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Action of Antioxygens⁽¹⁾ in the Oxidation
of Unsaturated Fatty Oils.

II. Inhibitory Effect of Diphenylamine, Diphenyl-
guanidine and Hydroquinone.

By

Bunnosuke YAMAGUCHI, *Rigakusi*,

Member of the Institute.

Abstract.

As a continuation to the previous communication, this paper describes the results of investigations on the antioxygenic action of diphenylamine, diphenylguanidine and hydroquinone in the oxidation of olive oil. The results of experiments can be well explained by the theory of mechanism of inhibition which has been developed in the earlier paper. A modified equation has been established in order to calculate the form of the velocity curve for the case of diphenylamine, and it has been shown that the theory agrees satisfactorily with the actual results of experiment.

(1) According to the reason lately stated by Moureu and his coworkers [Ind. Eng. Chem., 22, 551 (1930)], the author will adopt the name of "antioxygens" for the material possessing the property of preventing the action of free oxygen on a wide range of autoxidizable substances, although the term "antioxydants" has been used by him in the previous paper.

Introduction.

In the previous investigation⁽¹⁾ the author has studied the anti-oxygenic action of α -naphthylamine and unsym. diphenylhydrazine in the oxidation of olive oil and has ascertained that the actual rate of oxidation of the oil in the presence of α -naphthylamine can be expressed well by an equation based on Christiansen's theory of chain mechanism. In the present paper the action of other antioxygens such as diphenylamine, diphenylguanidine and hydroquinone in the oxidation of olive oil has been studied. The method of investigation is quite similar to that used in the previous investigation. The rate of oxidation of olive oil at 100°C in the presence and in the absence of antioxygen has been determined by the measurement of the decrease in iodine value. The olive oil used in the present experiments has been purified in the same way as before. This purified oil has an iodine value of 85.73 and contains no free acid (Olive Oil C).

Results of Experiments.

(a) Effect of diphenylamine.

Table I and the left-hand curve in Fig. 1 show the result for the oxidation of Olive Oil C in the absence of antioxygen. In agreement with the previous observation, the oxidation does not apparently start at once, i.e., oil remains seemingly unchanged during a period of incubation. (Different olive oils have respectively different induction periods. The period for Olive Oil C has been found to be 6.1 hours.) Once the oxidation started, the reaction proceeds unimolecularly with an appreciable rate, and accordingly the decrease of iodine value due to the oxidation can be expressed by Equation (I) given in the previous paper.

(1) Report of the Aeronautical Research Institute, Tokyo Imperial University, No. 61 [Vol. V, 196 (1930)].

TABLE I.
Oxidation of Olive Oil C without antioxygen.

Oxidation time (hours)	Observed iodine value (corrected†)	Logarithm of iodine value	$k = \frac{1}{t-6.1} \ln \frac{a}{a-x}$
0	85.73	1.93313	
7.00	83.88	1.92367	0.0242
11.67	74.55	1.87247	0.0250
16.50	65.64	1.81719	0.0256
23.00	54.22	1.73419	0.0271
30.00	45.26	1.65575	0.0267
			mean 0.0257

† The correction due to the weight increase of oil resulting from oxidation has been added.

