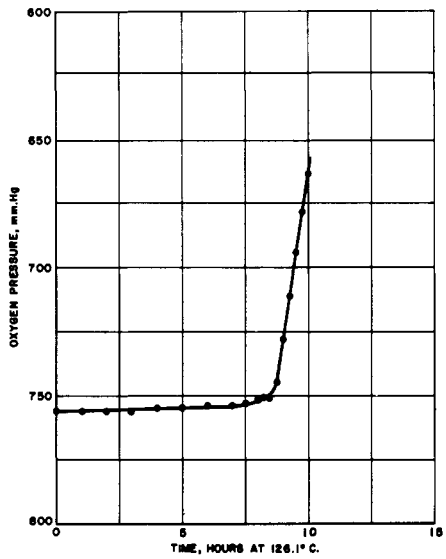

Figure 4. Oxygen intake of Polyglycol 15-200 with 0.0125% phenothiazine

ever, neither appears to be very effective under these experimental conditions.

The flash point test may be considered to be, in essence, a highly standardized and very accelerated aging test; and the inherent hazards associated with overinterpretation of accelerated aging tests are all present here. One of the best high temperature antioxidants for polyglycols, AgeRite Resin D, gives only a relatively modest flash point elevation of 70° F. Nevertheless, if the roughness of the flash point elevation is kept in mind, the correlation is useful. A criterion of elevation of at least 50° F. eliminates most of the ineffective antioxidants and passes all those showing real efficacy in this system at 126° C.

Oxygen Contact and Oxygen Pressure. Agitation of relatively viscous liquids under oxygen may lead to diffusion-controlled autoxidations, particularly with readily oxidizable substrates. This possibility for the present system was investigated by carrying out a series of oxygen-consumption runs at various controlled rates of stirring. The results are summarized in Table I. Diethylene glycol, which is nearly independent of stirrer rate at lower temperatures (*22*), is seen to be sharply dependent at 126° C. Polyglycol 15-200 is relatively insensitive to stirrer rate; its rate of oxidation is quite independent of stirrer rate above 300 r.p.m. Polyglycol E-400 is independent of stirrer rate over the entire accessible range. In all cases, the induction period reaction, in which oxygen is consumed very slowly, appears to be insensitive to stirrer rate.

However, the autoxidation rates of polyglycols are sensitive to oxygen pressure. Since the autoxidation rate of Polyglycol 15-200 is insensitive to stirrer rate, the observed oxygen pressure dependency exponent of 0.7 (Table IV) appears to be of kinetic significance. Although hydrocarbons seldom exhibit an oxygen pressure dependency in this oxygen pressure range (*31*), diethylene glycol has similarly been found to show a significant dependency (*22*).

The effect of oxygen pressure upon the induction periods of inhibited Polyglycol 15-200 is shown in Table V. The dependency exponents, shown in the right-hand column, are strikingly uniform in view of the wide chemical differences among the three antioxidants. The uniformity of this dependency, and its agreement with the oxygen pressure dependency for free autoxidation of this polyglycol (Table IV) argue against the explanation of inherent vulnerability of antioxidants to direct oxygen oxidation (*20*) under these conditions. For these systems at 126° C. it appears more reasonable to interpret the oxygen pressure dependency of the induction period in terms of a primary dependency arising from some other process.

Table III. Performance of Antioxidants with Polyglycol 15–200

Antioxidant Present at 0.50% Concentration	Flash Point Elevation, ° F.	Induction Period[a] under 1 Atm. Oxygen at 126.1° C., Hours
None	...	0.6
Triethanolamine	10	0.9
Styphen I[b]	25	1.4
AgeRite 3112[c]	35	2.2
Antioxidant 10323[d]	40	1.5
Bisphenol A[e]	50	1.3
Mercaptobenzothiazole	60	4.5
AgeRite Resin D[f]	70	>110
Hydroquinone	105	100
AgeRite White[g]	110	>110
Pyrocatechol	115	73
Phenothiazine	120	>110
Nordihydroguaiaretic acid	125	68
Gallic acid	130	86

[a] Time required for uptake of 0.05 mole oxygen/liter polyglycol. [b] Mixed α-methylbenzylphenols (Dow Chemical Co.). [c] A polyalkyl polyphenol (R.T. Vanderbilt Co.). [d] A resinous copolymer containing mixed cresols (Dow Chemical Co.). [e] 4,4′-Isopropylidenediphenol (Dow Chemical Co.). [f] Polymerized trimethyldihydroquinoline (R.T. Vanderbilt Co.). [g] *N,N′*-Di(2-naphthyl)-*p*-phenylenediamine (R.T. Vanderbilt Co.).

