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THE EFFECT OF METALLIC NAPTHENATES ON THE OXIDATION OF LINOLEIC ACID

BY

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A

THESIS

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Approved by- William J. James

Assistant Professor of Chemistry

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INTRODUCTION

Certain vegetable oils, known as "drying oils" polymerize to form solid films. Linseed oil, a typical drying oil, is a mixed glyceride of oleic acid ($HOOC(CH_2)_7CH{=}CH(CH_2)_7CH_3$), linoleic acid ($HOOC(CH_2)_7CH{=}CH{-}CH_2{-}CH{=}CH(CH_2)_4CH_3$), and linolenic acid ($HOOC(CH_2)_7CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_2{-}CH{=}CHCH_2CH_3$). The polymerization reaction by which these oils form films is known as drying.

It has been known for many years that certain metallic soaps catalyse the drying of oils. A great deal of information is available concerning the use of these soaps, but there is little knowledge of the actual manner in which the soaps catalyse drying. As the drying is known to be an autoxidation reaction, it is generally believed that the soaps must affect the oxidation of the oil in some way. The work described in this thesis was undertaken to gain some knowledge of the mechanism of the catalysis, and to correlate the effect of the soaps on the drying reaction with the electronic structure of the metals involved.

A review of the literature concerning drying oils and driers (the common term used to describe the metallic soaps mentioned above) shows many inconsistencies in data concerning the effect of driers on the autoxidation of oils. Much of this inconsistency may be attributed to the difficulties encountered in studying the reaction. Some of these difficulties are:

1. The composition of drying oils from different sources may vary. Therefore, the oils may behave differently during oxidation.
2. The composition, purity, and quantities used of the soaps influence their effect on the reaction.
3. The conditions under which the reaction is carried out affect the course of the reaction.

For these reasons, it is difficult to correlate data from one worker with that from another. In addition, much of the published work in this field has been incomplete. In many cases only a few soaps were studied. In others the products of the reaction were only partially investigated.

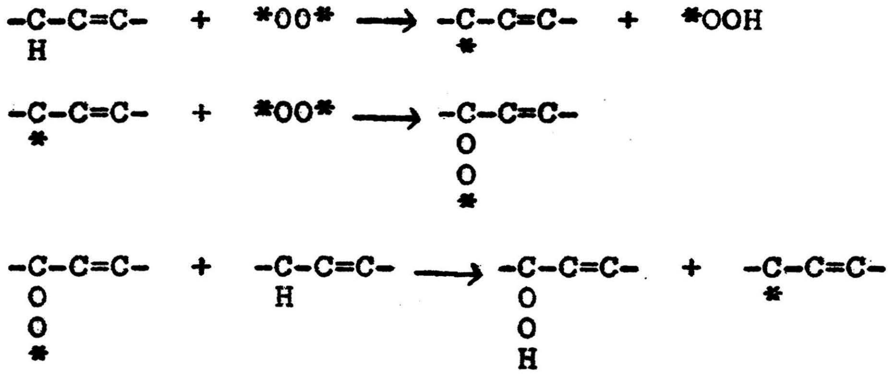
The aim of this work was to avoid as many of the above sources of error as possible. The oxidation was performed on linoleic acid instead of a natural drying oil. Linoleic acid was oxidized in the presence of several metallic soaps. An apparatus was assembled which permitted temperature, oxygen pressure and oxygen flow to be held constant during the oxidation. Soaps of a uniform composition were used. These soaps were of the metals of the first transition series with the exception of scandium and titanium. Thus, almost all the possible electron structures of that series were included. The course of the reaction was followed by collecting and analysing samples of the product at frequent intervals. Additional analyses were run on the final product of oxidation.

In addition, the effect of the soaps on the drying time of refined linseed oil was measured. By comparing the results of these measurements and the results of chemical analysis of oxidation products of linoleic acid, it was possible to suggest a mechanism for the drying. Finally, by comparing the effect of the soaps on drying time and on the course of the reaction, it was possible to suggest a mechanism for the catalysis.

REVIEW OF LITERATURE

The following changes are observed in films of drying oils (1). The film initially gains in weight, then loses some of this weight, but dries with a net increase in weight. This gain is due to oxygen absorbed from the atmosphere above the film. Volatile products are also given off during the drying. Among these products are carbon dioxide, water, formic acid, acetic acid, and hydrogen peroxide. The iodine number decreases, but not in proportion to the amount of oxygen absorbed. The peroxide value increases to a maximum, then decreases, but does not become zero. There is an increase in the amount of conjugated double bonds in the film. Viscosity does not begin to increase until peroxide decomposition begins. Non-volatile materials such as short chain acids, aldehydes, ketones and alcohols are found in the dry film.

The first step in this process is the addition of oxygen to the oil molecule. There have been many investigations of this reaction, but the actual mechanism is still somewhat uncertain. Farmer (2) suggested that the oxygen adds at a carbon adjacent to a double bond and initiates a free radical reaction which results in the formation of other hydroperoxides. In these reactions and others which will be shown, H will be included in structural formulas only when it is entering the reaction. The symbol * will be used to represent a free radical end. The symbol R will be used to represent an unoxidized oil or acid molecule.

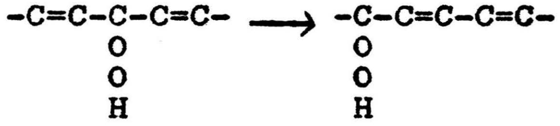


$$\underset{H}{-C}-C=C- \;+\; {*}OO{*} \longrightarrow \underset{*}{-C}-C=C- \;+\; {*}OOH$$

$$\underset{*}{-C}-C=C- \;+\; {*}OO{*} \longrightarrow \underset{\substack{O\\O\\*}}{-C}-C=C-$$

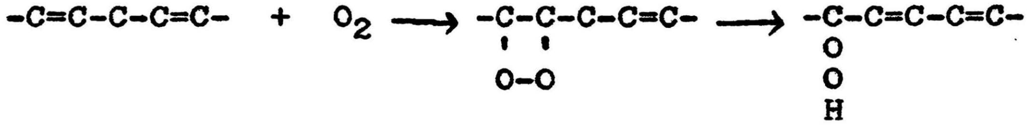
$$\underset{\substack{O\\O\\*}}{-C}-C=C- \;+\; \underset{H}{-C}-C=C- \longrightarrow \underset{\substack{O\\O\\H}}{-C}-C=C- \;+\; \underset{*}{-C}-C=C-$$

Bolland and Gee (3) share this view. The increase in conjugation during the oxidation may be caused by a rearrangement of the peroxide.



$$-C=C-\underset{\substack{O\\O\\H}}{C}-C=C- \longrightarrow \underset{\substack{O\\O\\H}}{-C}-C=C-C=C-$$

Gunstone and Hilditch (4) later proposed that the oxygen added at the double bond and Farmer (5) accepted this mechanism.



$$-C=C-C-C=C- \;+\; O_2 \longrightarrow \underset{\substack{|\quad|\\O-O}}{-C-C}-C-C=C- \longrightarrow \underset{\substack{O\\O\\H}}{-C}-C=C-C=C-$$

Most of the workers in the field of drying oils accept this mechanism, although Allen and Kummerow (6) indicate that both reactions take place to some extent. In either case the result is a hydroperoxide adjacent to a conjugated double bond.

Almost all suggested mechanisms for drying involve the decomposition of this peroxide. Lundberg (7) has offered the following possible mechanism.

$ROOH \longrightarrow ROO{*} \;+\; {*}H$

$ROO{*} \;+\; RH \longrightarrow ROOH \;+\; R{*}$

$$R^* + R^* \longrightarrow R{-}R$$

$$R^* + ROO^* \longrightarrow ROOR$$

A similar mechanism has been suggested by Williamson (8).

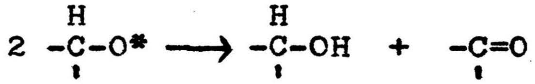
$$ROOH \longrightarrow RO^* + {}^*OH$$

$$RO^* + RH \longrightarrow ROH + R^*$$

$${}^*OH + RH \longrightarrow H_2O + R^*$$

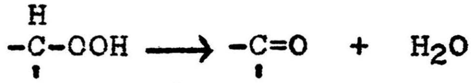
$$R^* + R^* \longrightarrow R{-}R$$

There also may be side reactions to form ketones.



$$2\ {-}\overset{H}{\underset{|}{C}}{-}O^* \longrightarrow {-}\overset{H}{\underset{|}{C}}{-}OH + {-}\underset{|}{C}{=}O$$

or



$${-}\overset{H}{\underset{|}{C}}{-}OOH \longrightarrow {-}\underset{|}{C}{=}O + H_2O$$

O'Neill (9) has suggested a mechanism similar to that of Williamson and states that the conjugated double bonds of the molecule are also attacked by excess oxygen with the formation of short chain scission products. This is in accord with the views of Weiss (10), who found that conjugated systems are in some cases more easily oxidized.

All these mechanisms for the polymerization of oils involve the formation and decomposition of peroxides. The manner in which driers affect these reactions is still uncertain. The simplest explanation is that the driers catalyse the formation of peroxides. A mechanism for this type of catalysis has been presented by Myers and Zettlemoyer (11).

$$Co^{++} + O_2 \longrightarrow (Co^{++}{-}OO^*)$$

$$(Co^{++}{-}OO^*) + RH \longrightarrow ROOH + Co^{++}$$

Another might be the decomposition of the peroxide as suggested by O'Neill (12).

$$\mathrm{ROOH} + \mathrm{Co}^{++} \longrightarrow \mathrm{Co}^{+++} + \mathrm{RO}^{*} + \mathrm{OH}^{-}$$

$$\text{or}$$

$$\mathrm{Co}^{+++} + \mathrm{RO}^{-} + {}^{*}\mathrm{OH}$$

$$\mathrm{Co}^{+++} + \mathrm{OH}^{-} \longrightarrow \mathrm{Co}^{++} + {}^{*}\mathrm{OH}$$

$$\mathrm{Co}^{+++} + \mathrm{RO}^{-} \longrightarrow \mathrm{Co}^{++} + \mathrm{RO}^{*}$$

Polymerization then proceeds in the manner already described. Mueller (13) has suggested another mechanism for the catalysis of the decomposition of the peroxide.

$$\mathrm{ROOH} + \mathrm{Co}^{++} \longrightarrow \mathrm{Co}^{+++} + \mathrm{RO}^{*} + \mathrm{OH}^{-}$$

$$\mathrm{ROOH} \rightleftharpoons \mathrm{ROO}^{-} + \mathrm{H}^{+}$$

$$\mathrm{ROO}^{-} + \mathrm{Co}^{+++} \longrightarrow \mathrm{ROO}^{*} + \mathrm{Co}^{++}$$

Several workers (14-20) have studied the effects of driers on the oxidation of oils. The results have often been inconsistent. Most of the workers have found that Co and Mn are good catalysts and Ca and Zn are poor catalysts. The other metals of the first transition series have shown varying activities as catalysts, depending on the method of investigation.

Perhaps the most complete study has been made by Skellon (21) who investigated the effect of several metal oleates on the oxidation of oleic acid. He found Co to be a good catalyst, Zn a poor catalyst, and V, Mn, Ni and Cu to be of intermediate activity. Jackson and Kummerow (22) investigated the oxidation of linoleic acid in the presence of Co, Mn, and Zn napthenates and found the order of activity as catalysts decreased in that order.

EXPERIMENTAL

The oxidation procedure was similar to that described by Gunstone and Hilditch (23) and Skellon (24). Oxygen was bubbled through acid maintained at an elevated temperature. At frequent intervals samples of the oxidation product were taken and analysed. Details of the procedure are given in the following paragraphs.

Apparatus

A three neck 250 ml. flask was fitted with an air condenser in the central neck. Of the remaining necks, one was fitted with a piece of glass tubing as an outlet for collecting samples and the other with a thermometer. Cork stoppers were used at all three necks as rubber stoppers were found to deteriorate on prolonged contact with heated linoleic acid. A glass tubing with the end drawn to a jet was inserted through the air condenser and served as an inlet tube for the oxygen. The top of the air condenser was fitted with a rubber stopper through which the inlet tube entered the flask. The oxygen escaped through another glass tube in the same stopper. A magnetic stirrer was placed in the bottom of the flask. The flask was immersed in a bath of motor oil in a large evaporating dish. An electric knife blade heater with a temperature control was used to regulate the temperature of the bath. A detailed drawing of the reaction flask is shown in Figure 1.

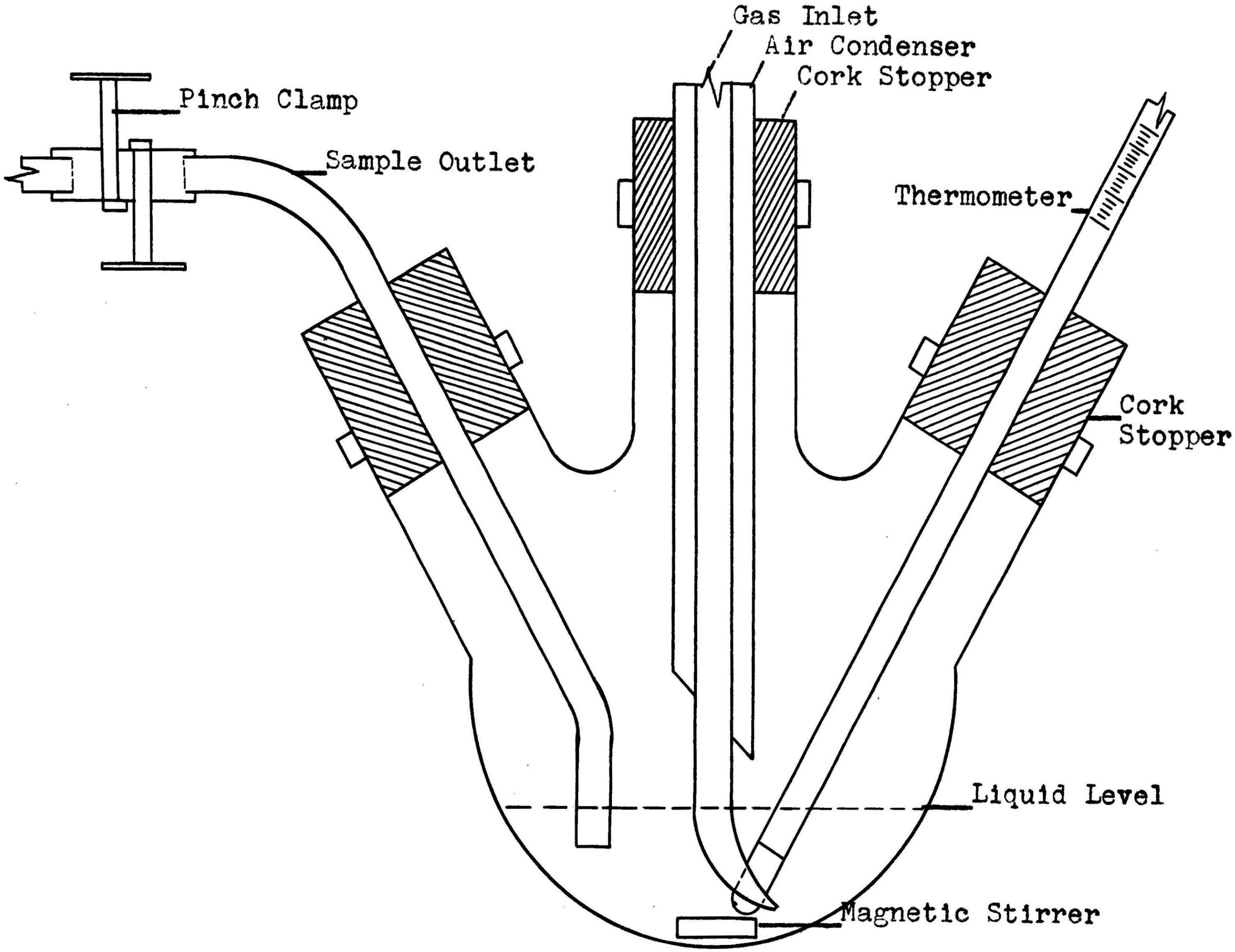
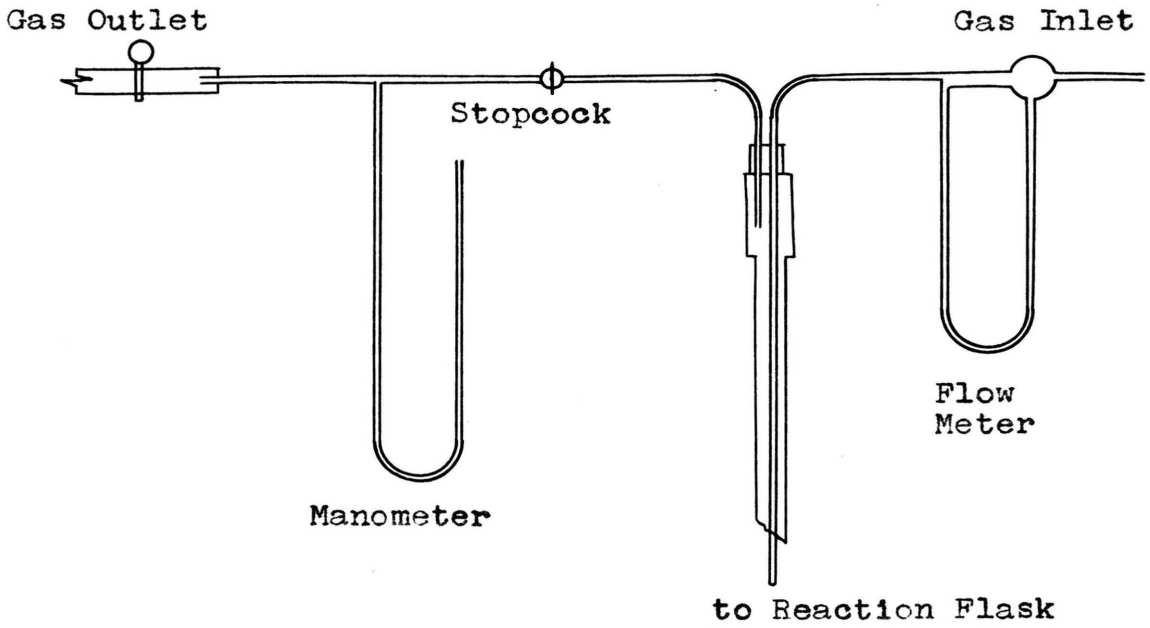


Figure 1
Reaction Flask

Commercial tank oxygen was used in all the oxidations. The gas was led from the tank through the gas inlet tube previously described. A flow meter was installed in the system between the tank and reaction flask. Escaping gases passed out the top of the air condenser. A stopcock was installed between the reaction flask and gas outlet so that the reaction flask could be closed completely if necessary. A differential manometer filled with water was connected between the stopcock and outlet. A diagram of the gas inlet and outlet system is shown in Figure 2.