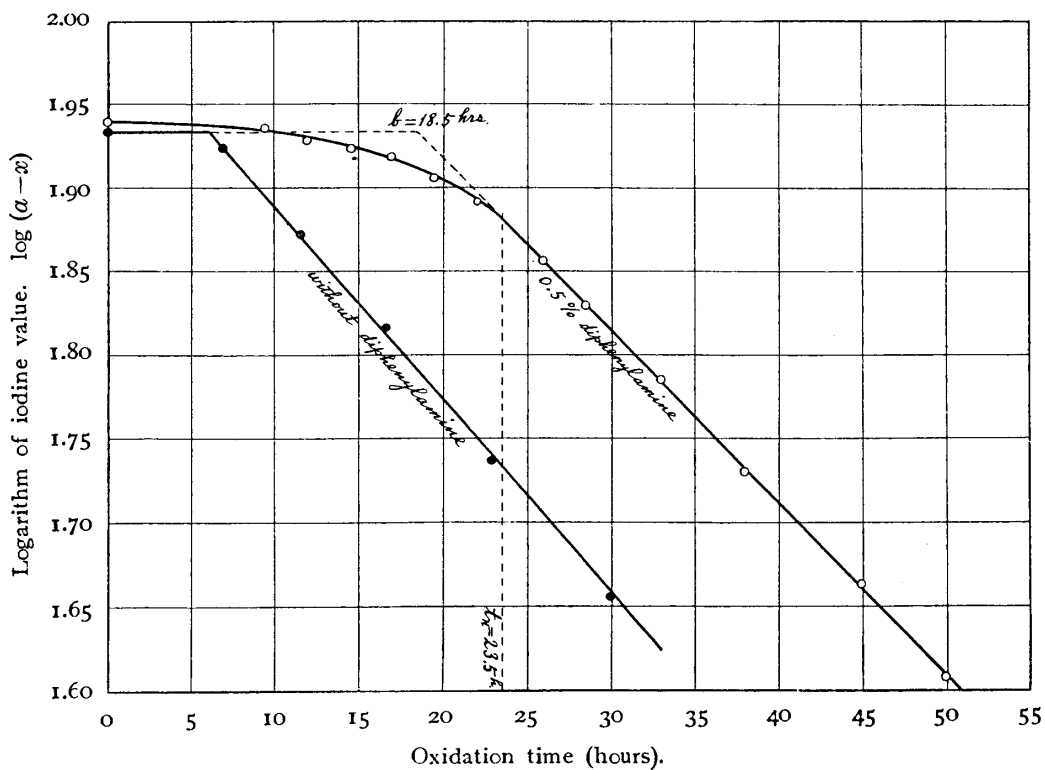


Fig. 1.

$$\ln \frac{a}{a-x} = k(t-b) \quad (1)$$

where a expresses the initial iodine value of the oil ($a=85.73$) and $(t-b)$ the time after the end of induction period.

The value of velocity coefficient k in the equation has been determined to be 0.0257 as shown in Table 1.

TABLE 2.
Effect of 0.5% diphenylamine.

Oxidation time. (hours)	Observed iodine value. (corrected†)	Logarithm of iodine value.	$k = \frac{1}{t-18.5} \ln \frac{a}{a-x}$	Calculated iodine value. J	
0	87.03	1.93967	} before t_n	86.80	
9.50	86.15	1.93528		85.48	
12.00	84.73	1.92802		84.95	
14.67	83.93	1.92393		83.47	
17.00	82.89	1.91851		82.31	
19.50	80.45	1.90555		80.70	
22.00	77.90	1.89154		78.38	
26.00	71.88	1.85663		0.0235	71.82*
28.50	67.59	1.82991		0.0237	67.71*
33.00	61.00	1.78532		0.0235	60.89*
38.00	53.85	1.73118	0.0238	54.11*	
45.00	46.11	1.66376	0.0234	45.87*	
50.00	40.59	1.60837	0.0238	40.77*	
			mean 0.0236		

† The correction due to the weight increase of oil resulting from oxidation has been added.

Table 2 and the right-hand curve in Fig. 1 show the result of investigation on the effect of 0.5% diphenylamine upon the oxidation of the oil at 100°C. Diphenylamine acts as an inhibitor of the reaction, lowering its velocity in a remarkable degree. The oxidation of the oil containing diphenylamine starts initially with a very small but sensible rate just after a length of time equal to the induction period for the

oil containing no antioxygen. The rate, however, increases slowly with time of oxidation until a point of time marked by t_n is reached, after which the oxidation is found to proceed completely unimolecularly. In this respect the antioxygenic effect of diphenylamine is quite analogous to that of α -naphthylamine. All the values of velocity coefficient which have been calculated by Equation (I) for different times of oxidation greater than t_n are found to be consistent as shown in Table 2, the average value being 0.0236. (The value of b which must be introduced in these calculations has been found to be 18.5 hours by the method already given in the earlier paper.) The value of velocity coefficient thus obtained, $k=0.0236$ is, however, slightly smaller than that for the oxidation without antioxygen, $k=0.0257$. The difference between them can not be allowed to be neglected. (In Fig. 1, the slope of straight part is greater for the left curve than the right one.) This result may be explained in the following manner.

The amount of diphenylamine added to the oil as an antioxygen decreases gradually with time of oxidation. The decrease of diphenylamine may be caused not only by its oxidation and evaporation, but also by some reaction with certain oxidation products of oil. Owing to the gradual loss of diphenylamine, the rate of oxidation increases slowly till t_n , at which the antioxygen should have been just completely lost from the oil in order that the reaction may begin to take a unimolecular course. Now if we assume that a certain substance which may be gradually formed from diphenylamine in the course of oxidation acts as a weak antioxygen, and that this substance is neither removed from the oil by evaporation nor destroyed by oxidation, the velocity coefficient of the unimolecular oxidation which the oil containing diphenylamine undergoes after t_n may be slightly smaller than that for the oxidation of the oil without antioxygen.

Under this assumption Equation (VIII) which has been deduced from Equation (IV) in the previous paper⁽¹⁾ can not be used without

(1) loc. cit.

some modification, because we must take in consideration a new factor due to the effect of the weak antioxygen which is assumed to be gradually formed in the course of oxidation.

Thus, Equation (IV) is substituted by the formula

$$v = \frac{dx}{dt} = \frac{Nk_r}{k_i c_i + k'_i c'_i + k_s} (a - x) \quad (\text{IV})'$$

where c'_i denotes the concentration of the antioxygen gradually formed in oil, k'_i a constant expressing the specific antioxygenic power of the substance, and the other letters have the same meanings as for Equation (IV).

