No. 74.

Action of Antioxygens in the Oxidation of Unsaturated Fatty Oils.

III. The Relation between the Induction Period in Oxidation and the Catalytic Effect of Driers.

By

Bunnosuke YAMAGUCHI, *Rigakusi*,

Member of the Institute.

Abstract.

As a continuation to the previous communications, this paper describes the results of investigation on the occurrence of induction period and the action of driers in the oxidation of unsaturated fatty oil.

Introduction.

In the previous papers[1] the author has ascertained that the oxidation of unsaturated fatty oils such as olive oil and castor oil does not apparently start during a certain length of induction period, but the reaction, when once started, proceeds unimolecularly with an appreciable rate. It has been also ascertained that the effect of antioxygens is mainly to prolong the induction period. The present study has been carried out to investigate whether the action of agencies known as driers is only limited to the shortening of induction period or they have also effects on the velocity of reaction which the oil undergoes

---

(1) Report of the Aeronautical Research Institute, Tokyo Imperial University, No. 61 (Vol. V, 196, 1930); No. 65 (Vol. V, 287, 1930).

B. Yamaguchi.

after induction period. As regards the effect of driers on the oxidation of linceed oil, a number of studies has been carried out since the investigation of Cloez.[1] Roger and Taylor[2] have arrived from their experimental results at the conception that driers act in the oxidation of oil as catalysts for the formation of autocatalytic substance formed during the reaction. The present author has a different opinion on this point, since we have, as will be shown later, some evidence that the oxidation induction period of unsaturated fatty oils is not the time needed for the formation or accumulation of the positive catalysts which have been considered by these investigators to be responsible for the autocatalytic nature of the oxidation, but it is due to the action of the natural antioxygen which the oil contains.

The method of investigation is quite similar to that used in the previous experiments. The rate of oxidation of olive oil at 100°C. in the presence and in the absence of catalyst has been determined by the measurement of the decrease in iodine value. Three kinds of olive oil (D,E and F) purified as before have been used. The catalysts used are copper oleate, lead oleate, manganese linoleate and stearic acid. These are soluble in olive oil within the extent of amount in which they have been added, and contain, according to analysis, the following percentage of metal.

Copper oleate	9·91% Cu
Lead oleate	25·95% Pb
Manganese linoleate	8·40% Mn.

Results of Experiments.

(a)   Effect of copper oleate.

Table I and Curves II, III and IV in Figure I show the results of investigation on the effect of 0·1, 0·3 and 0·5% copper oleate on the

(1)   Cloez: Compt. rend., **61**, 236, 321, 981 (1865). The résumé of the literature on the investigations up to 1926 has been given by Roger and Taylor in their paper (Jour. Phys. Chem., **30**, 1334, 1926).

(2)   Jour. Phys. Chem., **30**, 1334 (1926).

TABLE I.

The effect of copper oleate.

Amount of Cu-oleate. (%)	Oxidation time (hours)	Observed iodine value (corrected)*	Logarithm of iodine value.	$k=\dfrac{1}{t-b}\ln\dfrac{a}{a-x}$	Amount of CO_2 evolved.**
				($b=$1·4 hr·)	
	0	85·96	1·93430		0
	2·4	83·86	1·92357	0·0247	—
	4·0	80·58	1·90623	0·0249	16·03
	7·0	74·22	1·87053	0·0262	44·30
0	10·0	69·18	1·83996	0·0252	82·44
	15·0	60·97	1·78515	0·0253	160·55
	20·0	54·11	1·73329	0·0245	247·07
	25·0	48·28	1·68375	0·0245	348·20
	30·0	42·37	1·62707	0·0247	456·98
				mean value 0·0251	
				($b=$0)	
	0	86·15	1·93526		0
	1·0	84·54	1·92706	0·0189	3·62
	3·0	81·04	1·90870	0·0204	19·56
	6·0	76·61	1·88426	0·0196	57·71
0·1	10·0	70·28	1·84683	0·0204	125·44
	15·0	64·02	1·80630	0·0198	231·97
	20·0	57·98	1·76331	0·0198	323·85
	25·0	53·40	1·72754	0·0191	425·60
	30·0	48·21	1·68310	0·0194	528·30
				mean value 0·0197	
				($b=$0)	
	0	85·58	1·93237		0
	0·5	84·81	1·92844	0·0181	—
	3·0	81·24	1·90977	0·0174	22·27
	6·0	77·11	1·88711	0·0174	63·13
0·3	10·0	71·76	1·85589	0·0176	136·80
	15·0	65·76	1·81795	0·0176	233·87
	20·0	60·22	1·77974	0·0176	335·28
	25·0	55·48	1·74415	0·0173	440·60
	30·0	50·93	1·70701	0·0173	547·92
				mean value 0·0175	
				($b=$0)	
	0	86·02	1·93461		
	0·5	85·51	1·93220	(0·0111)	
	3·25	81·40	1·91062	0·0170	
	5·5	78·33	1·89390	0·0170	
0·5	10·0	72·50	1·86034	0·0171	
	15·0	66·54	1·82308	0·0171	
	20·0	61·37	1·78797	0·0169	
	25·0	56·42	1·75146	0·0169	
	30·0	51·90	1·71517	0·0168	
				mean value 0·0170	