Figure 2

Gas Inlet and Outlet System



Oxidation of Linoleic Acid

A standard procedure was adopted in all oxidations. The apparatus was assembled and purged with oxygen. The heater was connected several hours before beginning oxidation and the oilbath temperature brought to approximately 80°C. A sample of acid was prepared and heated on a hot plate to approximately 80°C., stirred well, and introduced into the flask through the neck at which the thermometer was fixed. The thermometer was quickly replaced and the system allowed to come to temperature equilibrium. Small adjustments in the setting of the temperature control were made, if necessary, until the temperature of the sample was 80±0.5°C. This usually required ten to fifteen minutes.

Oxidation was then begun by passing oxygen through the system at a rate of about 1½ cubic feet an hour. Rate of flow was measured by the flow meter, and if adjustments were necessary, they were made by means of a valve on the oxygen tank. The clamp on the gas outlet was tightened until the pressure inside the system was 760±2 mm. of mercury. Temperature, pressure and flow rate were checked periodically and any necessary adjustments were made.

As soon as pressure and flow rate had been regulated, the first sample was taken. Samples were taken by opening the clamp on the end of the sample outlet tube and allowing the pressure in the flask to force material through the sample outlet tube. As the oxidation product became more viscous in the later stages of oxidation, it was sometimes necessary to close the stopcock so that the pressure in the flask would be increased. Before taking each sample, any material already in the sample tube was collected and discarded.

Samples were taken every half hour for four hours and once an hour for the next two hours. About one gram of each sample was collected in a 3-inch test tube. The sample was cooled, stoppered, and set aside for analysis. After six hours all the material remaining in the flask was collected in Gardner viscosity tubes. One tube was reserved for viscosity measurements and the rest of the material used for the necessary analysis of the product.

Oxidation of Linoleic Acid in the Presence of Catalysts

Linoleic acid was oxidized in the presence of a series of metallic soaps. The soaps (with the exception of those of vanadium and chromium), were samples of commercial napthenate driers. The properties and sources of the various driers are listed in Table I.

Table I

Soap	Source	Metal concentration	Amount used per 35 grams of acid
Calcium napthenate	NAFTONE*	4%	0.625 g
Manganese napthenate	"	6	0.572
Iron napthenate	"	6	0.580
Cobalt napthenate	"	6	0.612
Copper napthenate	"	6	0.660
Zinc napthenate	"	8	0.509
Nickel napthenate	ADVANCE**	6	0.610

* NAFTONE, INC., 515 Madison Avenue, New York 22, N. Y.
** ADVANCE SOLVENTS AND CHEMICAL CORP., 245 Fifth Ave., New York 16, N. Y.

Chromium and vanadium napthenates were prepared from soluble salts of the metals and napthenic acid by the method given by Skellon and Spence (25). Five tenths of a gram of napthenic acid (acid number-230) was dissolved in methyl alcohol and neutralized with 0.179 N NaOH. Excess alcohol was boiled off and the hot soap solution added to a solution of 0.25 grams of $Cr(NO_3)_3 \cdot 9H_2O$ in 10 ml. of water. The resulting precipitate was washed twice with water and twice with alcohol and dissolved in approximately one gram of mineral spirits. The mineral spirit solution was weighed and divided into fractions of 1/7 and 6/7. The smaller fraction was used for the drying time test and the larger for oxidation. Vanadium napthenate was prepared by the same method using

0.325 grams of napthenic acid and 0.986 grams of $VOCl_2$.

The linoleic acid used in this work was purchased from the Fisher Scientific Company. It had an acid number of 199 (calculated-200), iodine number of 180 (calculated-180), and no detectable peroxide content. Enough of each of the soaps to provide 5 atoms of drier metal for each 1000 molecules of linoleic acid was added to 35 grams of linoleic acid. These amounts are listed in Table I. The larger portions of the chromium and vanadium napthenates were added to 30 grams of linoleic acid instead of 35. The mixture of soap and linoleic acid was then stirred well and oxidized in the manner described for pure linoleic acid.

Analysis of Samples

Each sample was analysed for peroxide content and conjugation. Samples taken approximately one hour apart were analysed for iodine value. Samples of the final product were analysed for acid and saponification numbers and the viscosity and molecular weight measured.

Conjugation (26)

Approximately 0.6 grams of sample were weighed to the nearest milligram into a tared 10 ml. volumetric flask, dissolved in purified methanol and diluted to 10 ml. By three successive 1:10 dilutions with purified methanol the concentration of the solution was reduced to approximately 0.06 grams of sample per liter of solution. The transmission of ultraviolet radiation of 2340Å by this solution was measured on a Beckman spectrophotometer and the per cent conjugation calculated by the following equation.

$$\% \text{ Conjugation} = \frac{\text{Log}\left(\frac{I_o}{I_t}\right) \times 100}{L \times 115 \times \text{sample wt. per liter of sol.}}$$

where

I_o is the per cent transmitted by methanol

I_t is the per cent transmitted by the sample

L is the cell length

115 is the extinction coefficient.

The per cent conjugation as calculated in this manner represents the weight per cent of the sample which is composed of molecules having a conjugated double bond, assuming these molecules to be conjugated linoleic acid.

Peroxide number (27)

Two ml. of the original solution prepared for the measurement of conjugation were dissolved in a 60:40 solution of glacial acetic acid:chloroform in a 250 ml. Erlenmeyer flask. One-half ml. of a saturated solution of potassium iodide was run into the flask and the contents swirled for one minute. After one minute the solution was diluted with 100 ml. of distilled water and titrated with 0.01 N $Na_2S_2O_3$ obtained by dilution of the standardized $Na_2S_2O_3$ prepared for the iodine number determination. The peroxide number was calculated as follows:

$$\text{Peroxide number} = \frac{(\text{ml. } Na_2S_2O_3 \times \text{Normality} \times 500)}{\text{sample weight}}$$

The peroxide number as calculated in this manner is the number of ml. of 0.002 N $Na_2S_2O_3$ required to titrate one gram of sample.

Iodine number (28)

Approximately 0.1 of a gram of sample was weighed to the nearest milligram into a 250 ml. Erlenmeyer flask. The sample was dissolved in 10 ml. of chloroform and 25 ml. of Wijs solution (29) were added. The contents were shaken, the flask stoppered, and placed in a dark cabinet. Shaking was repeated every 10 minutes. After one hour the solution was diluted with 100 ml. of distilled water and 15 ml. of a 15 per cent solution of KI and titrated with 0.1 N $Na_2S_2O_3$.

Wijs solution was prepared by dissolving 13 grams of I_2 in one liter of glacial acetic acid. Chlorine gas was bubbled into about 900 ml. of the iodine solution until the color turned from brown to red. The remaining 100 ml. of the iodine solution was then added to this solution. The result was a solution of ICl in acetic acid with a slight excess of I_2.

Sodium thiosulfate solution was prepared by dissolving 25 grams of $Na_2S_2O_3 \cdot 5H_2O$ in one liter of freshly boiled distilled water. The solution was allowed to stand for one day and standardized against $K_2Cr_2O_7$ (30).

A blank was run using 25 ml. of the Wijs solution with the given amounts of chloroform and KI. The iodine number was then calculated as follows:

$$\text{Iodine number} = \frac{(\text{ml. } Na_2S_2O_3 \text{ for blank} - \text{ml. } Na_2S_2O_3 \text{ for sample}) \times (\text{N } Na_2S_2O_3) \times 127}{\text{sample weight}}$$

The iodine number is the number of milligrams of iodine required to react with one gram of sample.

Acid number (31)

One gram of sample was weighed to the nearest milligram into a 250 ml. Erlenmeyer flask and dissolved in 50 ml. of methanol. This solution was titrated with 0.2 N NaOH using phenolphthalein as an indicator. The sodium hydroxide was prepared by dissolving 10 grams of NaOH in 20 ml. of water and allowing to stand for several days. The solution was filtered, the filtrate diluted to one liter and standardized against oxalic acid. The acid number was calculated as follows:

$$\text{Acid number} = \frac{(\text{ml. NaOH}) \times (\text{N NaOH}) \times 56.11}{\text{sample weight}}$$

The acid number is the number of milligrams of KOH required to neutralize one gram of sample.

Saponification number (32)

One gram of sample was weighed to the nearest milligram into a 250 ml. Erlenmeyer flask and dissolved in about 25 ml. of methanol. Twenty-five ml. of a 0.5N solution of ethanolic NaOH were pipetted into the flask. The flask was fitted with an air condenser and the solution refluxed for one hour. The flask was cooled, the condenser rinsed well with distilled water and the solution in the flask diluted with distilled water. The excess NaOH was titrated with 0.5 N H_2SO_4 using phenolphthalein as an indicator.

Ethanolic NaOH was prepared by dissolving 10 grams of NaOH in 500 cc. of ethanol. This solution was allowed to stand several days and filtered. The filtrate was stored in a glass stoppered bottle. Twenty-five ml. of the solution were titrated with 0.5N H_2SO_4 as a blank.

The saponification number was calculated as follows:

$$\text{Sap. No.} = \frac{(\text{ml. } H_2SO_4 \text{ for blank-ml. for sample}) \times (\text{N } H_2SO_4) \times 56.11}{\text{sample weight}}$$

The saponification number is the number of milligrams of KOH required to saponify one gram of sample.

The ester number is calculated by subtracting the acid number from the saponification number.

<u>Molecular weight</u> (33)

Approximately one gram of sample and ten grams of camphor were weighed to the nearest milligram into a clean dry test tube. The test tube was fitted with a 0.1°C. thermometer and an air jacket. Tube and air jacket were immersed in a bath of concentrated sulfuric acid and heated until the contents of the tube had melted. At this point heating was stopped and the contents of the tube allowed to cool at the rate of 1-2°C. per minute. The freezing point was recorded at the point at which crystals could be observed forming in the melt. The molecular weight was calculated from the following equation:

$$\text{Mol. wt.} = \frac{\text{Sample wt. x molal freezing point depression constant of camphor x 1000}}{\text{Camphor wt. x freezing point depression}}$$

Viscosity

The sample collected in the viscosity tube was cooled to room temperature and its viscosity measured by comparison with Gardner viscosity standards.

Accuracy of Analysis

All results except those from conjugation were reported to the nearest whole number. Per cent conjugation was reported to the nearest one tenth of one per cent.

The limits of accuracy for each analysis were determined by calculating the limits of accuracy of each operation performed during the analysis and calculating what the maximum cumulative error would be. These limits of accuracy are tabulated in Table II.

Table II

Analysis	Limits
Peroxide value	±3
Iodine number	±2
Acid number	±1
Sap. number	±1
Molecular weight	±5

Drying Time

Thirty-five grams of refined linseed oil from the Archer Daniel Midlands Company were mixed with enough drier to make the weight per cent of the drier equivalent to that used in the oxidation of linoleic acid. A 0.003-inch thick film of the mixture was cast on a hiding power chart. The film was tested for dryness by the finger-touch method after every hour for eight hours, every four hours for the next sixteen hours and every twelve hours thereafter. Drying time was reported as the time that the film was tack-free (34).

Table IIIa

Results of Oxidation of Linoleic Acid
with
No Catalyst

		Per cent Conjugation			Peroxide Number	
Sample	Time (hrs)	Sample Weight (grams)	Percent UV Transmitted	Percent Conjugation	Ml. 0.0118N $Na_2S_2O_3$	Peroxide Number
1	0	0.626	72	2.0	0.3	16
2	0.5	0.619	50	4.2	3.4	88
3	1	0.821	45	3.7	3.7	134
4	1.5	0.684	47	4.2	3.3	145
5	2	0.605	52	4.1	3.5	172
6	2.5	0.612	45	4.9	3.4	166
7	3	0.664	44	4.6	3.4	154
8	3.5	0.678	40	5.1		
9	4	0.739	32	5.8		
10	5	0.718	33	5.8	3.4	140
11	6	0.881	27	5.6	4.0	135

Table IIIb

Results of Oxidation of Linoleic Acid
with
No Catalyst

Sample	1	3	5	7	9	10	11
Iodine Number							
Sample weight (grams)	0.123	0.164	0.121	0.133	0.148	0.144	0.176
Ml. 0.115 N $Na_2S_2O_3$	15.0	18.7	11.6	12.9	13.4	12.2	13.9
Iodine Number	178	167	140	149	132	124	115
Acid Number							
Sample weight (grams)							0.874
Ml. 0.208N NaOH							12.8
Acid Number							172
Saponification Number							
Sample weight (grams)							1.056
Ml. 0.485 N H_2SO_4							8.9
Saponification Number							230
Molecular Weight							
Sample weight (grams)							1.087
Camphor weight (grams)							10.423
Freezing Point Depression (°C)							13.7
Molecular Weight							305
Ester Number							58
Viscosity (stokes)							6
Drying Time (hours)							168

Table IVa

Results of Oxidation of Linoleic Acid with Calcium Catalyst

		Per cent Conjugation			Peroxide Number	
Sample	Time (hrs)	Sample Weight (grams)	Percent UV Transmitted	Percent Conjugation	Ml. 0.0115N $Na_2S_2O_3$	Peroxide Number
1	0	0.617	75	1.8	0.3	14
2	0.5	0.610	58	3.4	3.2	150
3	1	0.611	50	4.3	3.7	174
4	1.5	0.611	45	4.9	3.4	160
5	2	0.612	40	5.6	2.9	136
6	2.5	0.612	42	5.4	2.7	128
7	3	0.615	41	5.5		
8	3.5	0.613	40	5.6	2.7	128
9	4	0.602	41	5.6		
10	5	0.605	42	5.4	2.4	114
11	6	0.600	43	5.3	2.5	120

Table IVb

Results of Oxidation of Linoleic Acid with Calcium Catalyst

Sample	1	3	5	7	9	10	11
Iodine Number							
Sample weight (grams)	0.103	0.107	0.105	0.112	0.110	0.104	0.118
Ml. 0.100 N $Na_2S_2O_3$	14.0	13.5	12.5	12.4	11.4	10.2	10.7
Iodine Number	173	160	151	141	132	125	115
Acid Number							
Sample weight (grams)							1.086
Ml. 0.179 N NaOH							18.6
Acid Number							172
Saponification Number							
Sample weight (grams)							1.145
Ml. 0.468 N H_2SO_4							10.1
Saponification Number							232
Molecular Weight							
Sample weight (grams)							1.064
Camphor weight (grams)							10.932
Freezing Point Depression (°C)							12.6
Molecular Weight							310
Ester Number							60
Viscosity (stokes)							6
Drying Time (hours)							114