Antioxidant Concentration Effects. In inhibited autoxidations, the induction period may be considered to be inversely related to the rate of the antioxidant-consuming induction period reaction, whatever that process may be (*6, 37*). For simple systems, if the antioxidant is essentially completely consumed at the end of the induction period, the relationship between induction period, t_i, and initial antioxidant concentration, $(AH)_0$, may be expected to obey the simple relationship:

$$t_i = k(AH)_0^n \qquad (1)$$

Table IV. Effect of Oxygen Pressure upon Autoxidation Rate of Polyglycol 15–200 at 126.1° C.

Initial Oxygen Pressure (P_i), Atm.	Initial Rate of Pressure Drop (r_i), Mm./Hr.	$\frac{r_i}{(P_i)^{0.7}}$
0.995	89.8	90
0.485	54.3	90
0.210	29.4	88

Table V. Effect of Oxygen Pressure upon Induction Periods of Inhibited Polyglycol 15–200 at 126.1° C.

Antioxidant Present, %	Initial Oxygen Pressure (P_i), Mm. Hg	Induction Period (t_i), Hours	$\frac{-d(\log t_i)}{d(\log P_i)}$
Phenothiazine, 0.0125	160.6	18.9	
	362.4	11.0_5	0.6
	762.3	8.0	
Phenothiazine,[a] 0.0125	156.9	24.4	
	372.3	17.0	0.7
	752.6	8.6	
Hydroquinone, 0.0500	159.7	30.0	
	371.6	15.8_5	0.8
	764.8	8.0	
Phenyl-2-naphthylamine, 0.1250	160.1	8.8_5	
	366.6	8.6	0.6[b]
	763.3	5.4	

[a] With specially purified polyglycol. [b] Based upon data at the two higher pressures only.

Equation 1 in its logarithmic form corresponds to the empirical data-fitting expression formulated by Rosenwald and Hoatson (*30*), and later derived by Kennerly and Patterson (*20*) from kinetic considerations. To test its applicability to polyglycol systems, four antioxidants were added at various suitable concentrations to Polyglycol 15–200, and the induction periods at 126° C. determined. The antioxidants were chosen to represent major chemical types in current use (*10*): hydroquinone as a polyhydroxy-aromatic, phenyl-2-naphthylamine as a typical arylamine, phenothiazine as a sulfate-heterocyclic, and 2,6-di-*tert*-butyl-4-methylphenol as an alkylated phenol. A commercial antioxidant resin, AgeRite Resin D (R.T. Vanderbilt Co., polymerized trimethyldihydroquinoline) was also used. The degree of conformity to Equation 1 is indicated by the linearity of the plots of log t_i *vs.* log $(AH)_0$ (Figure 5).

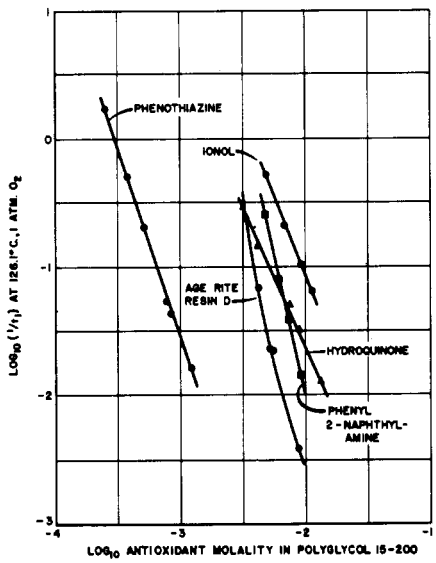

Figure 5. Effect of antioxidant concentration upon induction period of inhibited Polyglycol 15-200

Most of the data are close to linear in Figure 5, but the slopes are unusually steep. Values of n in Equation 1 are: phenothiazine, $n = 3.00$ (standard deviation $\pm$ 0.06); hydroquinone, $n = 2.15$ (standard deviation $\pm$ 0.06); phenyl-2-naphthylamine, $n \cong 4.3$ (standard deviation $\pm$ 0.27); and dibutylcresol, $n = 2.5$ (standard deviation $\pm$ 0.13). The curve for commercial resin is not linear, but is extremely steep.