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

** The amount of CO_2 is expressed by the number of c·c. of $N/10$ alkali solution needed to neutralize this gas.
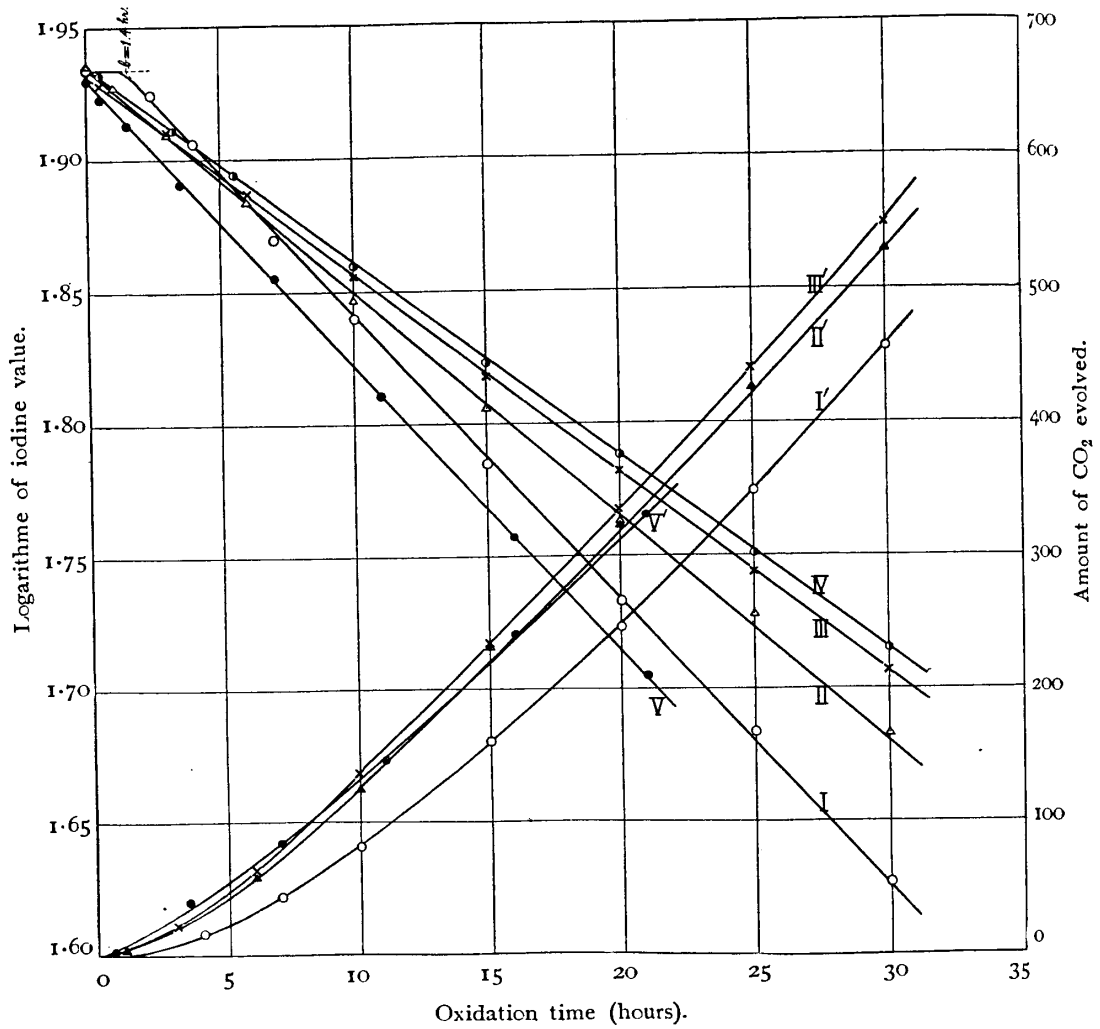
Fig. 1.