By putting $k = \frac{Nk_r}{k_s}$, $k_1 = \frac{k_i}{k_s}$ and $k_2 = \frac{k'_i}{k_s}$, the above equation becomes

$$\frac{dx}{dt} = \frac{k}{1 + k_1 c_i + k_2 c'_i} (a - x). \quad (\text{V})'$$

c_i , the amount of diphenylamine decreases with time of oxidation. As has already been stated, the antioxygen must have just been lost completely from the oil at the time t_n , if the oxidation after t_n is completely unimolecular. Furthermore, the decrease of diphenylamine is caused not only by oxidation and evaporation, but also by some reaction with certain decomposition products of oil resulting from oxidation. It may be assumed as in the previous paper that the total loss of diphenylamine in the oil is in direct proportion to time of oxidation and that substance vanishes at the time t_n .

$$\text{Thus} \quad c_i = k'_1 (t_n - t),$$

c'_i , the amount of the weaker antioxygen gradually formed from diphenylamine increases with time of oxidation until t_n . Since the term involving c'_i in Equation (V)' is merely a small correction, we may put approximately $c'_i = k'_2 t$ (where k'_2 is a constant), assuming that the formation of this antioxygen is proportional to the time of oxidation.

Equation (V)' then becomes

$$\begin{aligned} \frac{dx}{dt} &= \frac{k}{1 + k_1 k_1' (t_n - t) + k_2 k_2' t} (a - x) \\ &= \frac{k}{(1 + k_1'' t_n) + (k_2'' - k_1'') t} (a - x) \end{aligned} \quad \text{(VI)'}$$

where $k_1'' = k_1 k_1'$, $k_2'' = k_2 k_2'$.

Integrating the equation, we have

$$\log \frac{a}{a-x} = \frac{k}{k_1'' - k_2''} \log \frac{1 + k_1'' t_n}{(1 + k_1'' t_n) - (k_1'' - k_2'') t} \quad \text{(VII)'}$$

Here it should be noted that t and t_n in this equation are times measured from the end point of the induction period for the oil containing no antioxygen, i.e., times measured from the point at which, if the oil did not contain diphenylamine, the oxidation would have to start, and are not times measured from the point at which the bubbling of oxygen through the oil has been started. The former times are 6.1 hours less than the latter ones.

When k_2'' vanishes, Equation (VII)' becomes, of course, identical to Equation (VIII) given in the previous paper.

The four constants, k , k_1'' , k_2'' and t_n involved in Equation (VII)' are determined as follows. The value of k which is equal to $\frac{Nk_r}{k_s}$, representing the velocity coefficient in the absence of antioxygen (see Equation (V) in the previous paper), is 0.0257 as shown in Table 1.

The value of t_n is easily determined, since the point of time at which the reaction just begins to take a unimolecular course can be graphically decided from the oxidation curve such as Fig. 1.

Thus, we obtain

$t_n = 23.5 - 6.1 = 17.4$ hours for the oil containing 0.5% diphenylamine.

The evaluation of k_2'' also can be easily performed. When t is equal to t_n , Equation (VI)' reduces to

$$\frac{dx}{dt} = \frac{k}{1 + k_2''t}(a-x),$$

while on the other hand we have already observed that the velocity of oxidation just becomes unimolecular at the time t_n .

Accordingly we have the relation

$$\frac{k}{1 + k_2''t} = k_n,$$

where k_n represents the velocity coefficient of the unimolecular oxidation which the oil containing 0.5% diphenylamine undergoes after t_n , thus being equal to 0.0236.

Hence we obtain

$$k_2'' = \frac{k - k_n}{k_n t_n} = \frac{0.0257 - 0.0236}{0.0236 \times 17.4} = 0.00511.$$

Lastly, the value of k_1'' must be decided. As t_n is known and the iodine value at t_n can be calculated from Equation (I), the left side of Equation (VII)' is evaluated if the iodine value thus calculated is introduced in the equation. Then the value of k_1'' by whose introduction the right side of Equation (VII)' must become equal to that value of the left side can be easily determined by a graphical method. Thus the value of k_1'' has been found to be 0.470.

If Equation (VII)' is transformed into the form.

$$(a-x) = a \times \left[\frac{1 + k_1''t_n}{(1 + k_1''t_n) - (k_1'' - k_2'')t} \right] \frac{k}{k_2'' - k_1''} \quad (\text{VII})''$$

where $a = 85.73$, $t_n = 17.4$ hours, $k = 0.0257$, $k_1'' = 0.470$ and $k_2'' = 0.00511$, this equation gives the iodine value proper to oil itself at any instant in the course of oxidation. In order to calculate the iodine value of the oil

containing diphenylamine, we must, however, add a correction⁽¹⁾ due to the iodine absorption of diphenylamine. It is well known that this compound acts with halogens and forms tetrahalogen-substitution products. So if we assume that diphenylamine is completely transformed into tetraiododiphenylamine, when the measurement of iodine value of the oil containing diphenylamine is carried out by Wijs' method, a simple calculation leads us to assign an iodine value of 300.4 to diphenylamine. The initial iodine value of the oil containing 0.5% diphenylamine is then easily calculated and found to be

$$\frac{300.4 \times 0.5 + 85.73(100 - 0.5)}{100} = 87.03$$

This calculated value is in good agreement with the experimental value given in Table 2. (86.80).