Table Va

Results of Oxidation of Linoleic Acid with Vanadium Catalyst

		Percent Conjugation			Peroxide Number	
Sample	Time (hrs)	Sample Weight (grams)	Percent UV Transmitted	Percent Conjugation	Ml. 0.008N $Na_2S_2O_3$	Peroxide Number
1	0	0.586	65	2.8	0.6	22
2	0.5	0.591	55	4.0	1.0	35
3	1	0.590	49	4.8	1.2	42
4	1.5	0.580	49	4.8	0.9	32
5	2	0.576	44	5.6	0.6	22
6	2.58	1.146	20	5.5	1.3	22
7	3	0.592	44	5.4	0.7	24
8	3.66	0.586	46	5.4	0.6	20
9	4.75	0.586	45	5.3	0.6	20
10	6.33	0.587	45	5.3	0.6	20

Table Vb

Results of Oxidation of Linoleic Acid
with
Vanadium Catalyst

Sample	1	3	5	7	9	10
Iodine Number						
Sample weight (grams)	0.098	0.103	0.104	0.105	0.100	0.199
Ml. 0.101 N $Na_2S_2O_3$	12.4	12.3	11.5	10.9	10.7	10.3
Iodine Number	164	152	131	132	138	110
Acid Number						
Sample weight (grams)						1.012
Ml. 0.179 N NaOH						18.2
Acid Number						179
Saponification Number						
Sample weight (grams)						1.033
Ml. 0.468 N H_2SO_4						9.1
Saponification Number						231
Molecular Weight						
Sample weight (grams)						1.094
Camphor weight (grams)						11.123
Freezing Point Depression (°C)						11.1
Molecular Weight						351
Ester Number						52
Viscosity (stokes)						17
Drying Time (hours)						10

Table VIa

Results of Oxidation of Linoleic Acid

with

Chromium Catalyst

		Per cent Conjugation			Peroxide Number	
Sample	Time (hrs)	Sample Weight (grams)	Percent UV Transmitted	Percent Conjugation	Ml. 0.0101N $Na_2S_2O_3$	Peroxide Number
1	0	0.604	67	2.5	0.6	20
2	0.5	0.617	62	2.9	3.0	97
3	1	0.619	53	3.9	4.4	142
4	1.5	0.608	48	4.6	4.4	145
5	2	0.609	45	4.9	4.8	157
6	2.75	0.730	36	5.3	5.2	143
7	3.17	0.617	40	5.6	4.9	159
8	3.83	0.611	42	5.4	4.2	138
9	4.83	0.605	44	5.1	4.5	149
10	6	0.634	46	4.6	4.3	136

Table VIb

Results of Oxidation of Linoleic Acid with Chromium Catalyst

Sample	1	3	5	8	9	10
Iodine Number						
Sample weight	0.100	0.107	0.109	0.113	0.115	0.139
Ml. 0.101 N $Na_2S_2O_3$	13.0	13.2	12.4	11.1	10.4	11.7
Iodine Number	165	156	144	125	115	107
Acid Number						
Sample weight (grams)						1.031
Ml. 0.179 N NaOH						17.4
Acid Number						169
Saponification Number						
Sample weight (grams)						1.029
Ml. 0.468 N H_2SO_4						9.1
Saponification Number						232
Molecular Weight						
Sample Weight (grams)						1.162
Camphor weight (grams)						10.436
Freezing Point Depression (°C)						14.3
Molecular Weight						312
Ester Number						63
Viscosity (stokes)						6
Drying Time (hours)						120

Table VIIa

Results of Oxidation of Linoleic Acid with Manganese Catalyst

		Per cent Conjugation			Peroxide Number	
Sample	Time (hrs)	Sample Weight (grams)	Percent UV Transmitted	Percent Conjugation	Ml. 0.0115N $Na_2S_2O_3$	Peroxide Number
1	0	0.606			0.2	10
2	0.5	0.616	61	3.0	0.2	10
3	1	0.610	47	4.7	0.3	14
4	1.5	0.607	43	5.3	0.4	19
5	2	0.606	41	5.6	0.4	19
6	2.5	0.604	38	6.1	0.3	14
7	3	0.606	37	6.2	0.3	14
8	3.5	0.615	33	6.8		
9	4	0.600	38	6.1	0.3	14
10	5	0.609	35	6.5	0.3	14
11	6	0.607	36	6.4		

Table VIIb

Results of Oxidation of Linoleic Acid with Manganese Catalyst

Sample	1	3	5	7	9	11
Iodine Number						
Sample weight (grams)	0.119	0.111	0.116	0.115	0.114	0.109
Ml. 0.100 N $Na_2S_2O_3$	15.6	13.2	13.0	12.2	11.4	9.6
Iodine Number	167	151	143	135	127	111
Acid Number						
Sample weight (grams)						1.216
Ml. 0.208 N NaOH						18.6
Acid Number						179
Saponification Number						
Sample weight (grams)						1.046
Ml. 0.485 N H_2SO_4						8.8
Saponification Number						230
Molecular Weight						
Sample weight (grams)						0.895
Camphor weight (grams)						9.276
Freezing Point Depression (°C)						12.4
Molecular Weight						310
Ester Number						51
Viscosity (stokes)						6
Drying Time (hours)						8

Table VIIIa

Results of Oxidation of Linoleic Acid with Iron Catalyst

		Per cent Conjugation			Peroxide Number	
Sample	Time (hrs)	Sample Weight (grams)	Percent UV Transmitted	Percent Conjugation	Ml. 0.0100N $Na_2S_2O_3$	Peroxide Number
1	0	0.613	71	2.1	0.3	12
2	0.5	0.616	58	3.3	2.5	101
3	1	0.613	50	4.3	3.4	138
4	1.5	0.602	48	4.6	3.8	157
5	2	0.611	44	5.1	3.7	151
6	2.5					
7	3	0.601	43	5.3	3.0	125
8	3.5	0.603	43	5.3		
9	4	0.611	40	5.7	2.5	102
10	5	0.619	40	5.6	1.4	56
11	6	0.607	40	5.7	1.3	53

Table VIIIb

Results of Oxidation of Linoleic Acid
with
Iron Catalyst

Sample	1	3	5	7	9	10	11
Iodine Number							
Sample weight (grams)	0.107	0.105	0.103	0.104	0.102	0.103	0.119
Ml 0.101 N $Na_2S_2O_3$	14.4	12.6	11.8	11.1	10.4	9.8	11.0
Iodine number	173	154	147	137	131	122	118
Acid Number							
Sample weight (grams)							0.824
Ml 0.208 N NaOH							12.2
Acid Number							172
Saponification Number							
Sample weight (grams)							1.215
Ml 0.485N H_2SO_4							10.3
Saponification Number							230
Molecular Weight							
Sample weight (grams)							1.351
Camphor weight (grams)							12.455
Freezing Point Depression (°C)							13.8
Molecular Weight							314
Ester Number							58
Viscosity (Stokes)							8
Drying Time (hours)							17

Table IXa

Results of Oxidation of Linoleic Acid
with
Cobalt Catalyst

Sample	Time (hrs)	Per cent Conjugation Sample Weight (grams)	Per cent Conjugation Percent UV Transmitted	Per cent Conjugation Percent Conjugation	Peroxide Number Ml. 0.0109N $Na_2S_2O_3$	Peroxide Number Peroxide Number
1	0	0.616	68	2.4	0.2	9
2	0.5	0.607	47	4.7	0.5	21
3	1	0.623	47	4.6	0.4	16
4	1.5	0.615	40	5.6	0.2	9
5	2	0.607	37	6.2	0.2	9
6	2.5	0.604	38	6.1	0.1	5
7	3	0.605	38	6.1	0.1	5
8	3.5	0.609	38	6.0	0	0
9	4	0.602	34	6.8	0	0
10	5	0.602	38	6.1	0	0
11	6	0.603	38	6.1	0	0

Table IXb

Results of Oxidation of Linoleic Acid
with
Cobalt Catalyst

Sample	1	3	5	7	9	10	11
Iodine Number							
Sample weight (grams)	0.104	0.105	0.114	0.106	0.115	0.120	0.120
Ml 0.115N $Na_2S_2O_3$	11.9	11.4	11.1	10.5	10.0	9.7	8.8
Iodine Number	168	158	142	132	127	118	107
Acid Number							
Sample weight (grams)							0.953
Ml 0.208N NaOH							14.5
Acid Number							178
Saponification Number							
Sample weight (grams)							1.065
Ml 0.485N H_2SO_4							9.0
Saponification Number							229
Molecular Weight							
Sample weight (grams)							1.018
Camphor weight (grams)							7.814
Freezing Point Depression (^{o}C)							14.5
Molecular Weight							360
Ester Number							51
Viscosity (stokes)							17
Drying Time (hours)							3

Table Xa

Results of Oxidation of Linoleic Acid with Nickel Catalyst

Sample	Time (hrs)	Per cent Conjugation Sample Weight (grams)	Per cent Conjugation Percent UV Transmitted	Per cent Conjugation Percent Conjugation	Peroxide Number Ml. 0.0100N $Na_2S_2O_3$	Peroxide Number Peroxide Number
1	0	0.607	70	2.2	0.6	28
2	0.5	0.613	50	4.3	1.7	80
3	1	0.618	50	4.2	2.5	116
4	1.33	0.616	50	4.2	2.6	122
5	2	0.604			3.0	143
6	2.5					
7	3	0.600	40	5.8	3.2	153
8	3.66	0.605	40	5.8	3.5	166
9	4.66	0.619	42	5.3	3.1	144
10	6	0.602	40	5.8	2.7	129

Table Xb

Results of Oxidation of Linoleic Acid
with
Nickel Catalyst

Sample	1	3	5	8	9	10
Iodine Number						
Sample weight	0.104	0.110	0.101	0.102	0.114	0.112
Ml 0.101N $Na_2S_2O_3$	14.1	13.2	11.6	10.2	10.4	9.7
Iodine Number	172	152	149	128	117	111
Acid Number						
Sample weight (grams)						0.724
Ml 0.179N NaOH						12.4
Acid Number						172
Saponification Number						
Sample weight (grams)						1.021
Ml 0.468N H_2SO_4						9.1
Saponification Number						234
Molecular Weight						
Sample weight (grams)						1.104
Camphor weight (grams)						10.459
Freezing Point Depression (°C)						13.3
Molecular weight						317
Ester Number						62
Viscosity (stokes)						7
Drying Time (hours)						96

Table XIa

Results of Oxidation of Linoleic Acid with Copper Catalyst

		Per cent Conjugation			Peroxide Number	
Sample	Time (hrs)	Sample Weight (grams)	Percent UV Transmitted	Percent Conjugation	Ml. 0.0101N $Na_2S_2O_3$	Peroxide Number
1	0	0.621	70	2.2	0.2	8
2	0.5	0.615	66	2.6	1.6	65
3	1	0.618	57	3.4	2.2	89
4	1.5	0.630	48	4.4	2.0	80
5	2	0.620	45	4.8		
6	2.42	0.604	39	5.9	1.9	79
7	3	0.609	38	6.0	1.2	50
8	3.66	0.619	42	5.3	1.1	45
9	4.66	0.600	43	5.3	0.9	38
10	6.17	0.610	43	5.2	0.7	29

Table XIb

Results of Oxidation of Linoleic Acid
with
Copper Catalyst

Sample							
Iodine Number							
Sample weight (grams)	0.104	0.112	0.109	0.114	0.133	0.126	0.142
Ml 0.101N $Na_2S_2O_3$	13.2	13.8	12.4	12.2	13.7	11.9	12.5
Iodine Number	168	156	144	136	131	120	111
Acid Number							
Sample weight (grams)							1.000
Ml 0.179N NaOH							16.9
Acid Number							169
Saponification Number							
Sample weight (grams)							1.014
Ml 0.468N H_2SO_4							9.0
Saponification Number							232
Molecular Weight							
Sample weight (grams)							1.114
Camphor weight (grams)							12.821
Freezing Point Depression (°C)							11.1
Molecular Weight							314
Ester Number							63
Viscosity (stokes)							6
Drying Time (hours)							17

Table XII$_a$

Results of Oxidation of Linoleic Acid with Zinc Catalyst

		Per cent Conjugation*	Peroxide Number**	
Sample	Time (hrs)	Sample Weight (grams)	Ml. 0.0100N $Na_2S_2O_3$	Peroxide Number
1	0	0.123	0.1	4
2	0.5	0.122	2.2	90
3	1.	0.122	3.5	145
4	1.5	0.123	4.1	165
5	2	0.121	4.0	165
6	2.5	0.121	4.0	165
7	3	0.124	3.4	135
8	3.5	0.121	3.8	155
9	4.58	0.121	3.5	145
10	6.16	0.120	3.2	132

*A portion of the oxidized product was insoluble in methyl alcohol. This resulted in very low values for conjugation.

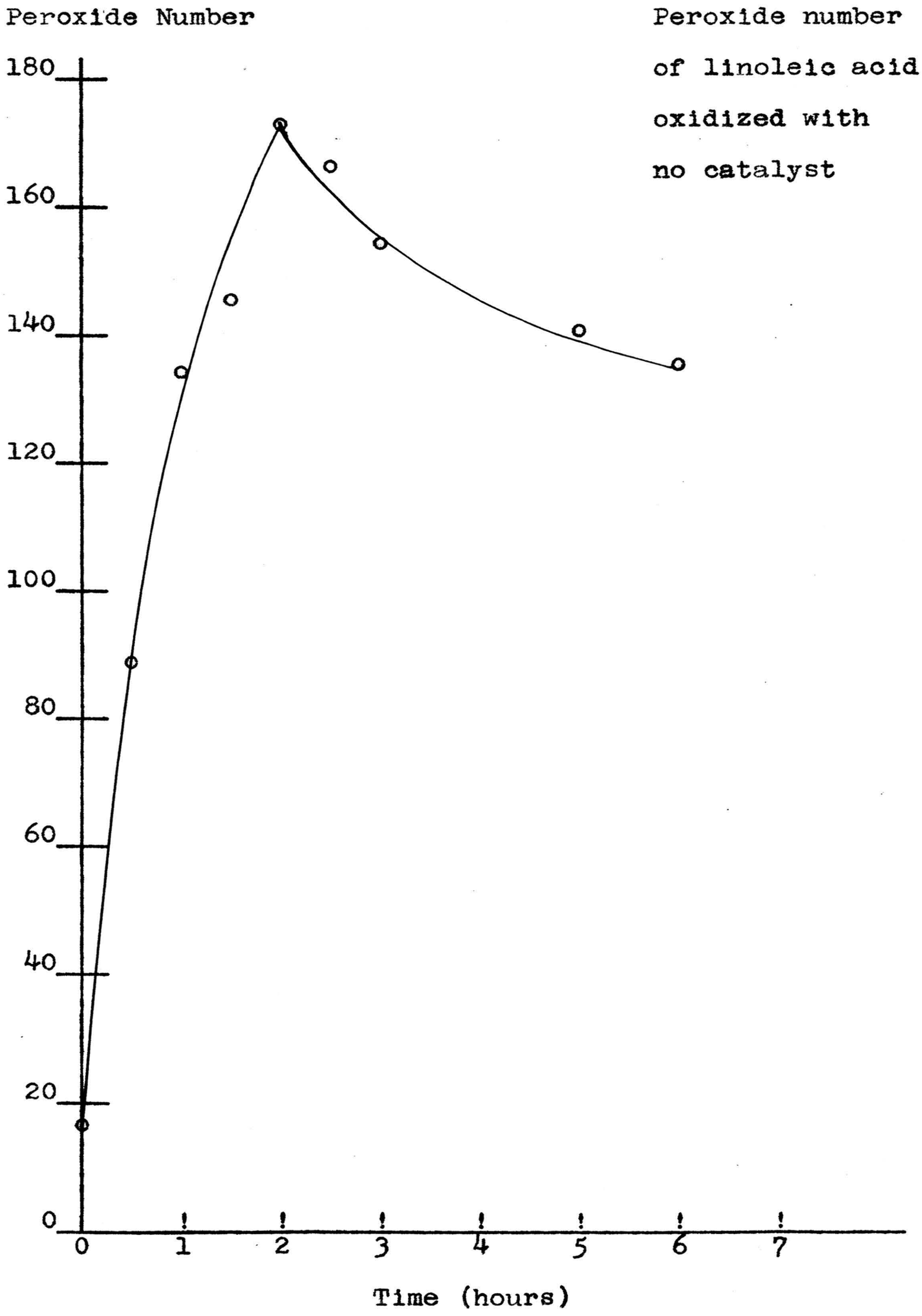
**Peroxide number determinations were run on the amounts listed without dissolving in methyl alcohol.