Curve I : Iodine value curve for pure olive oil.
Curve II : Iodine value curve for olive oil containing 0·1% Cu-oleate.
Curve III : Iodine value curve for olive oil containing 0·3% Cu-oleate.
Curve IV : Iodine value curve for olive oil containing 0·5% Cu-oleate.
Curve V : Iodine value curve for olive oil containing 0·3% Pb-oleate.
Curve I′ : Carbon dioxide curve for pure olive oil.
Curve II′ : Carbon dioxide curve for olive oil containing 0·1% Cu-oleate.
Curve III′: Carbon dioxide curve for olive oil containing 0·3% Cu-oleate.
Curve V′ : Carbon dioxide curve for olive oil containing 0·3% Pb-oleate.

oxidation of Olive Oil D. In agreement with the previous observation, the oxidation of the oil without catalyst apparently starts with a uni-molecular rate after an induction period of 1·4 hour as shown by Curve I. The copper catalyst acts to shorten the induction period in a re-markable degree. From Curves II, III and IV it is seen that the induction period is eliminated in all cases independently of the amount of catalyst and accordingly the decrease in iodine value is always found to proceed from the biginning with a unimolecular rate. Therefore, if we put $b = 0$ in Equation (I) given in the previous paper and calculate the values of velocity coefficient for different times of oxidation, we have always concordant constants as shown in Table 1. The following table, in which the mean values of the coefficients thus calculated for the oils containing different amounts of copper oleate are compared, shows that the rate of change in iodine value resulting from oxidation decreases with the increase in amount of copper oleate.

Added amount of copper oleate (%).	Velocity coefficient.
0	0·0251
0·1	0·0197
0·3	0·0175
0·5	0·0170

This is evident also from Figure 1, since the slope of iodine number curve decreases with the increase of copper oleate. The comparison of the iodine value of oil without catalyst with the values of oil with copper oleate after more than 5 hours' oxidation indicates that the former is always smaller than the latter. From this point of view it may be said that the copper catalyst rather acts as a negative catalyst. The observations on the evolution of carbon dioxide resulting from oxidation show an interesting contrast with the above results. The rate of evolution for the oils containing 0, 0·1 and 0·3% copper oleate are illustrated by Curves I', II' and III' in Figure 1. In this figure the

　　　　　　　　B. Yamaguchi.

ordinate denotes the number of c.c. of $\dfrac{N}{10}$ NaOH solution needed to neutralize the evolved carbon dioxide (see the last column in Table 1). From these curves it is seen that the rate of evolution of carbon dioxide after induction period increases, on the contrary to the change in iodine value, with the increase in amount of copper oleate.

TABLE 2.

Oxidation time. (hours)	Observed iodine value. (corrected)	Logarithm of iodine value.	Amount of CO_2 evolved.**
0	86·28	1·93591	0
2·0	84·00	1·92427	5·24
4·0	79·83	1·90219	18·11
7·0	74·00	1·86925	45·26
10·0	68·75 †	1·83272 †	82·21
	68·86	1·83797	
15·0	63·25	1·80107	210·76
20·0	57·93	1·76290	318·71
25·0	53·60	1·72917	427·07
30·0	49·11	1·69118	529·95

(86·28 to 68·75 bracketed: Before the addition of Cu-oleate. 68·86 to 49·11 bracketed: After the addition of Cu-oleate.)

The figure with † represents the iodine value immediately after the addition of 0·3% copper oleate.