These power dependencies are markedly higher than those reported for various phenolic and arylamine antioxidants in cracked motor fuel (*30*), diisobutylene (*30*), styrene (*29*), cyclohexane (*15*), and Tetralin (*16, 23*), in all of which studies n was found to have a value of unity or less. A value of 2 has been reported for n in the case of several sulfur-containing antioxidants in mineral oil (*20*). The much higher concentration dependence observed with Polyglycol 15–200 emphasizes the importance of substrate in determining the qualitative as well as quantitative behavior of added antioxidants.

The tendency of four of the antioxidants to group together in Figure 5 again suggests that the predominant antioxidant-consuming reaction is sacrificial transfer and is determined principally by the radical-generating reactions of the polyglycol. Hydroquinone is about twice as effective as dibutylcresol in this system. The extremely high efficacy of phenothiazine may be attributed to the fact that its oxidation products themselves possess antioxidant activity (*27*). The magnitude of n for the two amines may reflect the known tendencies of arylamines to catalyze hydroperoxide decomposition (*18*).

Effect of Temperature. The effect of temperature upon induction period at constant antioxidant loading may be seen by examining the induction periods of various aliquots of inhibited Polyglycol 15–200, subjected to oxidation at 100° to 141° C. (212° to 286° F.). Logarithms of induction periods are plotted against reciprocal absolute temperature (Figure 6). The approximate linearity of these Arrhenius plots permits estimation of the over-all activation energies of the induction period reactions. For phenothiazine, E_a = −28 kcal.; for dibutylcresol, E_2 = −51 kcal. Rough estimates of E_a for hydroquinone and phenyl-2-naphthylamine are −50 kcal. and −53 kcal., respectively—i.e.,

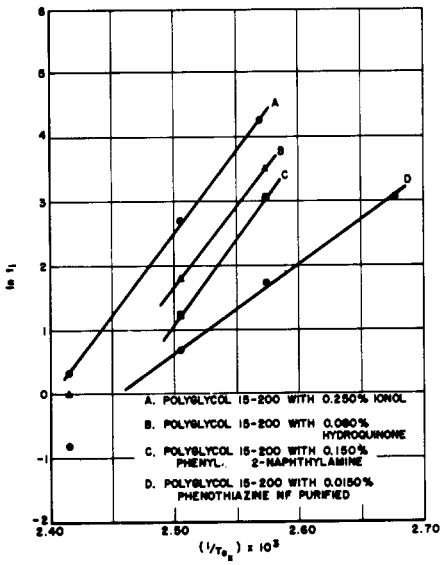

Figure 6. Temperature dependency of induction periods of inhibited Polyglycol 15-200

about the same as for dibutylcresol. This substantial identity of E_a's for these three different types of antioxidant further strengthens the inference noted above that the rate-determining step(s) of antioxidant consumption in these systems involve radical-generating reactions of the polyglycol. A similar argument has been advanced by Bawn (*2*), based upon similarities of activation energies of induction periods in the inhibited low-temperature autoxidation of benzaldehyde.

At temperatures of 150° C. and higher, most conventional antioxidants lose their efficacy (*9*), probably because of their inherent susceptibility to direct oxidation by oxygen (*20*). Of the group of antioxidants examined in this study, only phenothiazine and AgeRite Resin D show much efficacy at 150° C. Taking advantage of the fact that the great preponderance of oxidative degradation products of polyglycols are volatile at elevated temperatures, the efficacies of these two antioxidants may be compared by following the weight losses of inhibited polyglycol samples placed in open Petri dishes in a vented oven. Results of tests at 150° C. (302° F.) and 175° C. (347° F.) are shown in Table VI. Phenothiazine offers limited protection at the lower temperature, and virtually no protection at the higher temperature. This is in fair agreement with other findings (*9, 27*) with bis(2-ethylhexyl)sebacate inhibited with phenothiazine. AgeRite Resin D, however, confers excellent protection upon the polyglycol at 150° C., and affords appreciable protection (more than 24 hours at 0.50% loading) at 175° C.

Table VI. Weight Losses of Polyglycol 15–200 at 150° and 175° C.[a]

Temp., ° C.	Additive[b]	Hours: 24	96	144
		Per Cent Loss		
150	None (control)	63	89	90
150	Phenothiazine	<1	7	70
150	AgeRite Resin D	<1	<1	<1
175	None (control)	81	90	92
175	Phenothiazine	29	90	92
175	AgeRite Resin D	1	90	93

[a] All data, averages of duplicate determinations with 10.00-gram samples in 3.5 inch i.d. shallow-form Petri dishes in a vented convection oven.
[b] At 0.50% concn.