Table XIIb

Results of Oxidation of Linoleic Acid
with
Zinc Catalyst

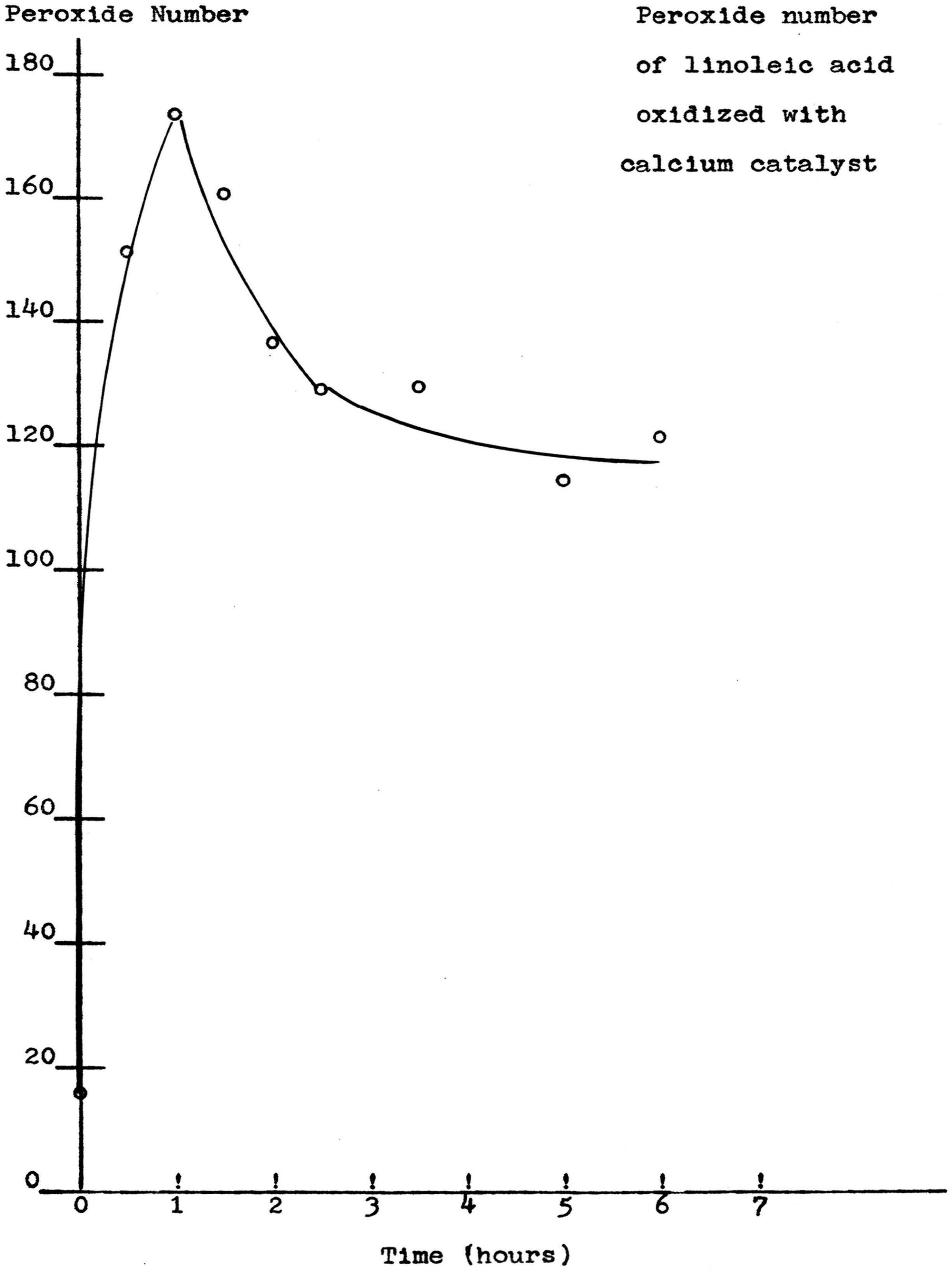
Sample						
Iodine Number						
Sample weight (grams)	0.101	0.118	0.119	0.109	0.121	0.120
Ml 0.100N $Na_2S_2O_3$	13.8	14.9	14.3	12.1	12.3	11.1
Iodine Number	173	161	153	141	129	117
Acid Number						
Sample weight (grams)						0.710
Ml 0.208 N NaOH						10.5
Acid Number						172
Saponification Number						
Sample weight (grams)						1.247
Ml 0.485N H_2SO_4						10.6
Saponification Number						232
Molecular Weight						
Sample weight (grams)						1.553
Camphor weight (grams)						10.03
Freezing Point Depression (^oC)						18.7
Molecular weight						330
Ester Number						60
Viscosity (stokes)						6
Drying Time (hours)						120

Figure 3



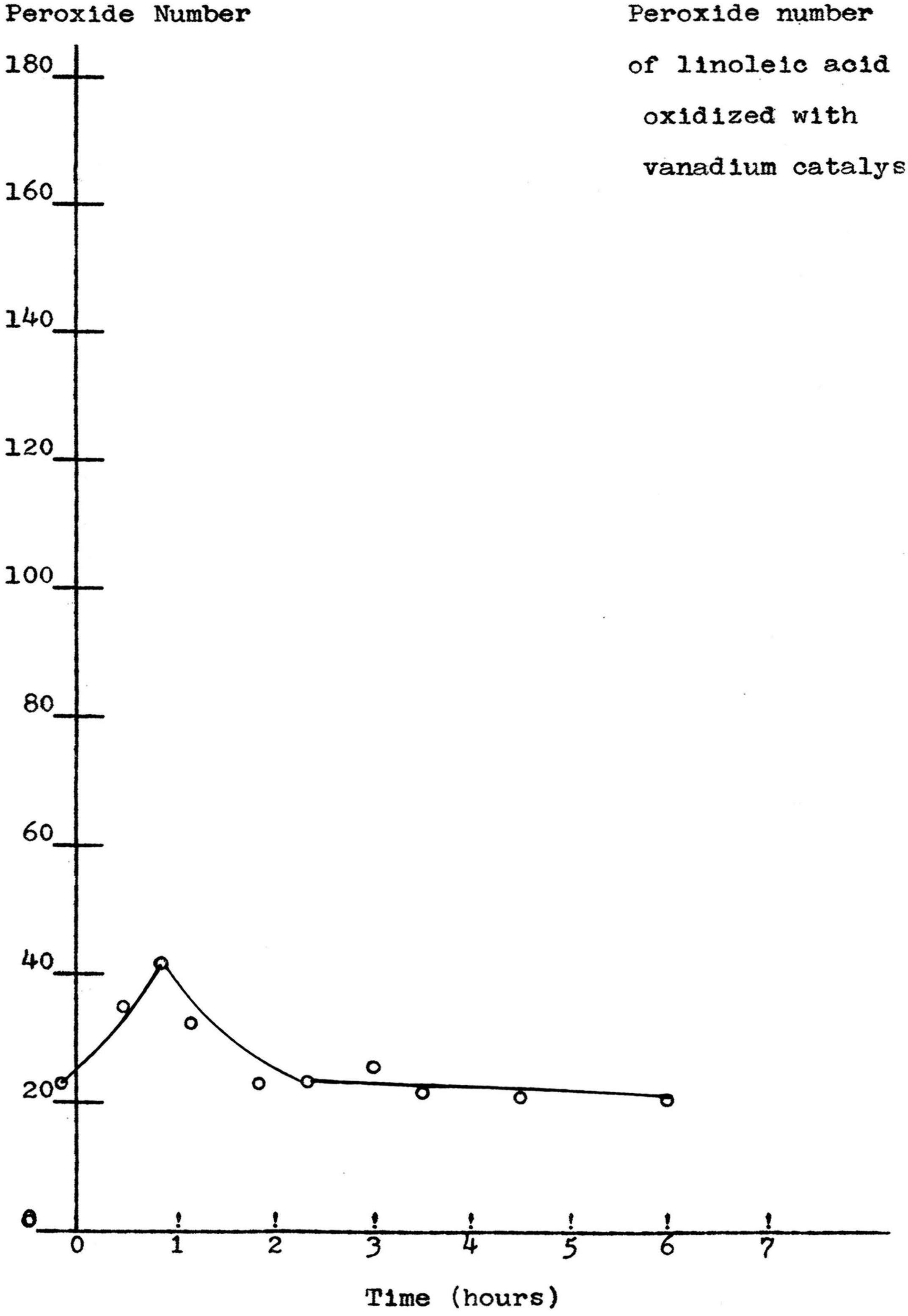
Peroxide number
of linoleic acid
oxidized with
no catalyst

Figure 4



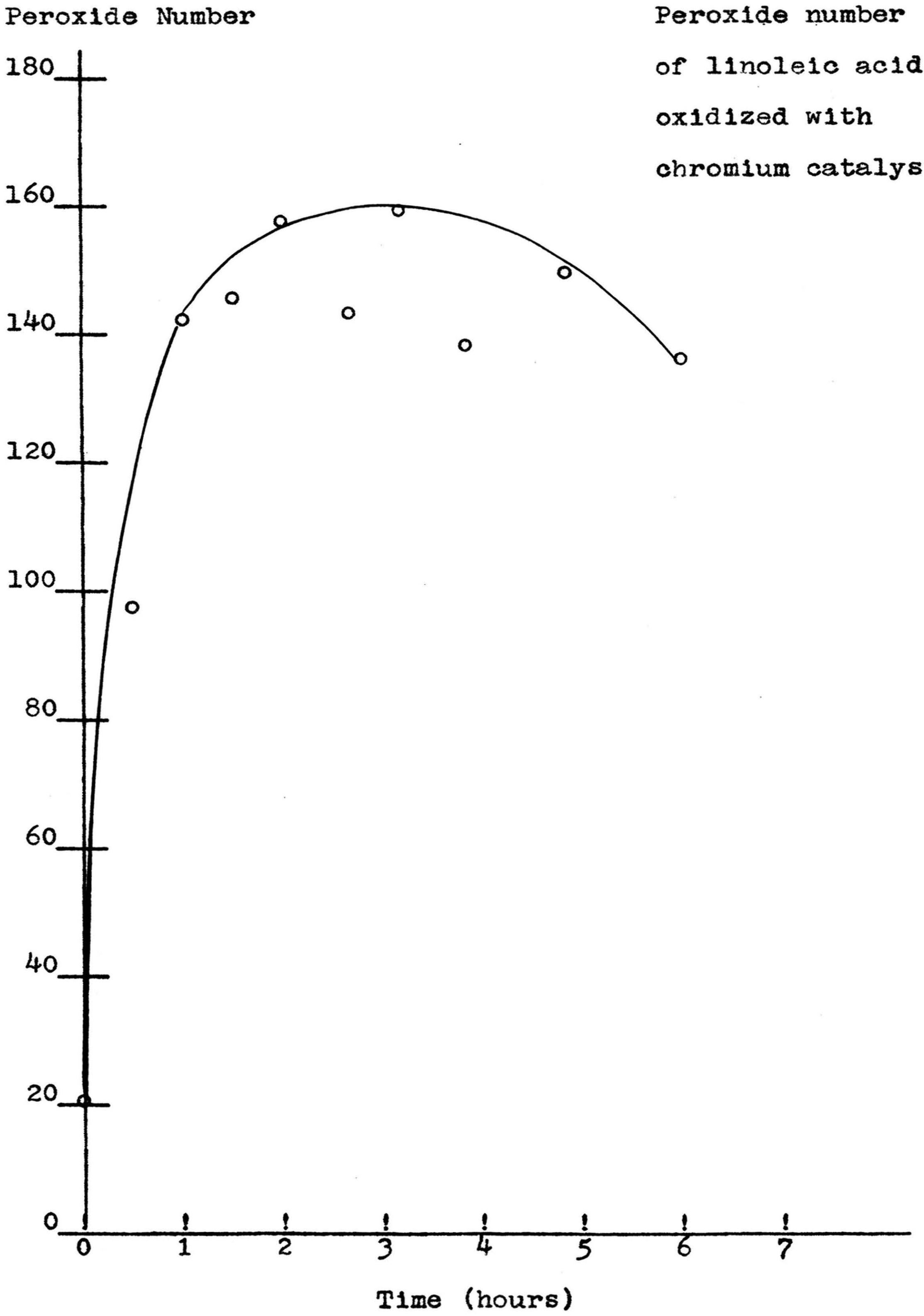
Peroxide number of linoleic acid oxidized with calcium catalyst

Figure 5



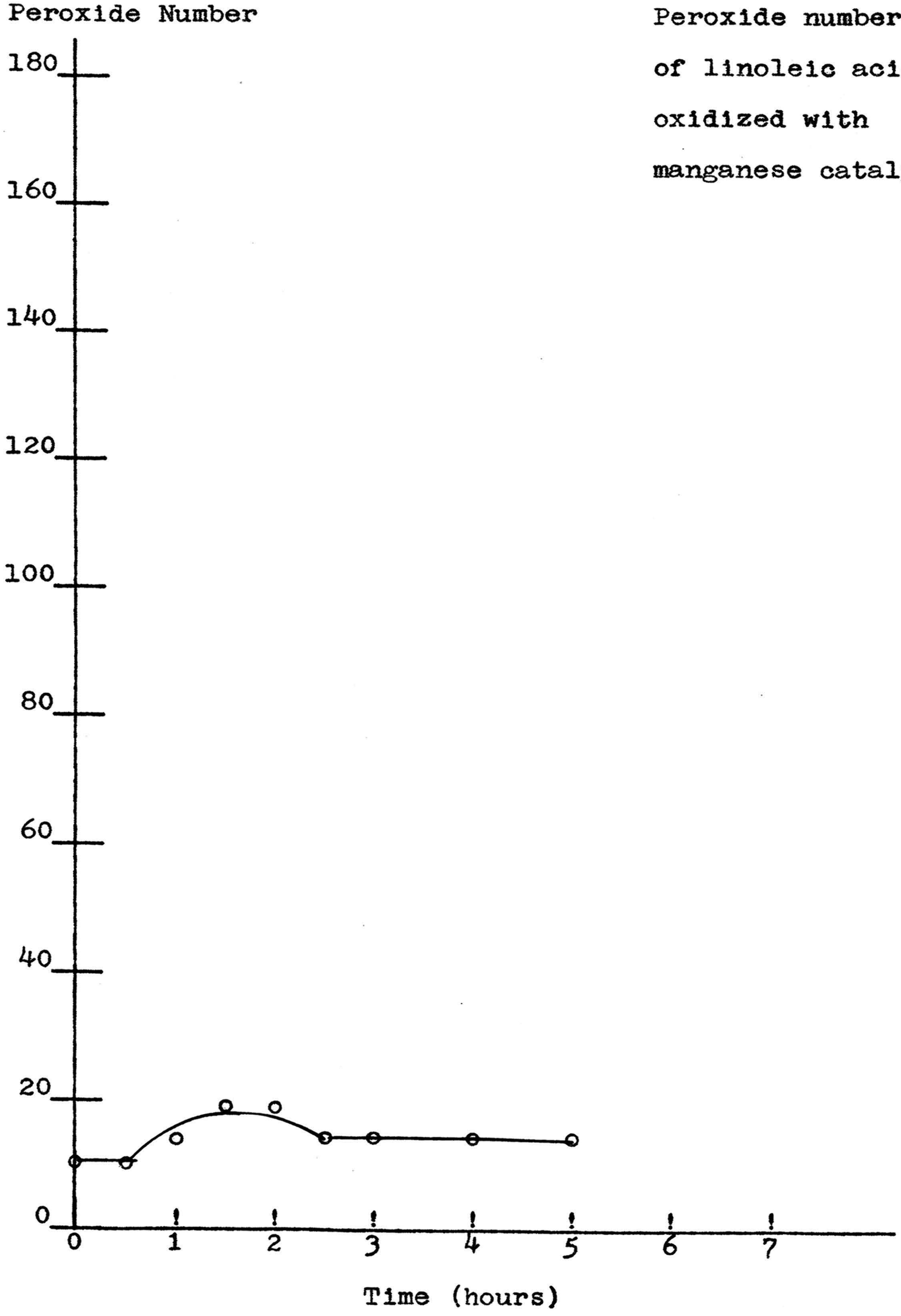
Peroxide number of linoleic acid oxidized with vanadium catalyst