** The amount of CO_2 is expressed by the number of c.c. of $N/10$ alkali solution needed to neutralize the gas.

Table 2 and Figure 2 show the effect of adding copper oleate after the oxidation has started. After 10 hours' oxidation of Olive Oil D, 0·3% copper oleate was added to the oil and the oxidation continued. In Figure 2, for comparison, the oxidation curves for the oils containing no catalyst and containing initially 0·3% copper oleate are also replotted (shown by broken lines). This figure indicates that the rate of change in iodine value is appreciably decreased by addition of copper oleate, and the curve representing this change is found after the addition to become almost parallel to that for the oil to which the same amount of copper oleate has been added before oxidation. The
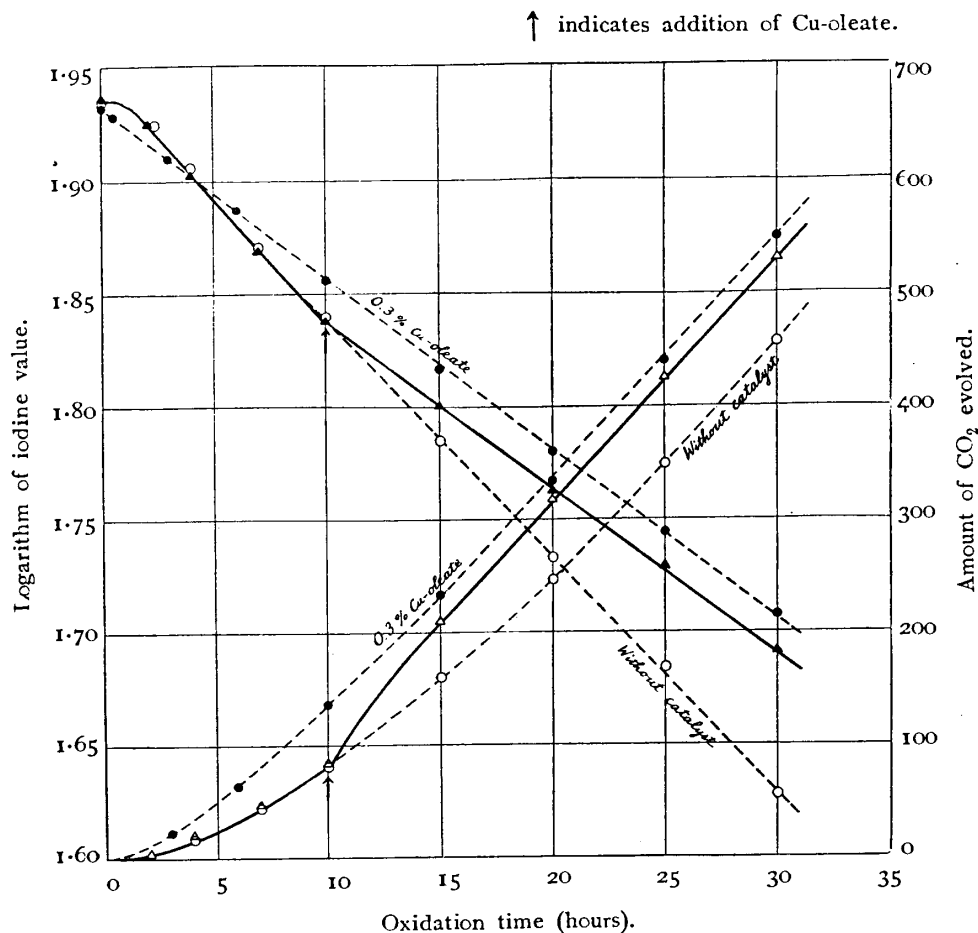
↑ indicates addition of Cu-oleate.

Fig. 2.

evolution of carbon dioxide is rapidly acceralated by the addition of the catalyst and after a few hours' continuation of oxidation the rate of evolution becomes comparable with that of the oil to which the same amount of the copper catalyst has been added before oxidation. A quite similar result has been attained also for the Olive Oil E. (Table 3 and Figure 3). The induction period of this oil, as compared with that of Olive Oil D, is much longer and has been found to be more than 19 hours. Nevertheless this period is almost completely eliminated by the addition of 0·3% copper oleate and the oxidation

TABLE 3.

	Oxidation time. (hours)	Observed iodine value. (corrected)	Logarithm of iodine value.	$k=\dfrac{1}{t-b}\ln\dfrac{a}{a-x}$	Amount of CO_2 evolved.*
Without catalyst.				$(b = 19 \cdot 3$ hrs.$)$	
	0	87·16	1·94032	—	0
	19·7	85·54	1·93218	(0·0469)	4·40
	21·0	83·75	1·92297	0·0235	8·74
	23·0	79·58	1·90080	0·0246	19·71
	27·0	70·98	1·85112	0·0267	58·23
	31·0	63·88	1·80537	0·0267	109·07
	35·0	57·85	1·76229	0·0261	167·09
	39·0	52·14	1·71713	0·0262	235·25
	43·0	46·61	1·66845	0·0264	303·47
	48·0	41·48	1·61782	0·0259	394·09
				mean 0·0258	
0·3% Cu-oleate.				$(b = 0)$	
	0	87·11	1·94007	—	0
	1·3	84·69	1·92870	0·0201	2·75
	3·0	81·18	1·91202	0·0215	21·03
	6·0	75·92	1·88516	0·0211	63·09
	10·0	70·33	1·85425	0·0198	130·90
	14·0	65·04	1·82191	0·0194	205·28
	18·0	59·10	1·78189	0·0202	292·05
	22·0	55·33	1·75449	0·0194	372·91
	26·0	50·94	1·71959	0·0195	451·40
	30·0	46·82	1·68392	0·0197	532·89
				mean 0·0201	

* The amount of CO_2 is expressed by the number of c.c. of $\dfrac{N}{10}$ alkali solution needed to neutralize the gas.

starts from the beginning with a unimolecular rate.