At lower temperatures (up to about 125° C.), present data suggest that the rate of inhibitor consumption, and hence the extent of protection which can be afforded by a chain-transfer antioxidant, is primarily a function of the susceptibility of the substrate to initiation and branching processes. At temperatures of 150° C. and above, however, vast differences become apparent in the performances of different inhibitors in the same substrate, and, conversely, similarities emerge in the performances of the same inhibitor in different substrates. This suggests that the primary determinant of antioxidant efficacy at temperatures above 150° C. may well be the rate of the direct antioxidant-oxygen reaction.

Generalization to Other Polyglycols. Few extrapolations are more hazardous than those applying antioxidant information obtained with one substrate to an entirely different substrate. On the other hand, closely similar substances should behave similarly. The question here is whether or not the whole family of polyoxyalkylene compounds, all sharing the repeating structure $-CH_2-CHR-O-$, may be considered to be comparable with one another with respect to antioxidant stabilization. Results of a series of tests at 126° C., with two good antioxidants and a representative group of polyoxyalkylene compounds, are shown in Table VII.

Table VII. Antioxidant Stabilization of Various Polyglycols and Derivatives[a]

Polyglycol	Controls (No Additive)	Phenothiazine, 0.50% Added	AgeRite Resin D, 0.50% Added
	Hours		
Diethylene glycol	1.3 1.1	>110	>110
E-400[b]	0.4 0.4	>110	>110
P-400[c]	0.8 0.7	>110	>110
E-400[b] diether[d]	0.3 0.3	>110	1.4
P-400[c] diether[d]	0.35 0.35	>110	2.0
15–200[e]	0.6 0.6	>110	>110
Polyoxystyrenediol[f]	4.0 3.2	3.5	3.8

[a] At 126.1° C. under 1 atm. oxygen; induction period defined in Table III[a]. [b] Table I[d]. [c] Polyoxypropylenediol, molecular weight 400. [d] Methyl *sec*-butyl diether. [e] Table I[c]. [f] Average molecular weight 590.

These data show that diethylene glycol, a representative polyethylene glycol, a representative polypropylene glycol, and a mixed oxyethylene-oxypropylene polyglycol, are uniformly well protected by these antioxidants. But more profound changes, either in the character of the repeating unit or in terminal groups, significantly alter the response to antioxidants. Thus, polyoxystyrenediol is not stabilized by either of these antioxidants, and the two polyglycol diethers are well protected by phenothiazine, but not at all by AgeRite Resin D.

Failure of AgeRite Resin D to stabilize the two polyglycol diethers might be thought to be due to the specific structural character imparted by the terminal ether groups. However, it appears more likely that this failure is due to a gross medium effect. This is suggested by the results of autoxidations of 1:1 mixtures of diethylene glycol and the methyl *sec*-butyl diether of Polyglycol E-400. If diether molecules were not inhibited by antioxidant, one would expect to find the mixture autoxidizing in the presence of AgeRite Resin D, at a rate perhaps somewhat slowed up by dilution with inhibited diethylene glycol. However, results (Table VIII) show complete inhibition of this mixed system by the antioxidant. This constitutes an intriguing problem deserving further study.

More generally, the data of Tables VII and VIII indicate that application of antioxidant data to families of polyethylene and polypropylene glycols is at least qualitatively sound, but that any extrapolation of such data to polyoxyalkylene compounds of profoundly different structures, or to materially different environments, would be extremely hazardous.

DISCUSSION

The unusually high dependencies of induction period upon antioxidant concentration (Figure 5) may be due to the unusual character of polyglycol autoxidations, as compared with typical hydrocarbon autoxidations. At temperatures above 75° C. it has been shown that peroxide concentration in autoxidizing diethylene glycol rapidly reaches a level, steady-state value, and that this steady-state concentration falls sharply as temperature is increased (22). This implies a progressive shortening of chain length with increasing temperature. At 126° C., the steady-state peroxide level is too low to be measured by the usual methods, and the kinetic chain length of the autoxidation, even without inhibitor present, must be considered to be very short.