Figure 6



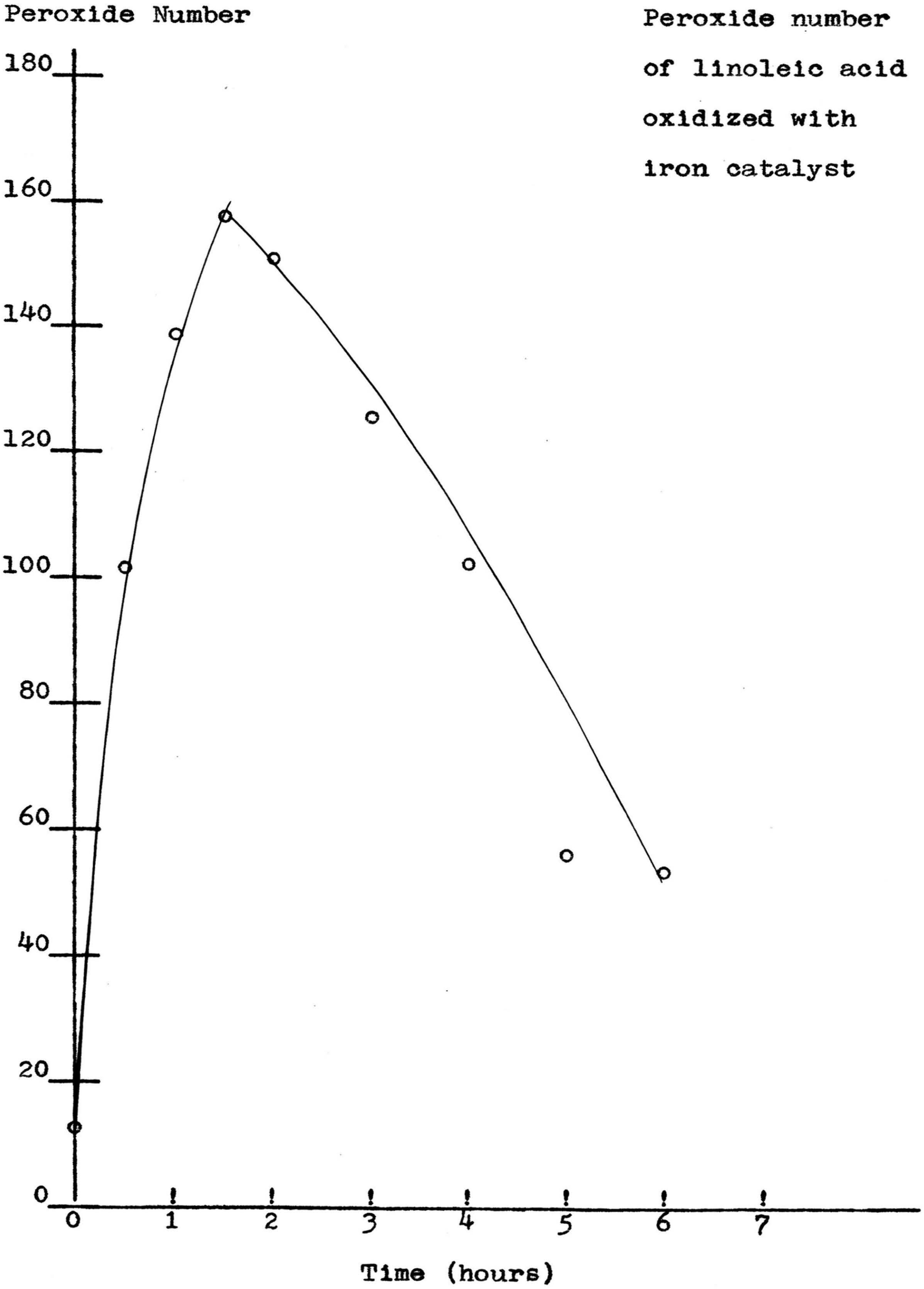
Peroxide number of linoleic acid oxidized with chromium catalyst

Figure 7



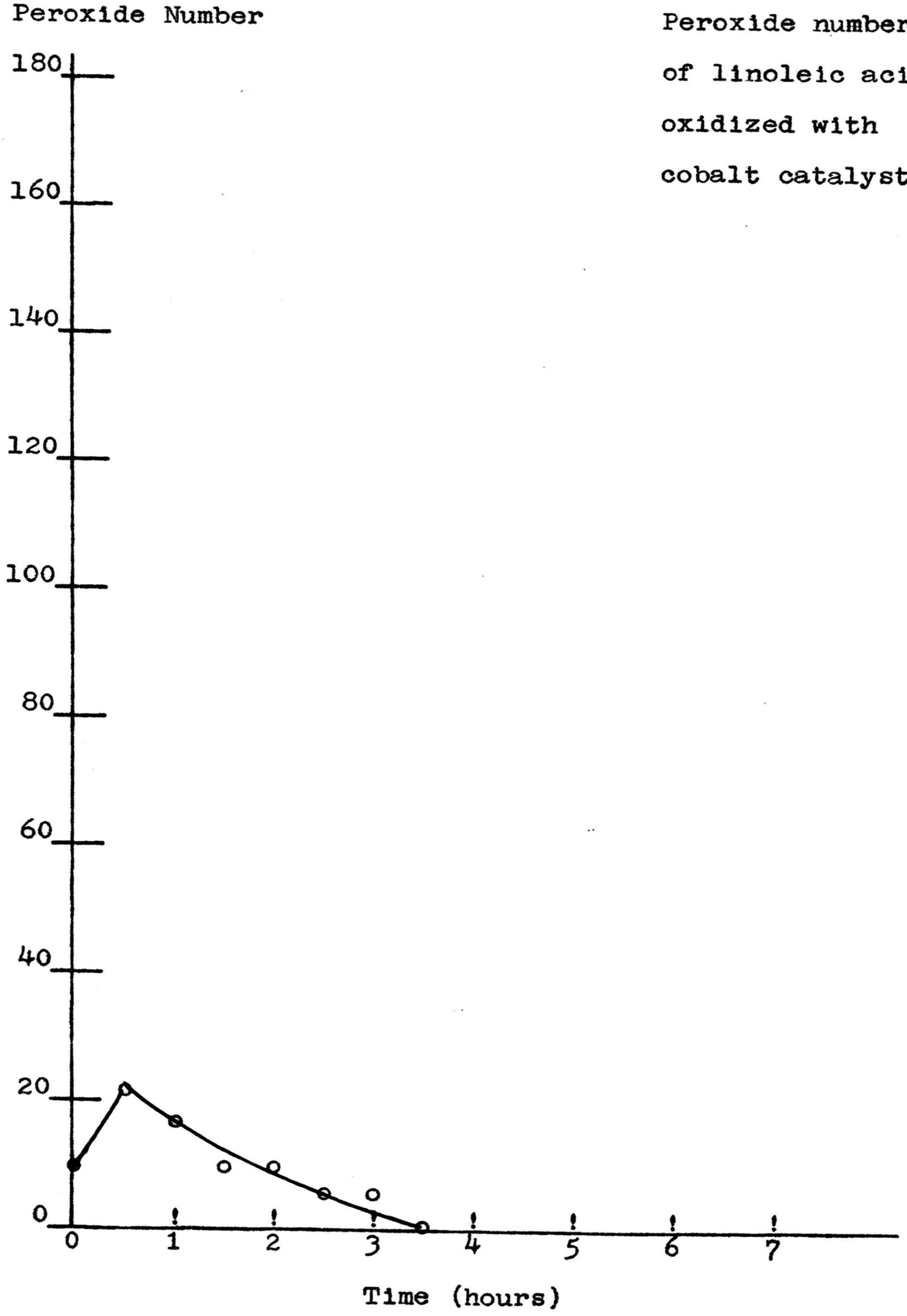
Peroxide number of linoleic acid oxidized with manganese catalyst

Figure 8



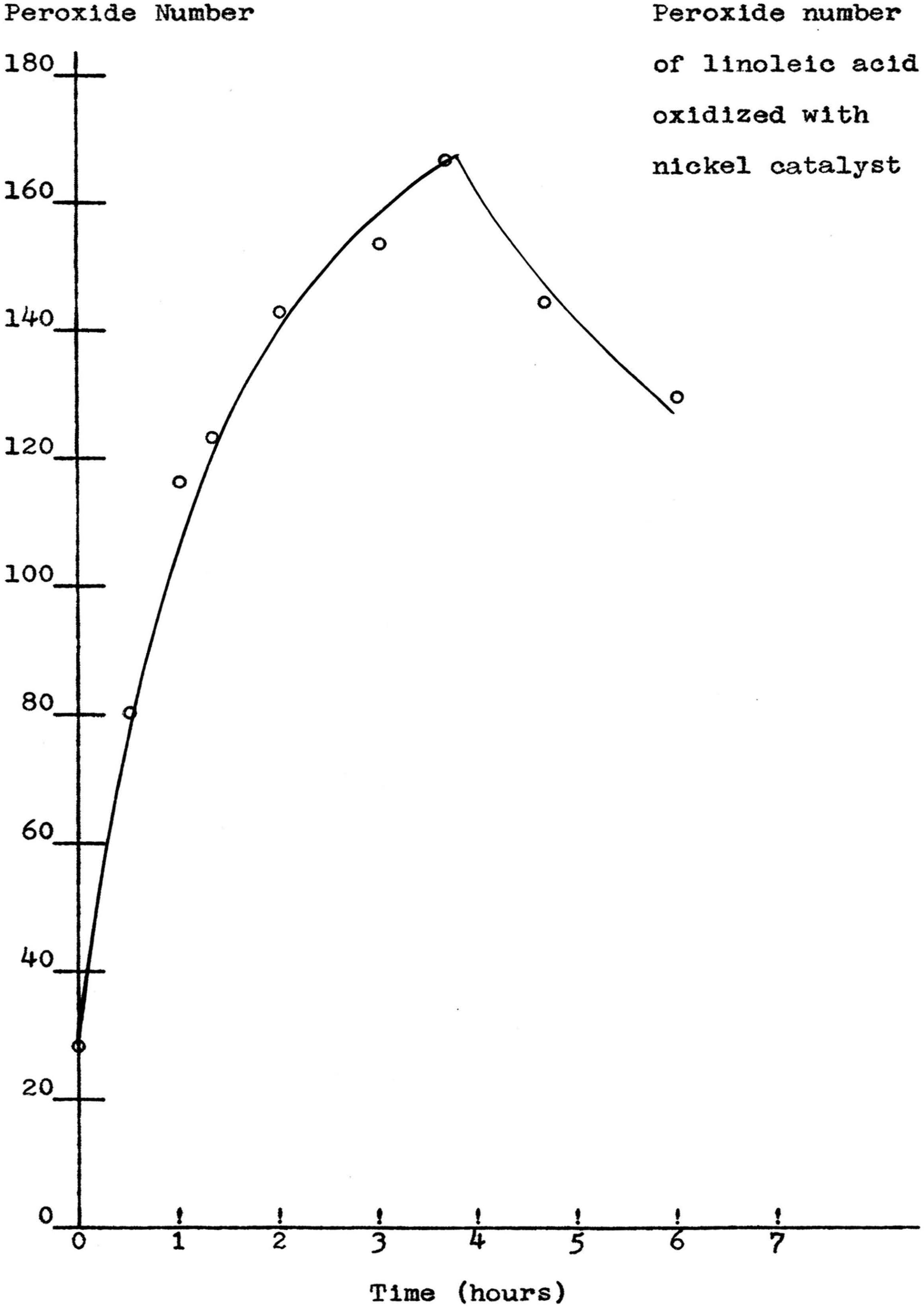
Peroxide number of linoleic acid oxidized with iron catalyst

Figure 9



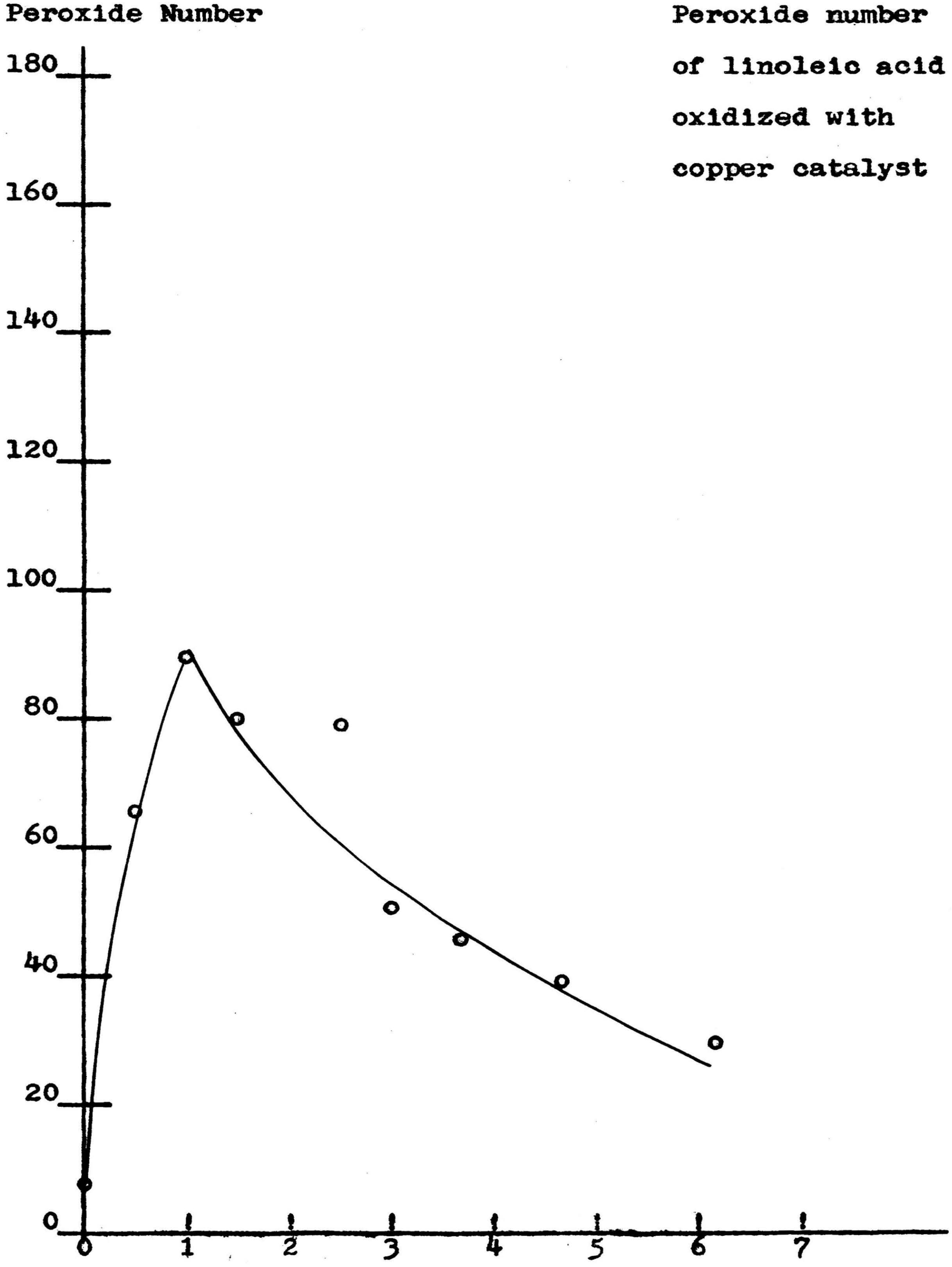
Peroxide number of linoleic acid oxidized with cobalt catalyst