Now the correction which must be added to Equation (VII)'' in order to obtain the iodine value at any time of oxidation of the oil containing 0.5% diphenylamine can be readily obtained, since it has been assumed that the amount of diphenylamine added to the oil decreases in direct proportion to time of oxidation and vanishes at the time t_n . Let the percentage of diphenylamine in the oil at a time of oxidation t (provided $t < t_n$) be q , then the iodine value J at that time can be calculated by the following formula⁽²⁾

$$J = \frac{300.4 \times q + (a-x)(100-q)}{100}, \quad \text{(VIII)'}$$

(1) When the amount of antioxygen added to the oil is so small that the iodine value of the oil containing the antioxygen is nearly equal to that of the pure oil, this kind of correction can approximately be neglected. This is the reason why such a correction has been neglected in the previous calculation for the oil containing α -naphthylamine.

(2) If we neglect q against 100 in Equation (VIII)', then the correction added to $(a-x)$, namely the correction due to the iodine absorption of diphenylamine will be given, in Fig. 2, simply by the vertical elevation of the line BN above AN which intersects with BN at t_n . The point A represents the initial iodine value (85.73) of the pure olive oil.

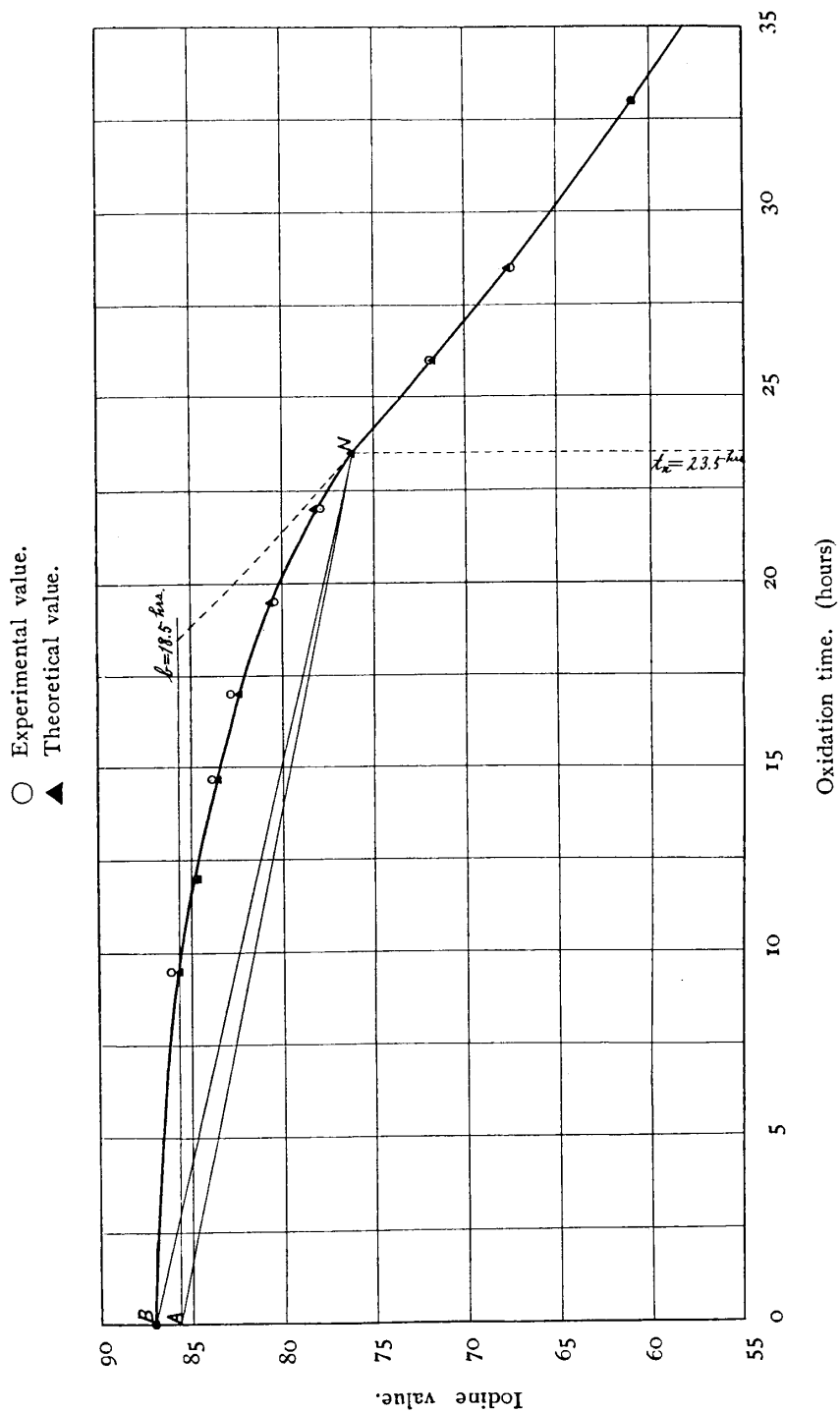


Fig. 2.

where $(a-x)$ is given by Equation (VII)'' and q can be evaluated by means of the equation

$$q=0.5-0.0313(6.1+t).$$

The iodine values calculated by Equation (VIII)' for different times of oxidation, as shown in Table 2 and Fig. 2, are in good agreement with the experimental values, the deviation being never beyond the range of experimental error. The figures marked with * in the table are the values calculated by Equation (I). ($t > t_n$). This striking agreement seems to justify the considerations which have been made to explain the mechanism of antioxygenic action.

(b) Effect of hydroquinone.