The effects of modifications of inhibition kinetics may be seen by considering the following group of reactions:

RH (heat, $h\nu$)	→	R·	(initiation)	(1)
R· + O_2	→	ROO·	(propagation)	(2)
ROO· + RH	→	R· + ROOH	(propagation)	(3)
ROO· + AH	→	inert	(termination I)	(4)
AH + O_2	→	inert	(direct oxidation)	(5)
ROOH	→	RO· + HO·	(branching)	(6)
RO· + RH	→	R· + HOR HO· HOH	(branching)	(7)
RO· + AH HO·	→	inert	(termination II)	(8)

For a simple, inhibited autoxidation (Reactions 1 to 4), steady-state approximation for the chain carrier radicals leads to an antioxidant consumption rate equal to the initiation rate:

$$-d(\mathrm{AH})/dt = \omega_i \qquad (2)$$

[For simplicity, it is assumed that antioxidant concentration at the end of the induction period, $(AH)_i$, is negligibly small.] However, the very property which makes an antioxidant effective—i.e., a high reactivity towards peroxy radicals—confers upon it an inherent susceptibility to direct

Table VIII. Stabilization of a Diether - Glycol Mixture[a]

Polyglycol			t_i, Hours	
Diethylene glycol, %	E-400 diether,[b] %	AgeRite Resin D, %	0.03 mole/liter	0.05 mole/liter
100	None	None	0.8	1.3
			0.6	1.1
100	None	0.50	54	>110
None	100	None	0.2	0.3
			0.2	0.3
None	100	0.50	0.9	1.4
50	50	None	0.2	0.4
50	50	0.50	67	>110

[a] At 126.1° C. under 1 atm. of oxygen.
[b] Table VII[b,d].

attack by molecular oxygen. When this process (Reaction 5) contributes significantly, then the antioxidant consumption rate takes on the form:

$$-d(\mathrm{AH})/dt = \omega_1 + k_5(\mathrm{O_2})(\mathrm{AH}) \quad (3)$$

Where the antioxidant is primarily a hydrogen donor, direct oxidation may be somewhat more deleterious than indicated by Reaction 5—e.g.,

$$\mathrm{AH} + \mathrm{O_2} \rightarrow \mathrm{HOO}\cdot + \text{inert} \quad (5a)$$

$$\mathrm{HOO}\cdot + \mathrm{RH} \ldots \rightarrow n\mathrm{R}\cdot \quad (5b)$$

But this does not affect the form of the antioxidant consumption expression:

$$-d(\mathrm{AH})/dt = \omega_1 + (n+1)k_{5a}(\mathrm{O_2})(\mathrm{AH}) \quad (4)$$

Equations 3 and 4 describe systems wherein induction periods are still almost linear with $(\mathrm{AH})_0$ at low antioxidant loadings, but fall off at higher loadings. Where Equation 1 is obeyed, n falls to values below unity. This is the commonly observed relationship between t_i and $(\mathrm{AH})_0$ for most inhibited hydrocarbon systems.

When the primary autoxidation product, ROOH, is itself subject to homolytic scission (Reaction 6), such that species ROOH itself becomes a transitory intermediate, Reaction 4 must be re-examined. It consists of hydrogen abstraction from the antioxidant (Reaction 4a), or of addition to the antioxidant to form an inert adduct (in which case, Reaction 4 remains an adequate representation), or of some combination of both these processes.

$$\mathrm{ROO}\cdot + \mathrm{AH} \rightarrow \mathrm{ROOH} + \text{inert} \quad (4a)$$

In this highly branching system, Reaction 4a is no longer a termination step. If f is the fraction of ROO· radicals undergoing Reaction 4a, and $(1 - f)$ is the fraction undergoing Reaction 4, then f must be less than 0.5 in order for the species AH to function as an antioxidant in this system. (For the limiting case of $f = 0.5$ in a strongly branching system, AH becomes kinetically invisible unless one includes other AH-involved reactions.) It can be easily shown that if M radicals are generated by other processes over some interval of time, and are consumed only by reactions with AH, then the total number of radicals ultimately reacting with the antioxidant species is $M/(1 - 2f)$. This line of argument leads to the conclusion that, within the framework of Reactions 4 and 4a, the only substances which could be effective antioxidants in highly branching systems are those which principally undergo addition reactions with peroxy radicals. But such a conclusion is contrary to a considerable body of experience. It is known that the antioxidant hydroquinone is converted largely to benzoquinone in oxidizing systems, and that trialkylphenols undergo first hydrogen abstraction, then addition (*3, 8, 12*). Both hydroquinone and trialkylphenols are effective inhibitors, in the present study and in other work carried out under deliberately branching conditions (*4, 21, 23*).