In order to explain these effects of copper oleate, we must know why the phenomenon of induction period occurs in the oxidation of oil. It has been already stated in the previous paper[1] that one possible explanation of it is to assume that oil contains some natural antioxygen
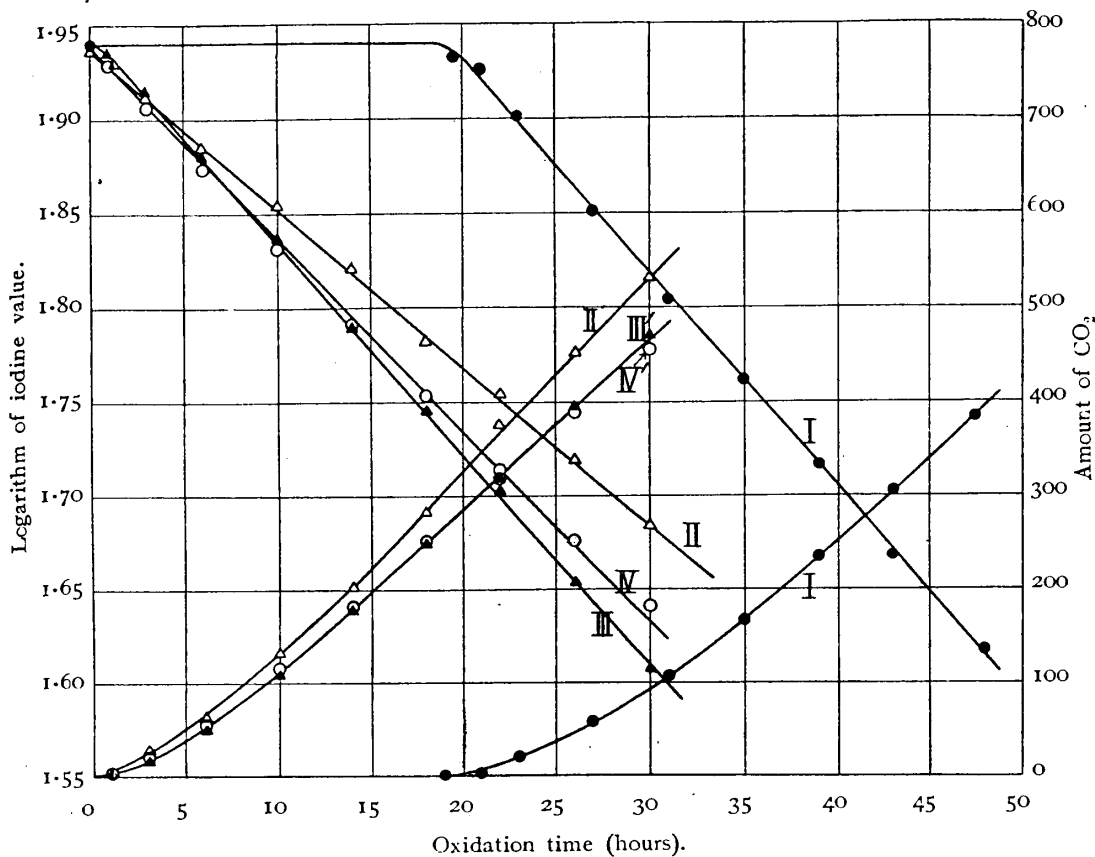
(1)   loc. cit.

Fig. 3.

Curve	I :	Iodine value curve for pure olive oil.
Curve	II :	Iodine value curve for olive oil containing 0·3% Cu-oleate.
Curve	III :	Iodine value curve for olive oil containing 0·3% Pb-oleate.
Curve	IV :	Iodine value curve for olive oil containing 0·3% Mn-linoleate.
Curve	I′ :	Carbon dioxide curve for pure olive oil.
Curve	II′ :	Carbon dioxide curve for olive oil containing 0·3% Cu-oleate.
Curve	III′ :	Carbon dioxide curve for olive oil containing 0·3% Pb-oleate.
Curve	IV′ :	Carbon dioxide curve for olive oil containing 0·3% Mn-linoleate.

which has not been removed by commercial purification. Very recently Mattill and Crawford[1] have observed that the susceptibility of corn oil to spontaneous oxidation increases with the decrease in amount of sterols which the oil contains. The inhibitory effect of sterols has been also ascertained by the present author in the following experiment.

(1) Ind. Eng. Chem., **22**, 341 (1930).

One sample of Olive Oil E was vigorously shaken at 60–70°C. with an excess of 1% alcoholic solution of digitonin so long that sterols contained in the oil was completely precipitated as digitonide. After adding a suitable amount of ether, the digitonide was then removed by filtration. From the filtrate thus obtained ether and alcohol were completely removed by distillation in vacuum, and the sample practically free from sterols was obtained. Parallel with this, another sample of the same oil was treated quite similarly but by alcohol instead of alcoholic solution of digitonin. The content of sterols of the oil was not altered in this case. These two samples with and without sterols were oxidized at 100°C to compare their induction periods. The results given in Table 4 and Figure 4 show that the induction period of the sterol-free oil is about 3 hours shorter than that of the other oil, indicating that the length of the period is decreased by the removal of sterols. This result together with the experiment of Mattill and Crawford lead us to believe that the occurrence of induction period in the oxidation of oil is at least partly due to the antioxygenic effect of sterols which the oil contains. Parallel with this study, the author has carried

TABLE 4.