Table 3 shows the results of investigation on the effect of 0.003%, 0.010% and 0.025% hydroquinone on the oxidation of Olive Oil C. The results are also illustrated by Fig. 3 in which the left-most straight line represents again the result for the oxidation without antioxygen. Hydroquinone acts as a very strong inhibitor in the oxidation of olive oil, prolonging the induction period in a remarkable degree. As seen from Fig. 3, the iodine value of oil remains seemingly unchanged during a period corresponding to the added amount of hydroquinone. Once the oxidation started, the reaction always proceeds unimolecularly with the same rate whether the reaction starts soon or has been delayed for a certain length of time by the antioxygen. In this respect the antioxygenic effect of hydroquinone resembles that of unsym. diphenylhydrazine which has been observed in the previous investigation. The velocity coefficient of such a unimolecular reaction can be calculated by Equation (I). The values of velocity coefficient for different oxidation times are always in good agreement with one another as shown in Table 3. From the fact that all the straight lines in Fig. 3 run almost parallel, it is easily perceived that the velocity coefficient k is practically independent of the amount of hydroquinone (see Table 4). The length of

TABLE 3.
Effect of hydroquinone.

Amount of Hydroquinone.	Oxidation time (hours)	Observed iodine value. (corrected)	Logarithm of iodine value.	$k = \frac{1}{t-b} \ln \frac{a}{a-x}$
0.003%	0	85.66	1.93278	$(b = 11.0 \text{ hours})$ 0.0250 0.0260 0.0261 0.0256 0.0248 mean: 0.0255
	10.58	85.43	1.93161	
	11.58	83.80	1.92325	
	12.58	82.40	1.91593	
	16.58	74.13	1.86998	
	20.58	66.75	1.82446	
	24.58	60.52	1.78196	
	29.58	54.16	1.73366	
0.010%	0	85.78	1.93339	$(b = 26.7 \text{ hours})$ 0.0247 0.0250 0.0258 0.0257 0.0261 0.0260 mean: 0.0256
	25.25	85.68	1.93288	
	26.75	84.96	1.92919	
	28.75	81.58	1.91158	
	32.75	73.71	1.86750	
	36.75	66.19	1.82082	
	40.75	59.73	1.77617	
	44.75	53.49	1.72828	
50.00	44.60	1.67045		
0.025%	0	85.74	1.93318	$(b = 54.5 \text{ hours})$ 0.0236 0.0251 0.0258 0.0263 0.0251 0.0258 0.0265 mean: 0.0255
	55.00	84.39	1.92630	
	57.00	80.82	1.90752	
	59.00	76.58	1.88411	
	63.00	68.82	1.83769	
	67.00	61.72	1.79040	
	71.00	56.66	1.75324	
	75.00	50.52	1.70344	
80.00	43.62	1.63970		