To explain this inhibition in branching systems, one is obliged to consider specific inhibition of the branching process. Chain transfer antioxidants cannot prevent the first-order homolytic decay of hydroperoxide (Reaction 6), but they can compete with the substrate, via Reaction 8, for the reactive products of homolysis. With this second kind of termination entering into the kinetics, the general form of the antioxidant consumption equation becomes:

$$-d(\mathrm{AH})/dt = \omega_1[1 + 2k_3(\mathrm{RH})/k_4(\mathrm{AH})] + k_5(\mathrm{O_2})(\mathrm{AH}) \quad (5)$$

This expression still fails to account for the parallel dependencies of t_i upon oxygen pressure (Table V). The similar dependency of free oxidation rate upon pressure (Table IV) indicates the existence of some oxygen-dependent process other than Reaction 5. A major change in the $(\mathrm{R}\cdot)/(\mathrm{ROO}\cdot)$ ratio, sufficient to alter the dominant biradical termination process for the free oxidation (sensitivity of Reaction 2 to oxygen pressure) is theoretically possible. This, however, is unattractive for two reasons: The range of oxygen pressures (150 to 760 mm. Hg) is considerably above that required for termination-controlled oxygen dependency; and, further, since both propagation and biradical termination are of little consequence in inhibited systems, such an explanation still fails to account for the dependencies observed in Table V.

Attention must, therefore, be directed to the one process which enters importantly into rate expressions for both free and inhibited systems: initiation. If, in addition to Reaction 1, an oxygen-involved initiation process is assumed,

$$\mathrm{RH} + \mathrm{O_2} \ldots \rightarrow m\mathrm{R}\cdot \quad (1a)$$

then for a simple system (Reactions 1 to 4) the antioxidant consumption expression corresponding to Equation 2 is:

$$-d(\mathrm{AH})/dt = \omega_1 + mk_{1a}(\mathrm{RH})(\mathrm{O_2}) \quad (2a)$$

and the expression for the inhibited branching system (Reactions 1 to 8) becomes:

$$-d(\mathrm{AH})/dt = [\omega_1 + mk_{1a}(\mathrm{O_2})(\mathrm{RH})]\cdot [1 + 2k_3(\mathrm{RH})/k_4(\mathrm{AH})] + k_5(\mathrm{O_2})(\mathrm{AH}) \quad (5a)$$

Under the experimental conditions at 126° C., direct oxidation of antioxidants appears to be unimportant in comparison with other antioxidant-consuming reactions. The oxygen dependency of the induction period, observed to be substantially the same for various antioxidants in the same substrate (Table V), appears to be best accounted for in terms of oxygen participation in an initiation process. The steep dependencies of t_i upon antioxidant concentration (Figure 5) reflect the importance of reaction between the antioxidant and the radical products of peroxide homolysis (compare the inverse functions of antioxidant concentration in Equations 5 and 5a) and, in some cases, concurrent antioxidant-catalyzed peroxide decomposition (*20*). A more explicit theoretical understanding of these dependencies must await detailed investigation of the unit processes.

DERIVATION OF KINETIC EQUATIONS

The several kinetic equations used are derived by solution of the simultaneous equations of the steady-state approximation.

Equations 5 and 5a, however, are too complicated to be intuitively obvious, and also involve an additional assumption (which is, however, quite defensible–v.i.). The following is the stepwise derivation of Equation 5.

This case assumes Reactions 1 through 8.

Then, steady-state for $(\mathrm{R}\cdot)$:

$$k_2(\mathrm{O_2})(\mathrm{R}\cdot) = \omega_1 + k_3(\mathrm{RH})(\mathrm{ROO}\cdot) + k_7(\mathrm{RH})(\mathrm{RO}\cdot) \quad (1')$$