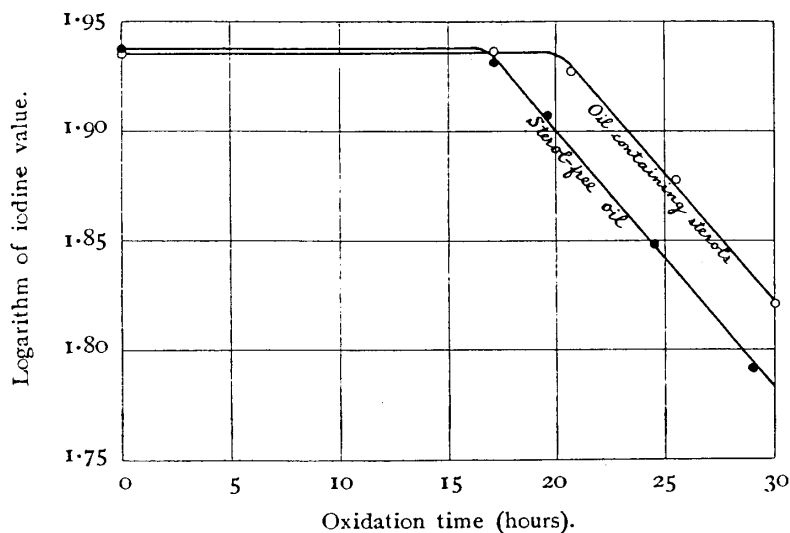|	Oxidation time. (hours)	Iodine value. (corrected)	Logarithm of iodine value.
Oxidation of the oil containing no sterol.	0	86·47	1·93687
	17·1	85·22	1·93054
	19·6	80·70	1·90686
	24·5	70·46	1·84792
	29·0	61·89	1·79161
Oxidation of oil containing sterols.	0	86·10	1·93500
	17·1	86·39	1·93645
	20·7	84·64	1·92756
	25·5	75·56	1·87826
	30·0	66.18	1.82075

Fig. 4.

out an investigation on the oxidation of triolein[1] at 100°C. and ascertained that the induction period of pure triolein is neglegibly short if it exists at all. It may be therefore concluded that the induction period, which the sterol-free olive oil has still possessed, is probably due to the effect of " unsaponifiable matters[2] " other than sterols. The fact that the induction period of Olive Oil E is much longer than that of Olive Oil D may, therefore, indicates that the former oil contains much amount of antioxygenic unsaponifiable matters than the latter oil. Indeed, the oxidation induction period of unsaturated fatty oil decreases in general with the progress of commercial purification.

The effect of copper oleate on the induction period can now be explained by assuming that the catalyst suppresses the inhibiting action of unsaponifiable matters. The fact that the copper oleate decreases the unimolecular rate of change in iodine value after induction period and

(1) The detailed results of this investigation are being published in the succeeding paper (Report of this institute No. 75).

(2) The author has used the term " unsaponifiable matters " for all the substances other than common glycerider contained in fatty oils. Phosphatides are also included in the " unsaponifiable matters," although they are saponifiable. The study on the effect of unsaponifiable matters on the oxidation of oil is being continued.

at the same time increases the rate of evolution of carbon dioxide—an interesting fact which could not be found if the rate of oxidation be measured either by the change-in-weight method or by the oxygen-absorption method—indicates that the copper catalyst, besides the effect of shortening induction period, has further powers to break the chains of the oxygen-addition reaction of oil and to accelerate the decomposition of its oxidation products. It is well known that copper acts as a good accelerator in the decomposition of the substance such as fatty acids.[1]

(b) Effect of lead oleate.

Table 5 and Table 6 respectively show the results of investigation on the effect of 0.3% lead oleate upon the oxidation of Olive Oil D and E. The results are illustrated also by Curve V in Figure 1 and* Curve III in Figure 3. This catalyst suppresses efficiently the antioxygenic

TABLE 5.

The oxidation of Olive Oil D with 0.3% Pb-oleate.

Oxidation time. (hours)	Observed iodine value. (corrected)	Logarithm of iodine value.	$k=\dfrac{1}{t}\ln\dfrac{a}{a-x}$	Amount of CO_2 evolved.*
0	85.15	1.93019		0
0.5	83.66	1.92253	(0.0353)	3.0
1.5	81.82	1.91285	0.0266	—
3.5	77.83	1.89155	0.0257	40.1
7.0	71.74	1.85578	0.0245	83.8
11.0	64.71	1.81099	0.0250	146.6
16.0	57.14	1.75690	0.0249	240.5
21.0	50.65	1.70459	0.0247	331.0
			mean 0.0252	

* The amount of CO_2 is expressed by the number of c.c. of $\dfrac{N}{10}$ alkali solution needed to neutralize it.