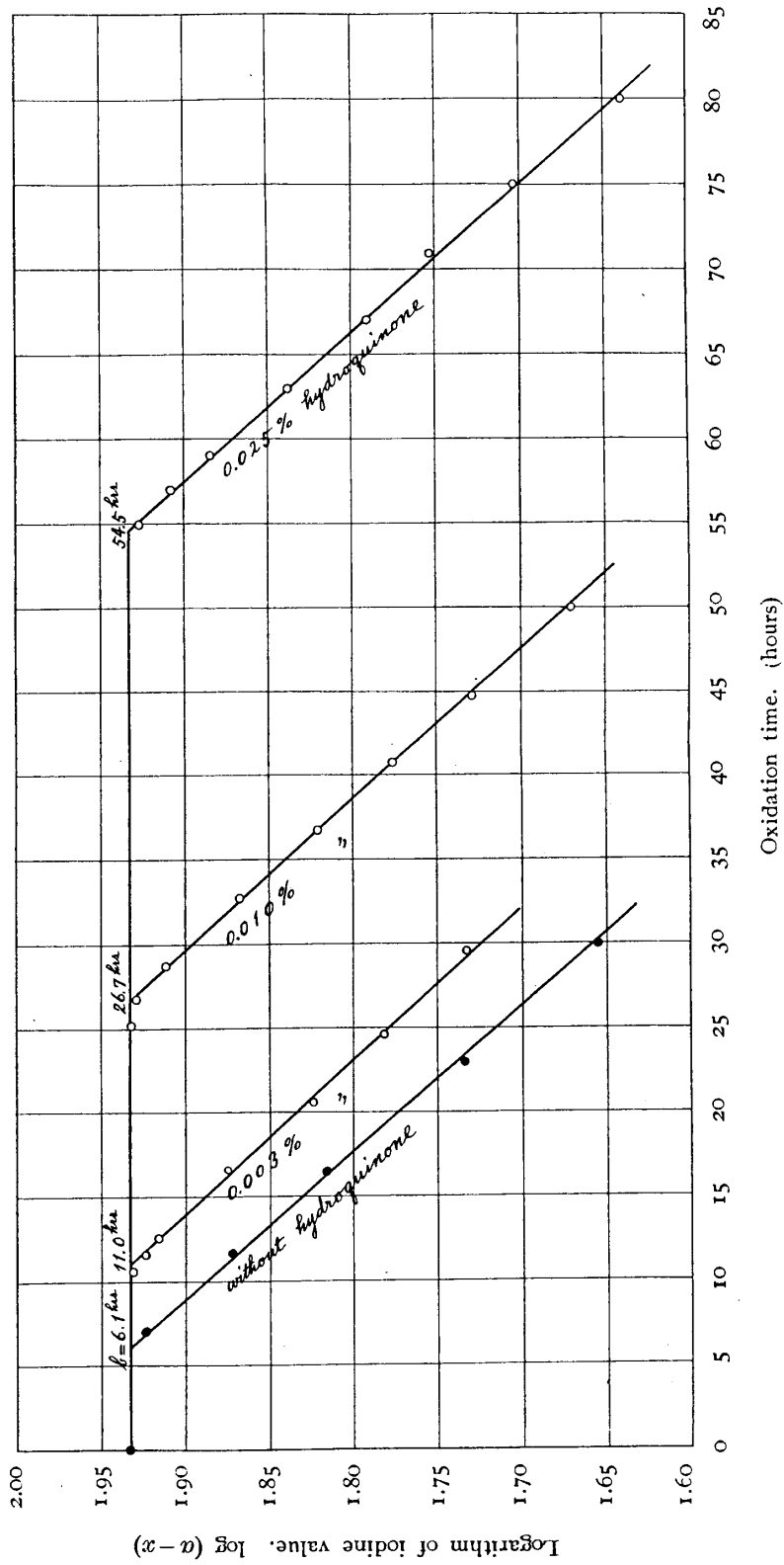


Fig. 3.

TABLE 4.

Added amount of Hydroquinone. (%)	Induction period (b). (hours)	$k = \frac{1}{t-b} \ln \frac{x}{a-x}$
0	6.1	0.0257
0.003	11.0	0.0255
0.010	26.7	0.0256
0.025	54.5	0.0255

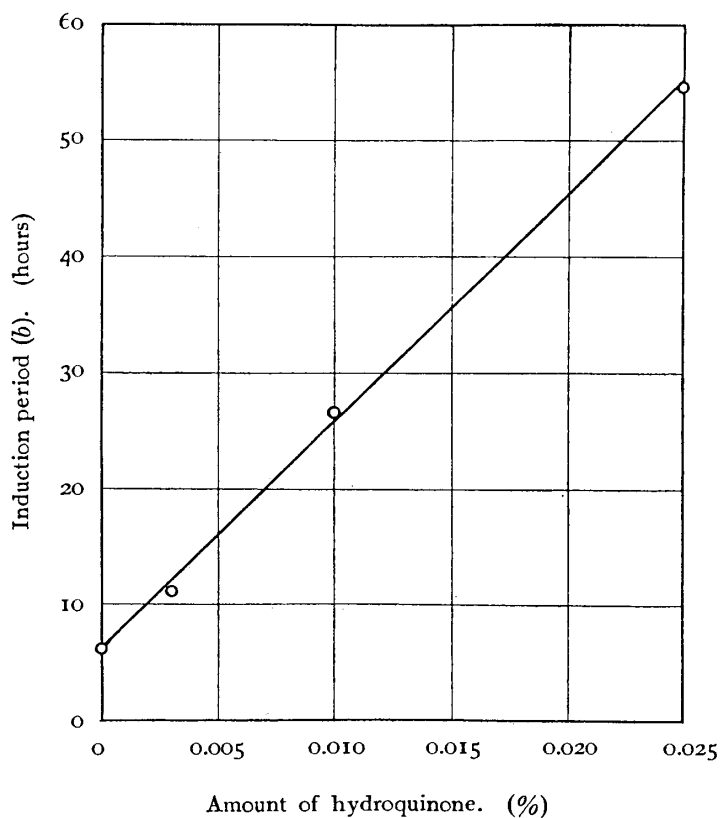


Fig. 4.