And, steady-state for $(\mathrm{ROO}\cdot)$:

$$k_2(O_2)(R\cdot) = k_3(RH)(ROO\cdot) + k_4(AH)(ROO\cdot) \quad (2')$$

And, steady-state for (ROOH):

$$k_6(ROOH) = k_3(RH)\,(ROO\cdot) \quad (3')$$

And, steady-state for (RO·):

$$2k_6(ROOH) = k_7(RH)(RO\cdot) + k_8(AH)(RO\cdot) \quad (4')$$

Now, Equation 1′ minus Equation 2′ gives

$$k_4(AH)(ROO\cdot) = \omega_1 + k_7(RH)(RO\cdot) \quad (5')$$

And, twice Equation 3′ minus Equation 4′ gives:

$$2k_3(RH)(ROO\cdot) = k_7(RH)(RO\cdot) + k_8(AH)(RO\cdot) \quad (6')$$

Solution of simultaneous Equations 5′ and 6′ gives:

$$(RO\cdot) = \frac{2\omega_1 \cdot k_3(RH)}{k_4(AH)\cdot k_7(RH) + k_4(AH)\cdot k_8(AH) - 2k_3(RH)\cdot k_7(RH)} \quad (7')$$

$$(ROO\cdot) = \frac{2\omega_1 \cdot k_3(RH)\cdot k_7(RH)}{k_4(AH)\left[k_4(AH)\cdot k_7(RH) + k_4(AH)\cdot k_8(AH) - 2k_3(RH)\cdot k_7(RH)\right]} + \frac{\omega_1}{k_4(AH)} \quad (8')$$

Now the last term in the denominators on the right-hand sides of Equations 7′ and 8′ must be very small in comparison with the other denominator terms. Thus,

(a) To stop the primary chain so as to obtain inhibition rather than just retardation, $k_3(RH)$ must be very small compared with $k_4(AH)$.

(b) The branching step ω_7 must be small in comparison with ω_8. If $k_7(RH)$ were even half the magnitude of $k_8(AH)$, branching would "run away" and, for an H-donor antioxidant, no induction period could be obtained.

Therefore, the product $k_3(RH)\cdot k_7(RH)$ is necessarily very small as compared with either of the preceding denominator terms, and is still smaller as compared with the sum of the other two denominator terms. Consequently this last term may be dropped without introducing significant error:

$$(RO\cdot) = \frac{2\omega_1 \cdot k_3(RH)}{k_4(AH)\left[k_7(RH) + k_8(AH)\right]} \quad (7a')$$

$$(ROO\cdot) = \frac{2\omega_1 \cdot k_3(RH)\cdot k_7(RH)}{k_4^2(AH)^2\left[k_7(RH) + k_8(AH)\right]} + \frac{\omega_1}{k_4(AH)} \quad (8a')$$

From Reactions 1 to 8:

$$-d(AH)/dt = \omega_4 + \omega_8 + \omega_5 \quad (9')$$

Expanding:

$$-d(AH)/dt = k_4(AH)(ROO\cdot) + k_8(AH)(RO\cdot) + k_5(O_2)(AH) \quad (9a')$$

Substituting 7a′ and 8a′ into 9a′:

$$\frac{-d(AH)}{dt} = \omega_1 + \frac{2\omega_1 \cdot k_3(RH)\cdot k_7(RH)}{k_4(AH)\left[k_7(RH) + k_8(AH)\right]} + \frac{2\omega_1 \cdot k_3(RH)\cdot k_8(AH)}{k_4(AH)\left[k_7(RH) + k_8(AH)\right]} + k_5(O_2)(AH) \quad (10')$$

Collection and cancellation of terms in Equation 10′ give:

$$-d(AH)/dt = \omega_1 + 2\omega_1 \cdot \frac{k_3(RH)}{k_4(AH)} + k_5(O_2)(AH) \quad (10a')$$

which is identical with Equation 5.

ACKNOWLEDGMENT

The author thanks W.T. Lippincott, University of Florida, Gainesville, Fla., for helpful discussions, and D.F. Wisniewski for assistance in obtaining many of the data. The experimental work was conducted in the Technical Service and Development Laboratory, The Dow Chemical Co. The pressure-recording apparatus was designed and constructed by Ormond Barstow and L.T. Finlayson, The Dow Chemical Co.