(1) Sabatier: La catalyse en chimie organique. P. 328 (1920).

<p style="text-align:center;">TABLE 6.</p>

<p style="text-align:center;">The oxidation of Olive Oil E with 0·3% Pb-oleate.</p>

Oxidation time. (hours)	Observed iodine value. (corrected)	Logarithm of iodine value.	$k = \dfrac{1}{t-0\cdot7}\ln\dfrac{a}{a-x}$	Amount of CO_2 evolved.*
0	87·31	1·94106	—	0
1·0	86·10	1·93500	(0·0465)	2·38
3·0	82·29	1·91533	0·0258	17·07
6·0	76·19	1·88187	0·0257	51·92
10·0	68·68	1·83684	0·0258	111·43
14·0	61·68	1·79012	0·0261	180·11
18·0	55·67	1·74563	0·0260	250·03
22·0	50·42	1·70259	0·0258	323·42
26·0	45·07	1·65390	0·0261	395·87
30·0	40·47	1·60715	0·0262	469·98
			mean 0·0259	

* The amount of CO_2 is expressed by the number of c.c. of $\dfrac{N}{10}$ alkali solution needed to neutralize it.

action of unsaponifiable matters. It eliminates almost completely the induction period of Olive Oil D and shortens that of Olive Oil E to less than one hour. The unimolecular rate of change in iodine value after induction period is, however, not altered by the presence of this catalyst as indicated by the parallelism of Curves I and V in Figure 1 and that of Curves I and III in Figure 3. The figures indicate furthur that the rate of evolution of carbon dioxide after induction period is practically not altered by the catalyst, although the starting of the gas evolution is exceedingly hastened by it. Lead oleate, therefore, acts neither as an inhibitor for the oxygen-addition reaction of oil, nor as an accelerator for the decomposition of its oxidation products, although the catalyst suppresses the inhibitory action of unsaponifiable matters which the oil contains.

(c) Effect of manganese linoleate.

The result of investigation on the effect of 0·3% manganese linoleate upon the oxidation of Olive Oil E is shown by Table 7 and Curve IV in

TABLE 7.

The effect of manganese linoleate.

Oxidation time. (hours)	Observed iodine value. (corrected)	Logarithm of iodine value.	$l.=\dfrac{1}{t}\ln\dfrac{a}{a-x}$	Amount of CO_2 evolved.*
0	87·16	1·94032	—	—
1·0	84·89	1·92884	0·0264	3·57
3·0	80·46	1·90558	0·0267	19·78
6·0	74·64	1·87299	0·0258	55·17
10·0	67·73	1·83080	0·0252	116·30
14·0	61·59	1·78953	0·0248	184·11
18·0	56·67	1·75332	0·0239	250·88
22·0	52·17	1·71742	0·0233	319·93
26·0	47·48	1·67651	0·0234	389·66
30·0	43·85	1·64199	0·0229	456·03
			mean 0·0247	

* The amount of CO_2 is expressed by the number of c.c. of $\dfrac{N}{10}$ alkali solution needed to neutralize it.

Figure 3. Similarly as copper oleate and lead oleate, this manganese catalyst suppresses efficiently the antioxygenic action of unsaponifiable matters which the oil contains, eliminating its induction period almost completely. Since Figure 3 shows that the slope of Curve IV is slightly slower than that of Curve I, manganese linoleate seems to act, like copper oleate, as an antioxygen for the oxygen-addition reaction of oil, although its action is much weaker than that of copper oleate. The approximate coincidence of Curve III′ and IV′ in Figure 3, by which the respective rates of evolution of carbon dioxide for the oils containing 0·3% lead oleate and 0·3% manganese linoleate are expressed, indicates that the manganese catalyst, similarly as lead oleate, does not practically accelerate the rate of decomposition of oxidation products of oil.

(d) ·Effect of stearic acid.

The effect of addition of stearic acid on the oxidation of Olive Oil F has been studied in the hope that some light might be cast on the action of organic acids formed during the oxidation of oil. Table 8 and Figure 5 show the results of the oxidation of oil with 1 and 2% stearic

TABLE 8.