Figure 10



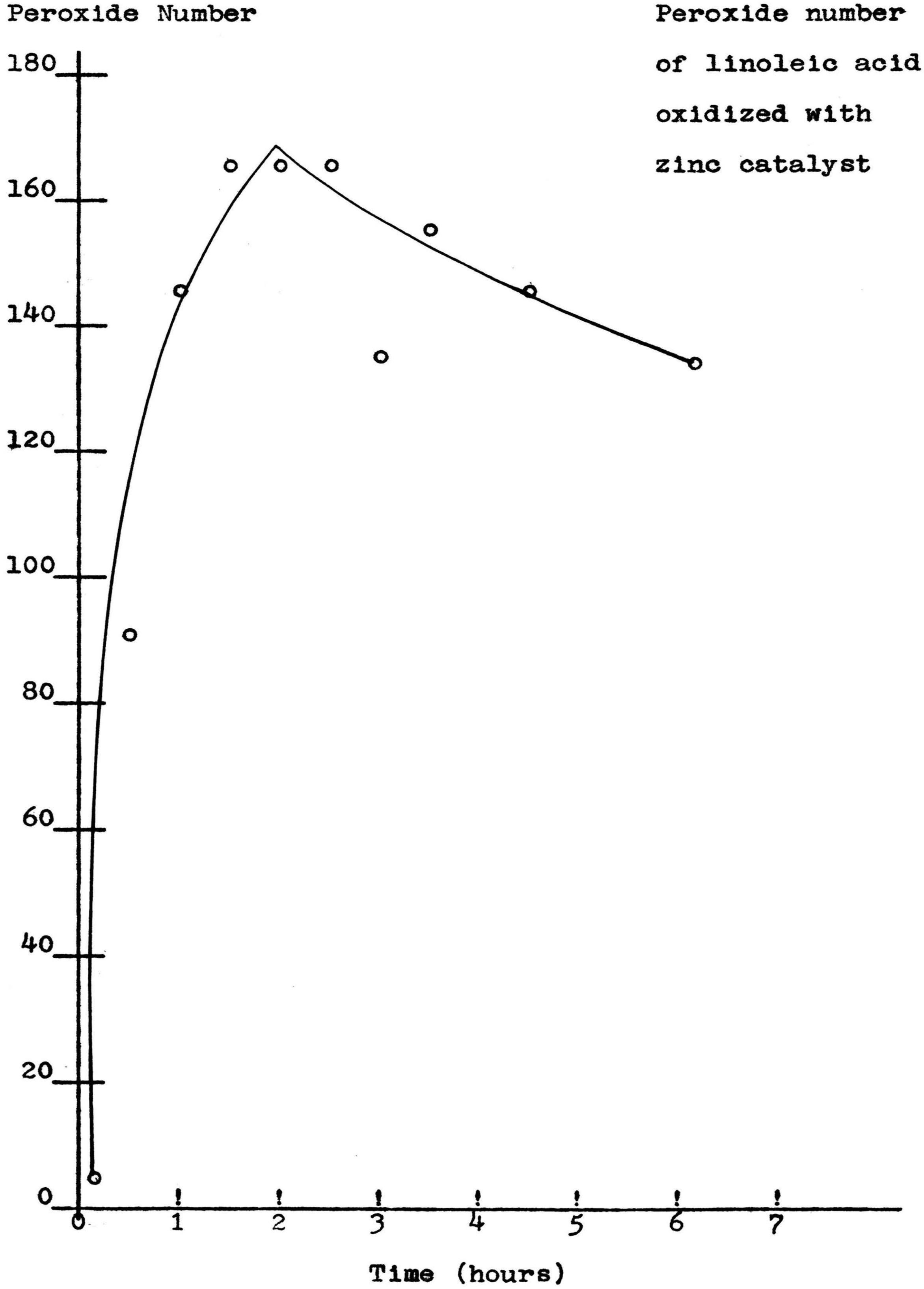
Peroxide number of linoleic acid oxidized with nickel catalyst

Figure 11



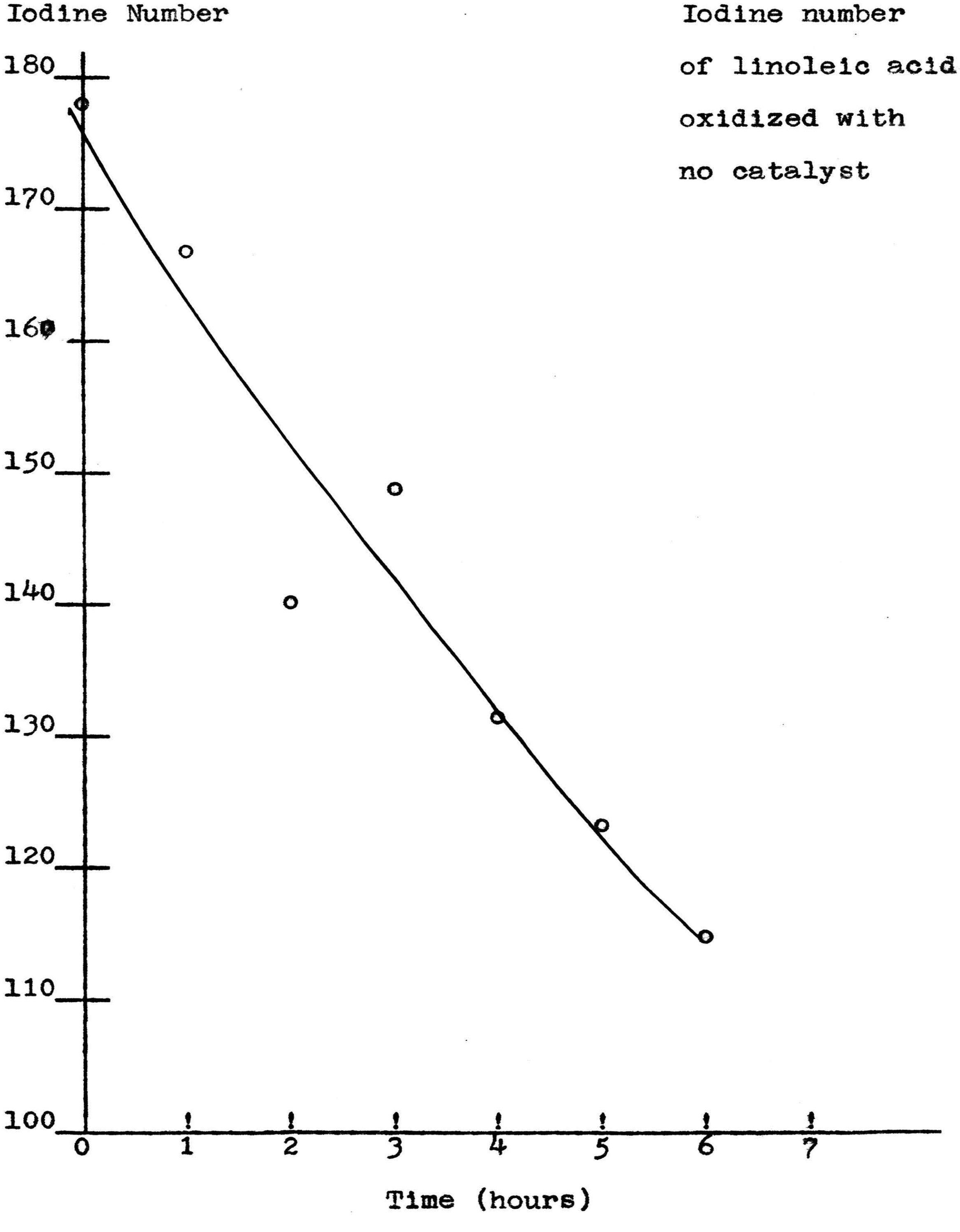
Peroxide number of linoleic acid oxidized with copper catalyst

Figure 12



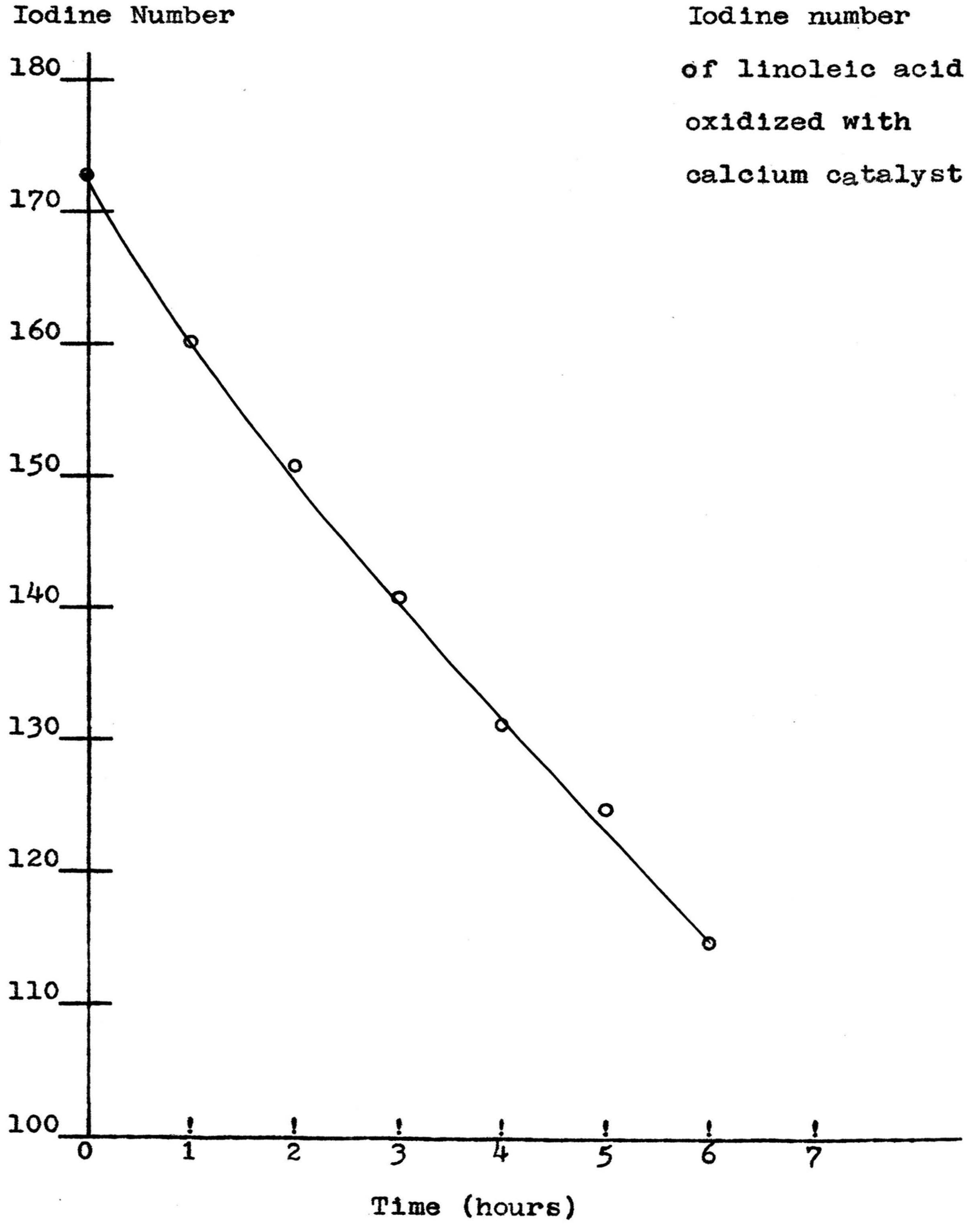
Peroxide number of linoleic acid oxidized with zinc catalyst

Figure 13



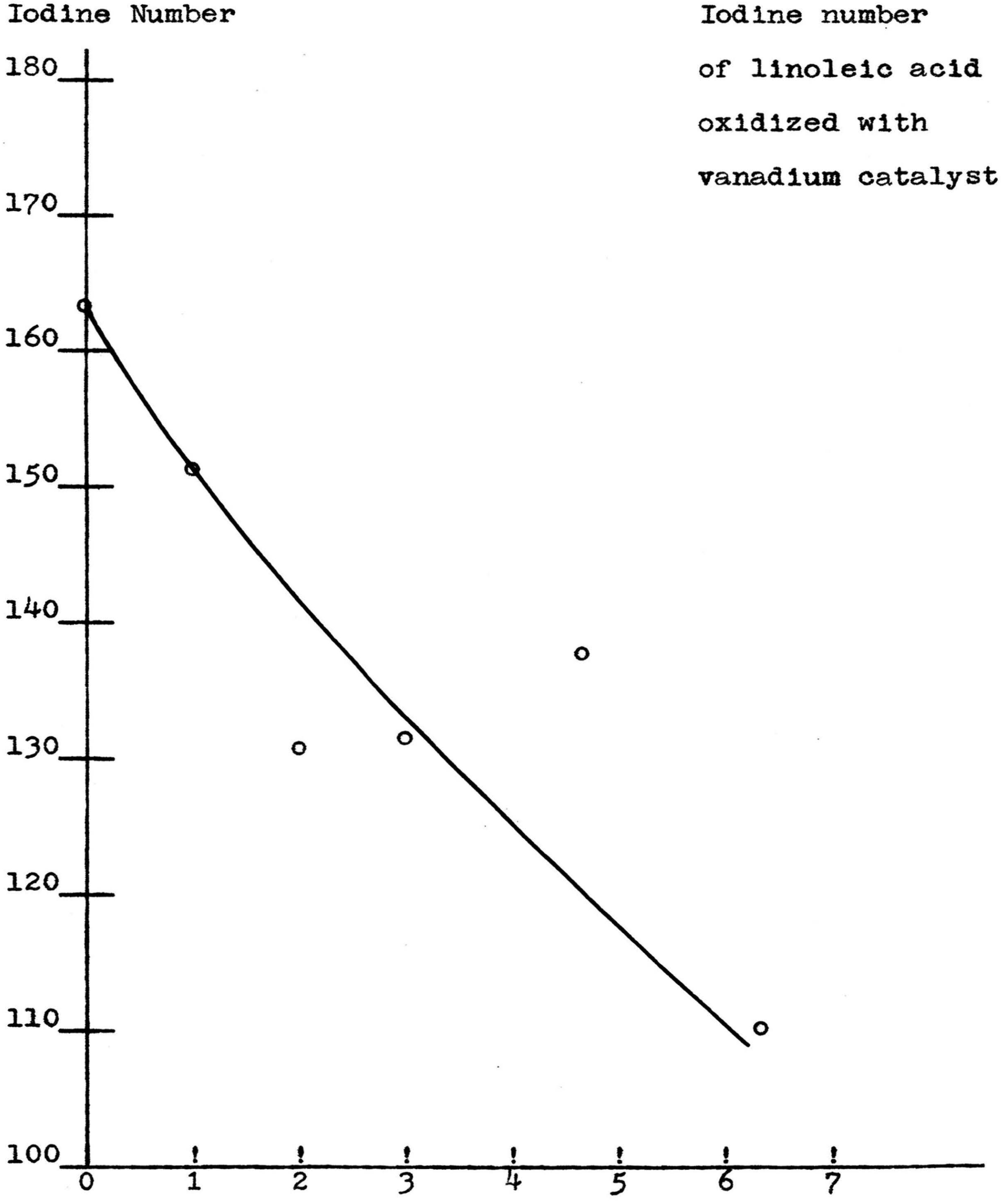
Iodine number of linoleic acid oxidized with no catalyst