LITERATURE CITED

(1) Am. Soc. Testing Materials, Philadelphia, Pa., "A.S.T.M. Standards," 1949, Procedure **D92-46**.
(2) Bawn, C.E.H., *Discussions Faraday Soc.* **14**, 181 (1953).
(3) Bickel, A.F., Kooyman, E.C., *J. Chem. Soc.* **1953**, 3211.
(4) Blanchard, H.S., *J. Am. Chem. Soc.* **82**, 2014 (1960).
(5) Britton, E.C., Sexton, A.R. (to Dow Chemical Co.), U.S. Patent **2,441,793** (May 1948).
(6) Brook, J.H.T., Matthews, J.B., *Discussions Faraday Soc.* **10**, 298 (1951).
(7) Caldwell, J.A., Lytle, M.L. (to Esso Research and Engineering Co.), U.S. Patent **2,799,649** (July 1957).
(8) Campbell, T.W., Coppinger, G.M., *J. Am. Chem. Soc.* **74**, 1469 (1952).
(9) Cohen, G., Murphy, C.M., O'Rear, J.G., Ravner, H., Zisman, W.A., *Ind. Eng. Chem.* **45**, 1766 (1953).
(10) Cole, J.W., Jr., *Ibid.*, **51**, 52A (May 1959).
(11) Collegeman, S.M., Belt, J.R., Am. Soc. Testing Materials *Spec. Tech. Publ.* **84**, 91 (1948).
(12) Cook, C.D., Nash, N.G., Flanagan, H.R., *J. Am. Chem. Soc.* **77**, 1783 (1955).
(13) Curme, G.O., Jr., Johnston, F.; "Glycols," pp. 176ff, 181, 277ff, Reinhold, New York, 1952.
(14) Dow Chemical Co., Brit. Patent **699,664** (November 1953).
(15) Dryer, C.G., Lowry, C.D., Jr., Egloff, G., Morrell, J.C., *Ind. Eng. Chem.* **27**, 315 (1935).
(16) George, P., Robertson, A., *Proc. Roy. Soc. (London)* **185A**, 309 (1946).
(17) Goldschmidt, A., Stewart, W.T., Harle, O.L. (to California Research Corp.), U.S. Patent **2,687,378** (August 1954).
(18) Horner, L., Schwenk, E., *Angew. Chem.* **61**, 411 (1949); *Ann. Chem. Liebigs* **566**, 69 (1949).
(19) Horsley, L.H., Britton, E.C. (to Dow Chemical Co.), U.S. Patent **2,733,272** (January 1956).
(20) Kennerly, G.W., Patterson, W.L., Jr., *Ind. Eng. Chem.* **48**, 1917 (1956).
(21) Lippincott, W.T., Lloyd, W.G., *J. Am. Chem. Soc.* **79**, 4811 (1957).
(22) Lloyd, W.G., *Ibid.*, **78**, 72 (1956).
(23) Lloyd, W.G., Ph.D. thesis, Michigan State Univ., East Lansing, Mich., 1957.
(24) Lloyd, W.G. (to Dow Chemical Co.), U.S. Patent **2,848,501** (August 1958).
(25) Lloyd, W.G., Taylor, F.C., Jr., *Ind. Eng. Chem.* **46**, 2407 (1954).
(26) Lourenco, A., *Compt. rend.* **49**, 619 (1859).
(27) Murphy, C.M., Ravner, H., Smith, N.L., *Ind. Eng. Chem.* **42**, 2479 (1950).
(28) Ohlmann, E.O., Thurber, W.S. (to Dow Chemical Co.), U.S. Patent **2,665,312** (January 1954).
(29) Rosenwald, R.H., Abstracts, p. 12M, Division of Organic Chemistry, 111th Meeting, ACS, April 1947.
(30) Rosenwald, R.H., Hoatson, J.R., *Ind. Eng. Chem.* **41**, 914 (1949).
(31) Russell, G.A., *J. Chem. Educ.* **36**, 111 (1959).
(32) Sexton, A.R. (to Dow Chemical Co.), U.S. Patent **2,441,848** (May 1948).
(33) Sexton, A.R., Alquist, F.N. (to Dow Chemical Co.), *Ibid.*, **2,441,849** (May 1948).
(34) Stewart, W.T., Goldschmidt, A., Harle, O.L. (to California Research Corp.), *Ibid.*, **2,687,377** (August 1954).
(35) Sweatt, C.H., Langer, T.W., *Mech. Eng.* **73**, 469 (1951); *Ibid.*, **74**, 162 (1952).
(36) Walters, E.L., Sipple, H.E. (to Shell Development Co.), U.S. Patent **2,514,982** (July 1950).
(37) Wilson, J.E., *Ind. Eng. Chem.* **47**, 2201 (1955).
(38) Youden, W.J., "Statistical Methods for Chemists," pp. 90ff, Wiley, New York, 1951.

RECEIVED for review August 25, 1960. Accepted March 28, 1961.