The effect of stearic acid.

| Amount of stearic acid. (%)	Oxidation time. (hours)	Observed iodine value. (corrected)	Logarithm of iodine value.	$k=\dfrac{1}{t-b}\ln\dfrac{a}{a-x}$
0	0	86.34	1.93622	(b=3.2 hr.) —
	4.0	84.64	1.92757	0.0249
	7.0	78.61	1.89549	0.0246
	12.0	68.71	1.83700	0.0260
	17.0	60.81	1.78394	0.0254
	22.0	53.08	1.72484	0.0259
	27.0	47.44	1.67611	0.0252
				mean 0.0253
1	0	85.60	1.93246	(b=1.6 hr.) —
	2.0	84.67	1.92773	0.0272
	5.0	79.19	1.89866	0.0229
	10.0	69.54	1.84225	0.0247
	15.0	60.04	1.77844	0.0265
	20.0	52.75	1.72222	0.0263
	25.0	47.16	1.67362	0.0255
				mean 0.0255
2	0	84.50	1.92685	(b=1.0 hr.)
	2.0	82.43	1.91611	0.0247
	5.0	76.78	1.88524	0.0240
	10.0	66.84	1.82506	0.0260
	14.0	59.87	1.77722	0.0265
	20.0	51.00	1.70758	0.0266
	23.0	47.20	1.67391	0.0243
				mean 0.0254
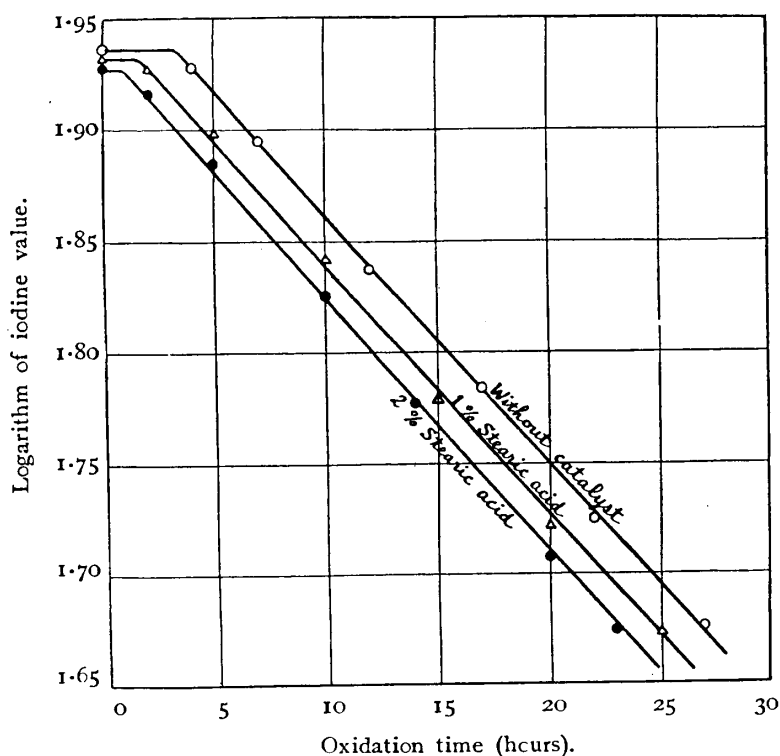
Fig. 5.

acid and without catalyst. Similarly as lead oleate, stearic acid shortens the induction period, suppressing the antioxygenic action of un-saponifiable matters contained in the oil, and does not alter the uni-molecular rate of change in iodine value after induction period. The effect of stearic acid is, however, much weaker than that of lead oleate. If the assumption is allowed that the action of organic acids formed during the oxidation of oil is similar to that of stearic acid, it may be said from the above result that such acids have no direct effect on the rate of oxygen-addition reaction of oil, although they suppress the in-hibitory action of unsaponifiable matters which the oil contains.

Summary.

(1) The occurrence of induction period in the oxidation of unsaturated fatty oil is due to the antioxygenic action of unsaponifiable matters including sterols which the oil contains.

(2) Copper oleate, lead oleate and manganese linoleate shortens efficiently the induction period of olive oil, suppressing the antioxygenic action of unsaponifiable matters.

(3) Copper oleate decreases the unimolecular rate of change in iodine value after induction period, thus acting in this respect as an antioxygen. Manganese linoleate seems to have a similar effect, although its antioxygenic power is very weak. Lead oleate does not possess such a power, having no effect on the rate of oxygen-addition reaction of oil.

(4) Copper oleate, acting further as an accelerator for the decomposition of oxidation products of oil, increases the rate of evolution of carbon dioxide. The catalyst, therefore, have at the same time three different effects: (i) the suppression of the antioxygenic action of unsaponifiable matters contained in oil, (ii) the retardation of the oxygen-addition reaction of oil and (iii) the acceleration of decomposition of oxidation products of oil.

(5) Stearic acid acts to shorten the oxidation induction period of oil in an appreciable degree but has no direct effect on the oxygen-addition reaction of oil.

(August, 1931)