Figure 14



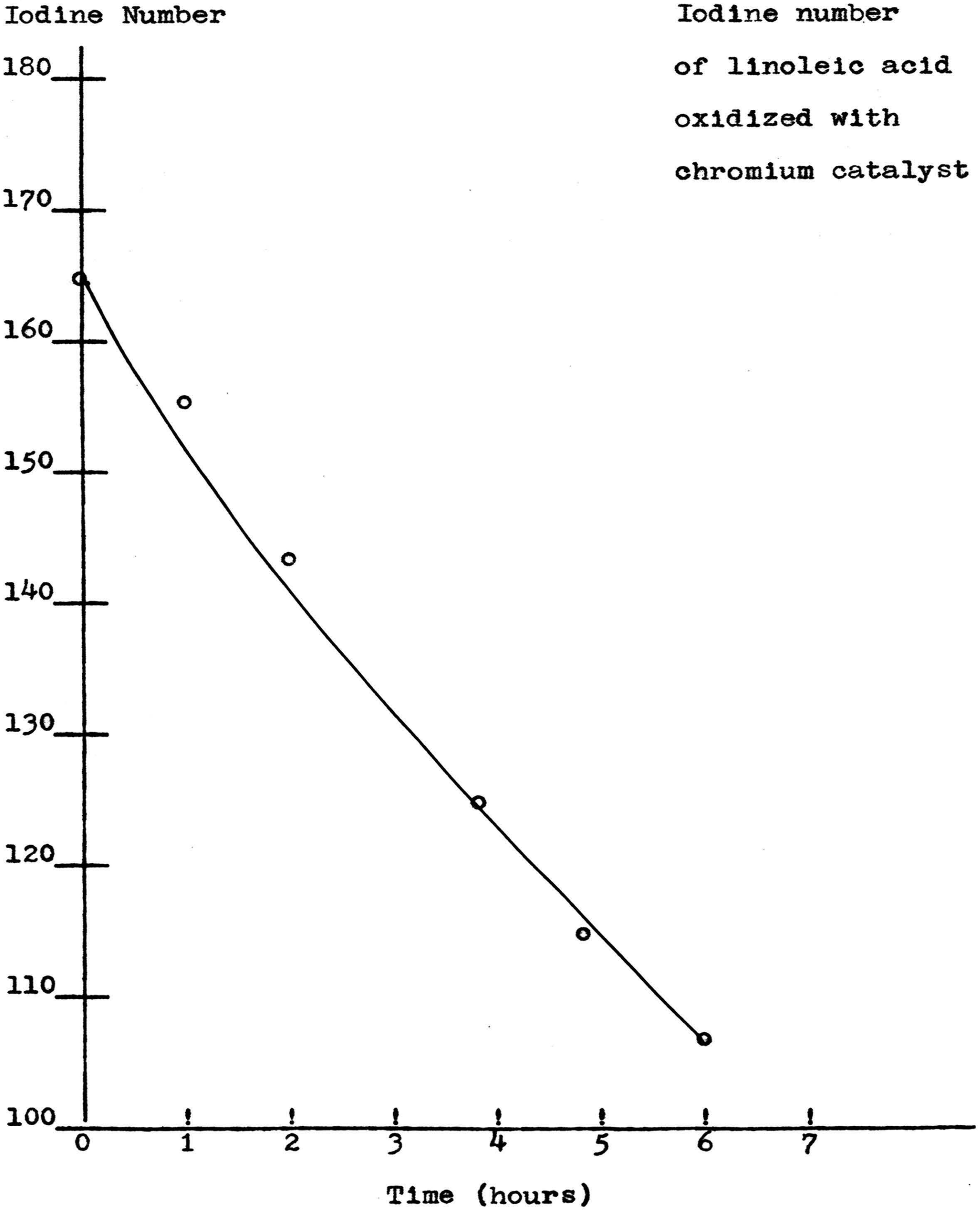
Iodine number of linoleic acid oxidized with calcium catalyst

Figure 15



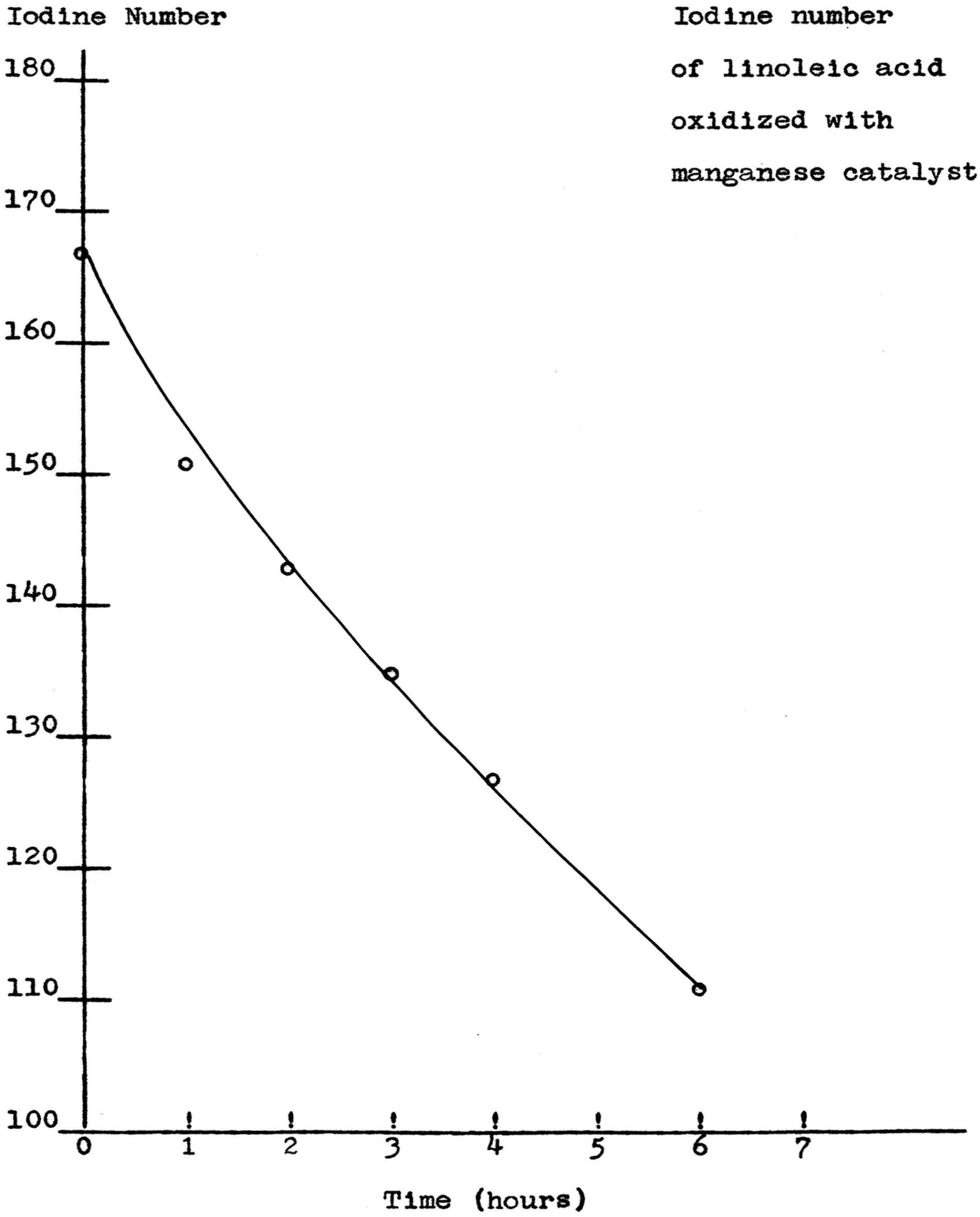
Iodine number of linoleic acid oxidized with vanadium catalyst

Figure 16



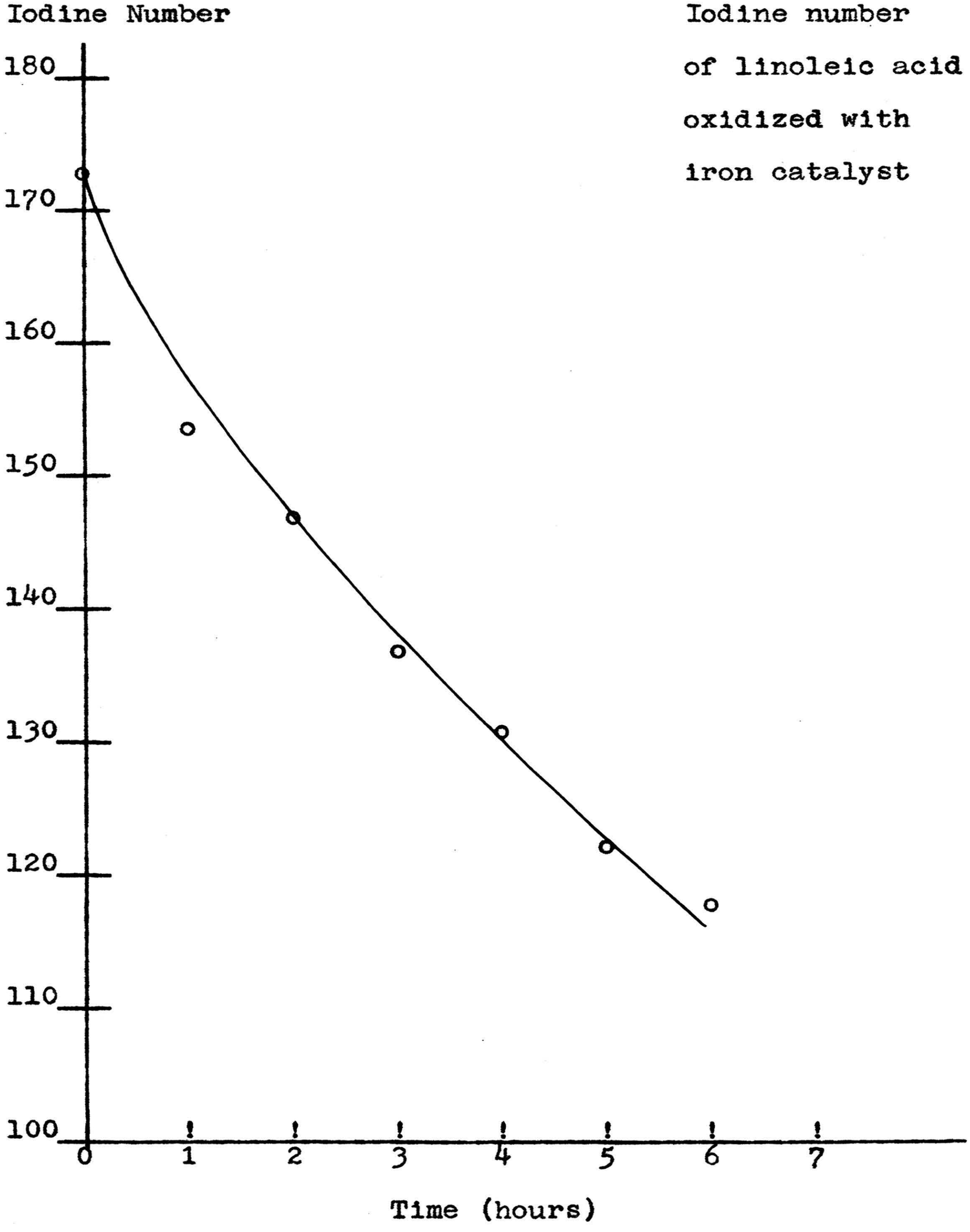
Iodine number of linoleic acid oxidized with chromium catalyst

Figure 17



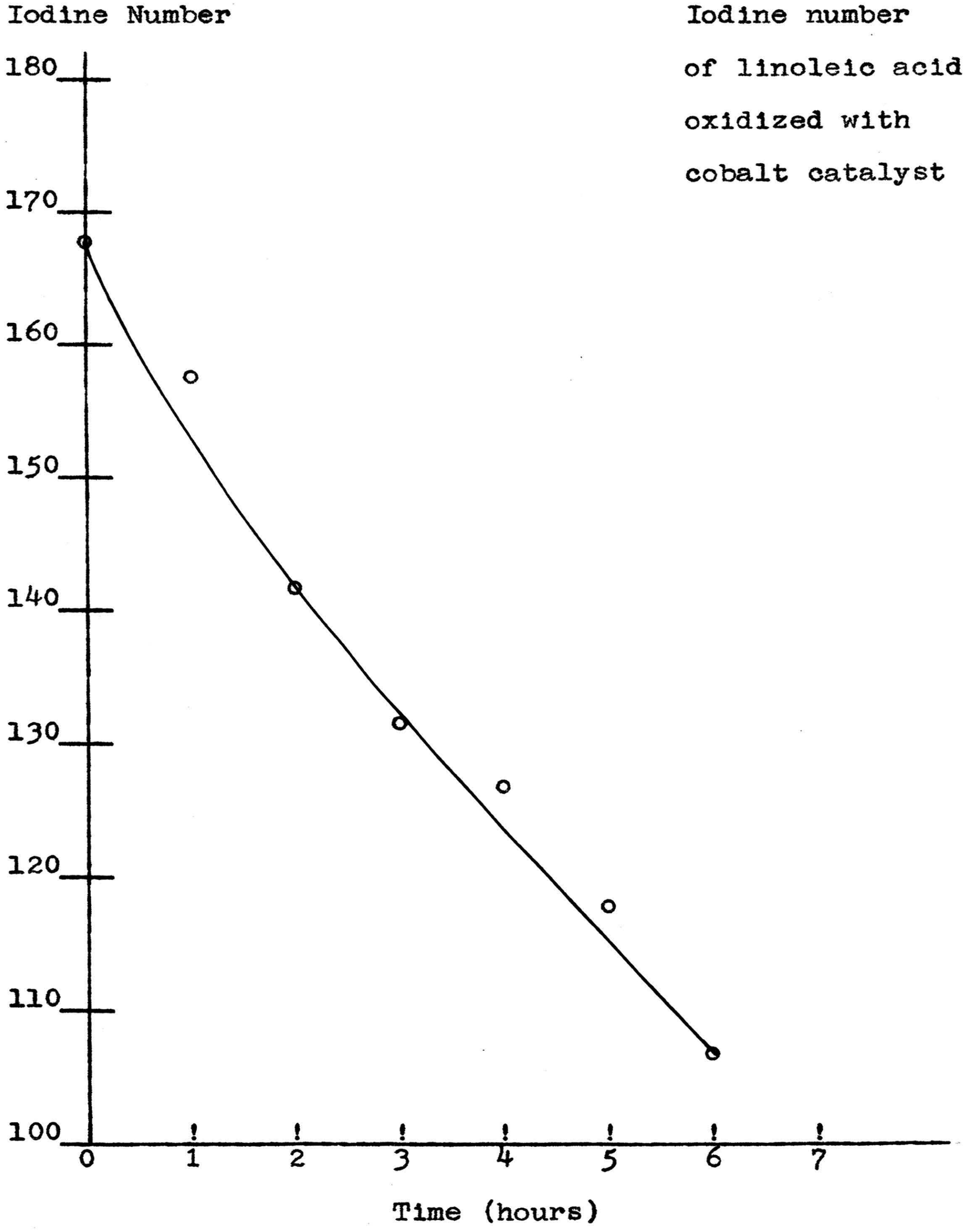
Iodine number
of linoleic acid
oxidized with
manganese catalyst

Figure 18



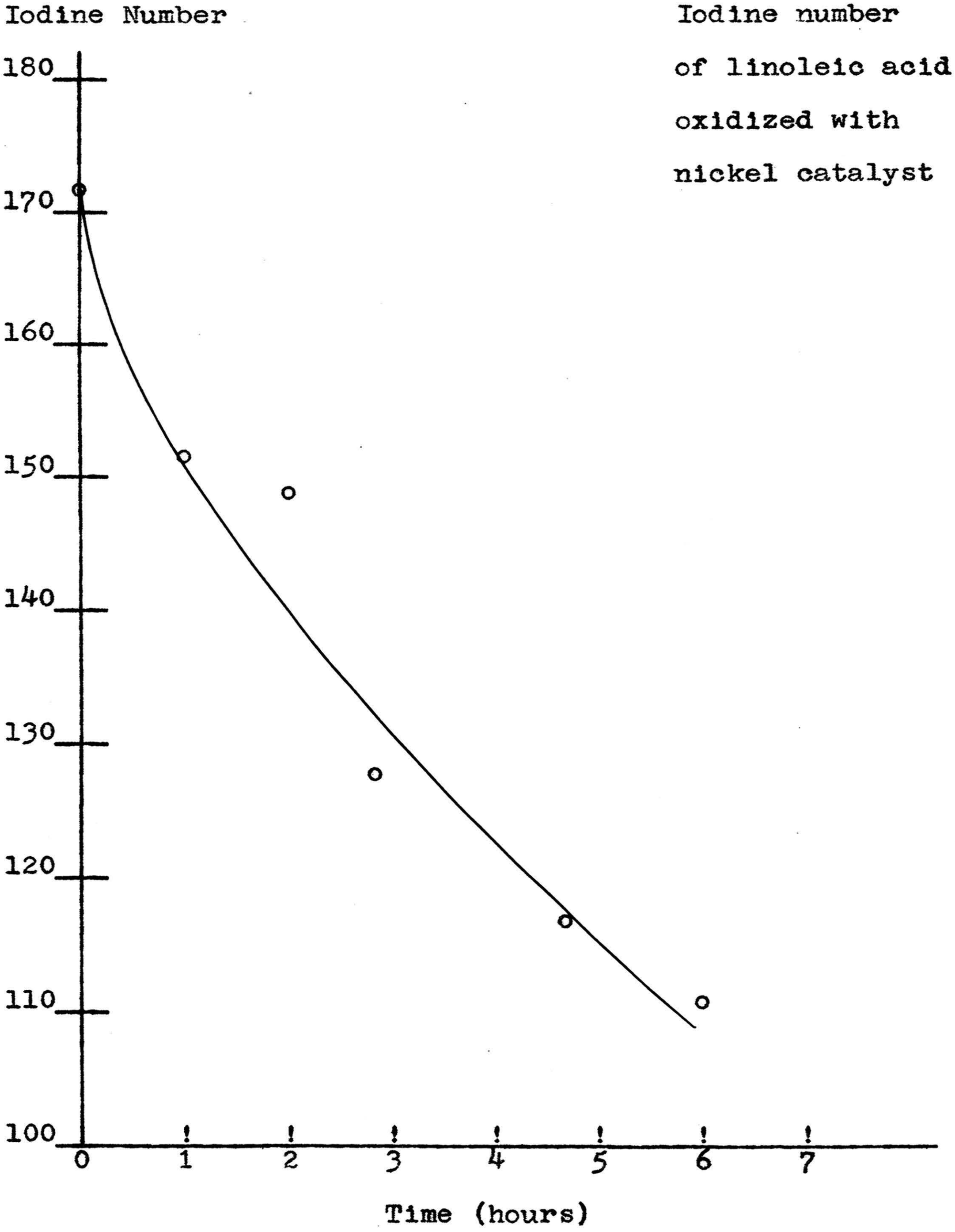
Iodine number
of linoleic acid
oxidized with
iron catalyst