induction period depends, as illustrated in Fig. 4, upon the added amount of hydroquinone and the former increases almost in direct proportion to the latter. The fact that the reaction, when once started, always proceeds at the same rate, leads us to the conviction that the

antioxygen must have been lost completely from the oil before the oxidation apparently starts, and that even a trace of hydroquinone can inhibit the oxidation very strongly as long as it remains in the oil.

The interpretation of mechanism which has been made in the previous paper in order to explain the inhibitory action of unsym. diphenylhydrazine can be directly applied to that of hydroquinone. If we assume that hydroquinone has a very strong power to break the chain of reaction, i.e., the specific inhibitory power represented by k_i in Equation (III) in the earlier paper is great enough so that the relation $k_i c_i + k_s \gg k_r c_r$ holds even for a very small value of c_i , then Equation (III) will reduce to

$$v = N.$$

Since N has been assumed to be very small, the velocity of oxidation will be, in agreement with actual results of experiment, so slow that the oil will remain seemingly unchanged until the antioxygen will have been almost completely lost from the oil.

The inhibitory power of hydroquinone is much superior to that of unsym. diphenylhydrazine as is evident from the experimental fact that the induction period for the oil containing 0.025% hydroquinone amounts to 54.5 hours, while that for the oil containing the same amount of unsym. diphenylhydrazine is about 14.0 hours⁽¹⁾. The addition of only 0.003% hydroquinone causes the oil to remain seemingly unchanged during a period of 11.0 hours, thus prolonging the period of incubation from 6.1 to 11.0 hours. If we assume for simplicity that the oil consists of triolein alone, a calculation will show that one molecule of hydroquinone can inhibit efficiently the oxidation of at least more than 4100 molecules of triolein or 12300 unsaturated linkages of triolein. The mechanism of such a trace-catalysis can not perhaps be explained, unless we have recourse to the theory of chain mechanism such as the author has adopted.

(1) See the previous paper cited before.

TABLE V.
Effect of diphenylguanidine.

Added Amount of diphenylguanidine. (%)	Oxidation time. (hours)	Observed iodine value. (corrected)	Logarithm of iodine value.	$k = \frac{1}{t-b} \ln \frac{a}{a-x}$
0.10%	0	85.50	1.93197	$(b = 16.5 \text{ hours})$ 0.0238 0.0244 0.0246 0.0260 0.0242 0.0258 0.0258 mean: 0.0247
	12.50	85.51	1.93202	
	16.50	84.35	1.92609	
	18.00	82.73	1.91766	
	20.00	78.72	1.89611	
	22.00	74.87	1.87429	
	25.00	68.77	1.83742	
	30.00	61.81	1.79106	
	35.00	53.15	1.72552	
	40.00	46.74	1.66973	
0.25%	0	85.48	1.93186	$(b = 34.5 \text{ hours})$ 0.0238 0.0212 0.0234 0.0224 0.0236 mean: 0.0229
	22.00	84.96	1.92921	
	34.00	83.73	1.92290	
	38.00	78.86	1.89686	
	41.00	74.46	1.87195	
	44.00	68.23	1.83643	
	49.00	61.95	1.79201	
	55.04	52.74	1.72217	

(c) Effect of Diphenylguanidine.

The results of investigation on the antioxygenic effect of 0.10% and 0.25% diphenylguanidine on the oxidation of Olive Oil C are given in Table 5 and Fig. 5. In this figure, the oxidation curve for the oil without antioxygen is also replotted (the left-most straight line). Although the inhibitory power of diphenylguanidine is stronger than that of diphenylamine and α -naphthylamine, it is much inferior to that of hydroquinone and unsym. diphenylhydrazine. As seen from Fig. 5, the oxidation curve for this antioxygen shows appreciably an autocatalytic

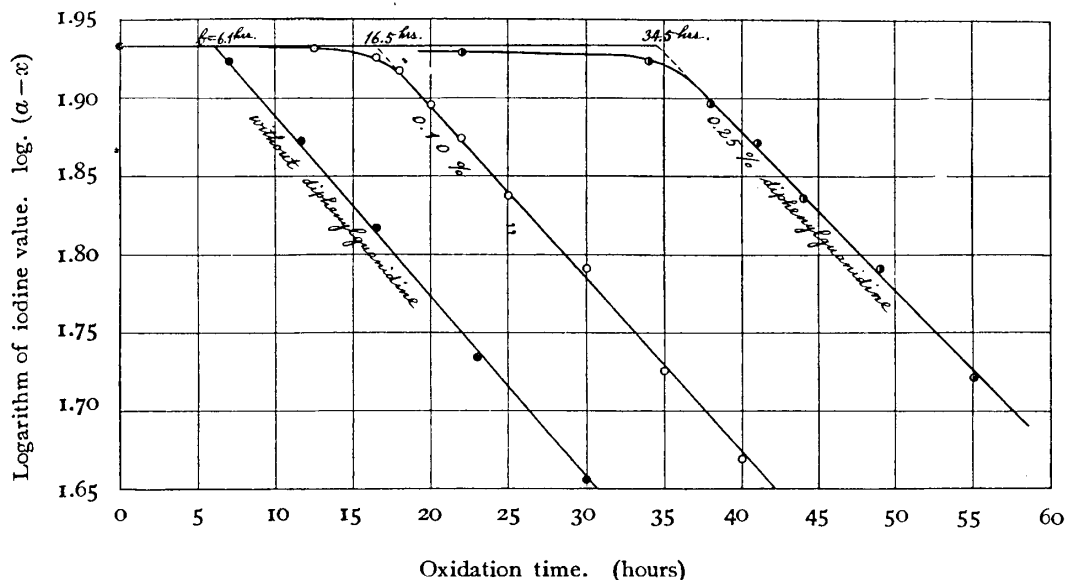


Fig. 5.

nature⁽¹⁾ resembling the curve for diphenylamine rather than that for hydroquinone. Diphenylguanidine, like diphenylamine, does not inhibit the oxidation so completely for a certain length of time as hydroquinone and diphenylhydrazine do: in the other words, the period of incubation is not apparently altered by the antioxygen, although the initial rate of oxidation is exceedingly lowered by it. The rate of oxidation which is extremely slow at the beginning increases gradually with time of oxidation till a point of time t_n after which the reaction proceeds completely unimolecularly.

All the values of velocity coefficient calculated by Equation (I) for different times of oxidation greater than t_n are found always consistent as shown in Table 5. (The value of b which must be introduced in the calculation has been decided in the same way as before. The value of velocity coefficient which the oil containing diphenylguanidine

(1) It should be noted that the autocatalytic effect is, in this case, obviously due to the gradual removal or destruction of the antioxygen contained in the oil, although the cause of autocatalytic effect is usually considered to consist in the formation and accumulation of positive catalyst in the course of reaction.

undergoes after t_n is slightly smaller than that for the oil without anti-oxygen. The difference between them is found to increase with the added amount of diphenylguanidine. The result, being quite analogous to that for the oil containing diphenylamine, can be explained similarly as in that case by assuming that there remains in the oil another weak antioxidant which may have been gradually formed from diphenylguanidine in the course of oxidation.

Summary.

(1) The antioxidant effects of diphenylamine, diphenylguanidine and hydroquinone on the oxidation of olive oil have been studied.

(2) Diphenylamine, acting as a good antioxidant, lowers the initial rate of oxidation in a remarkable degree, although it does not inhibit the oxidation so completely as unsym. diphenylhydrazine does. The oxidation of the olive oil containing diphenylamine starts initially with a very small but sensible rate just after the same length of time as the period of incubation for the oil containing no antioxidant. After the antioxidant has been completely lost from the oil in the course of oxidation, the reaction then proceeds unimolecularly as for the pure olive oil. The value of velocity coefficient of the unimolecular reaction is, however, found slightly smaller than that for the pure olive oil. This seems to be due to the effect of a certain weak antioxidant which may be gradually formed from diphenylamine in the course of oxidation either through its oxidation, thermal decomposition or through some reaction with certain oxidation products of oil.

(3) Hydroquinone acts as a very strong inhibitor, prolonging the induction period in a remarkable degree as unsym. diphenylhydrazine does. The length of the period thus prolonged depends upon the added amount of hydroquinone, and the former increases almost in direct proportion to the latter. After the period the oxidation proceeds as for the oil containing no antioxidant.

(4) The antioxygenic power of diphenylguanidine is superior to that of diphenylamine but inferior to that of hydroquinone. The oxidation curve for the oil containing diphenylguanidine resembles the curve for the oil with diphenylamine rather than that for the oil with hydroquinone.

(5) The results of experiments can be well explained by the theory of mechanism of inhibition developed in the previous paper. On the basis of the theory an equation has been deduced in order to calculate the form of the velocity curve for the oxidation of the oil containing diphenylamine and it has been shown that the equation agrees well with the actual results of experiments.

In conclusion the author wishes to express his cordial thanks to Prof. M. Katayama for his valuable advices during the work and also to Mr. Gengo Nara for his earnest assistance.

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