Figure 19



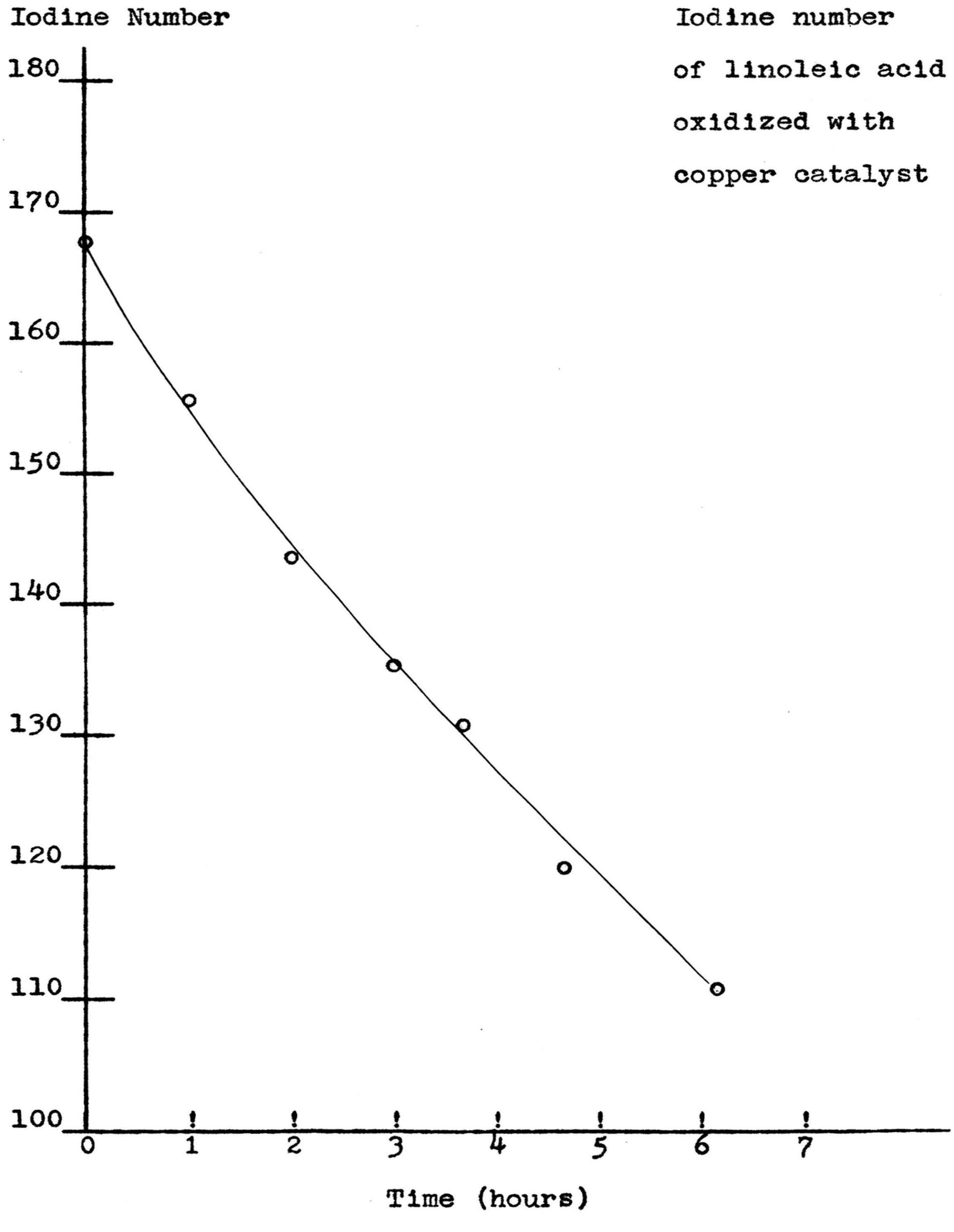
Iodine number
of linoleic acid
oxidized with
cobalt catalyst

Figure 20



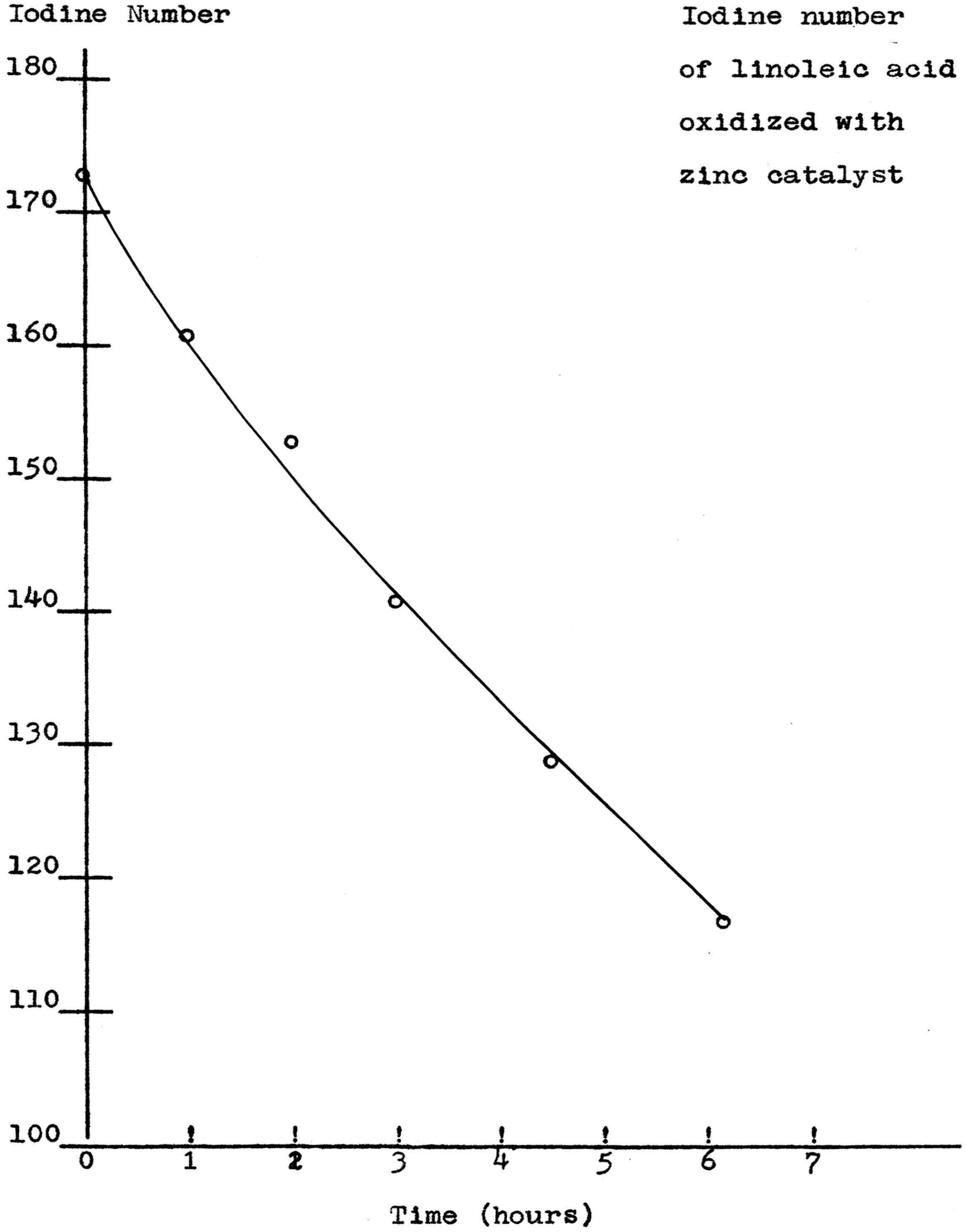
Iodine number
of linoleic acid
oxidized with
nickel catalyst

Figure 21



Iodine number of linoleic acid oxidized with copper catalyst

Figure 22



Iodine number of linoleic acid oxidized with zinc catalyst

Figure 23

Conjugation
of linoleic acid
oxidized with
no catalyst

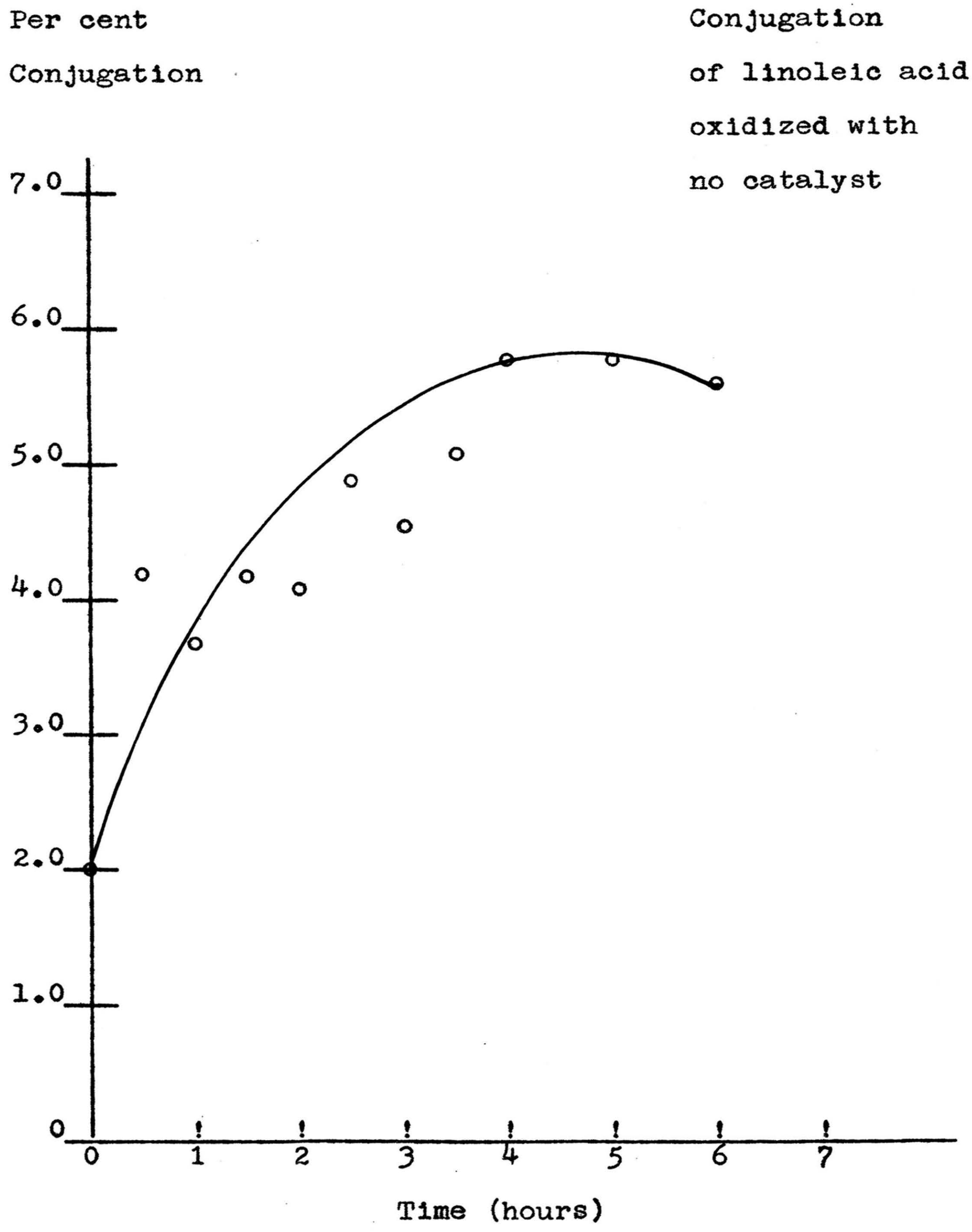
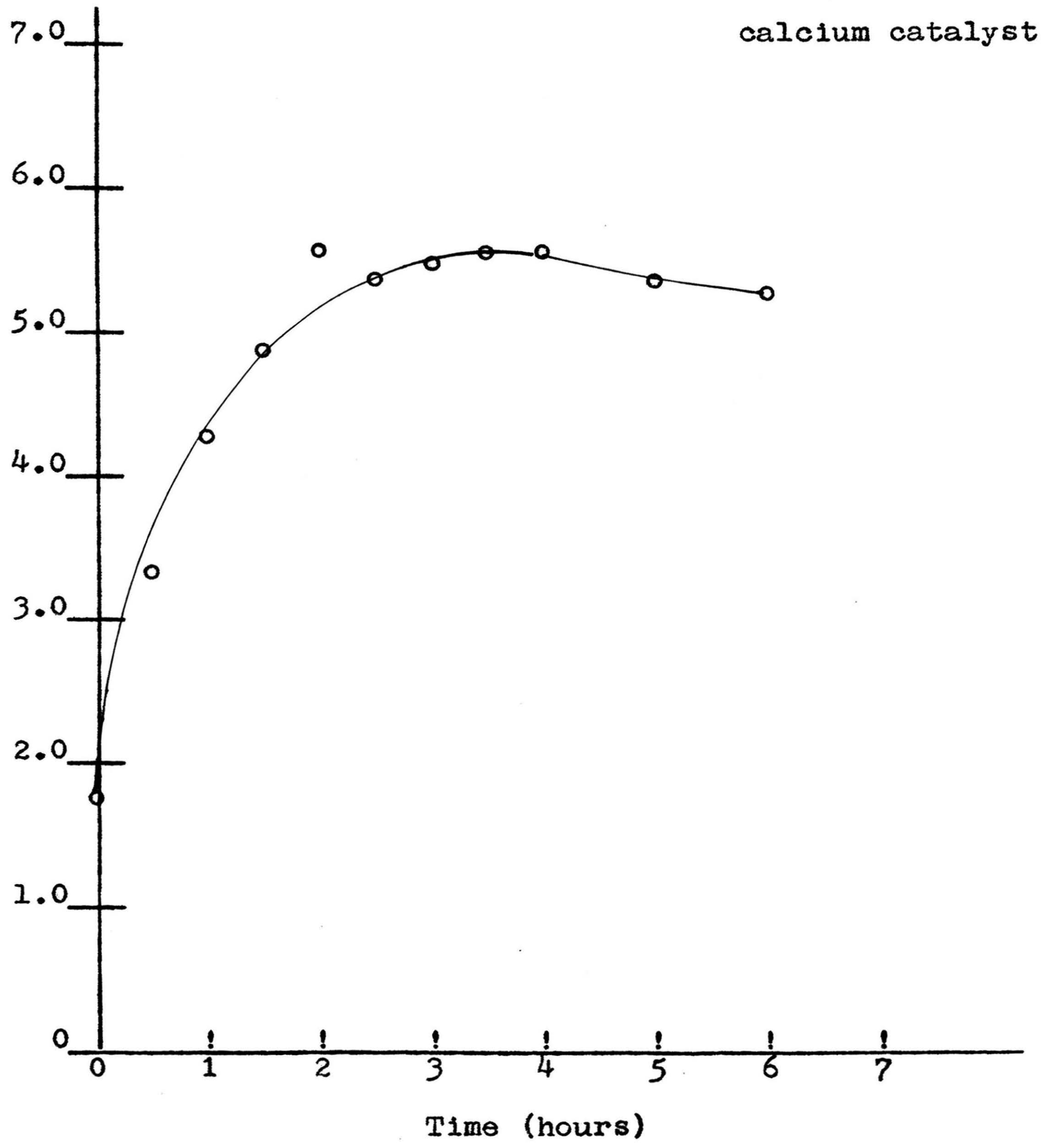
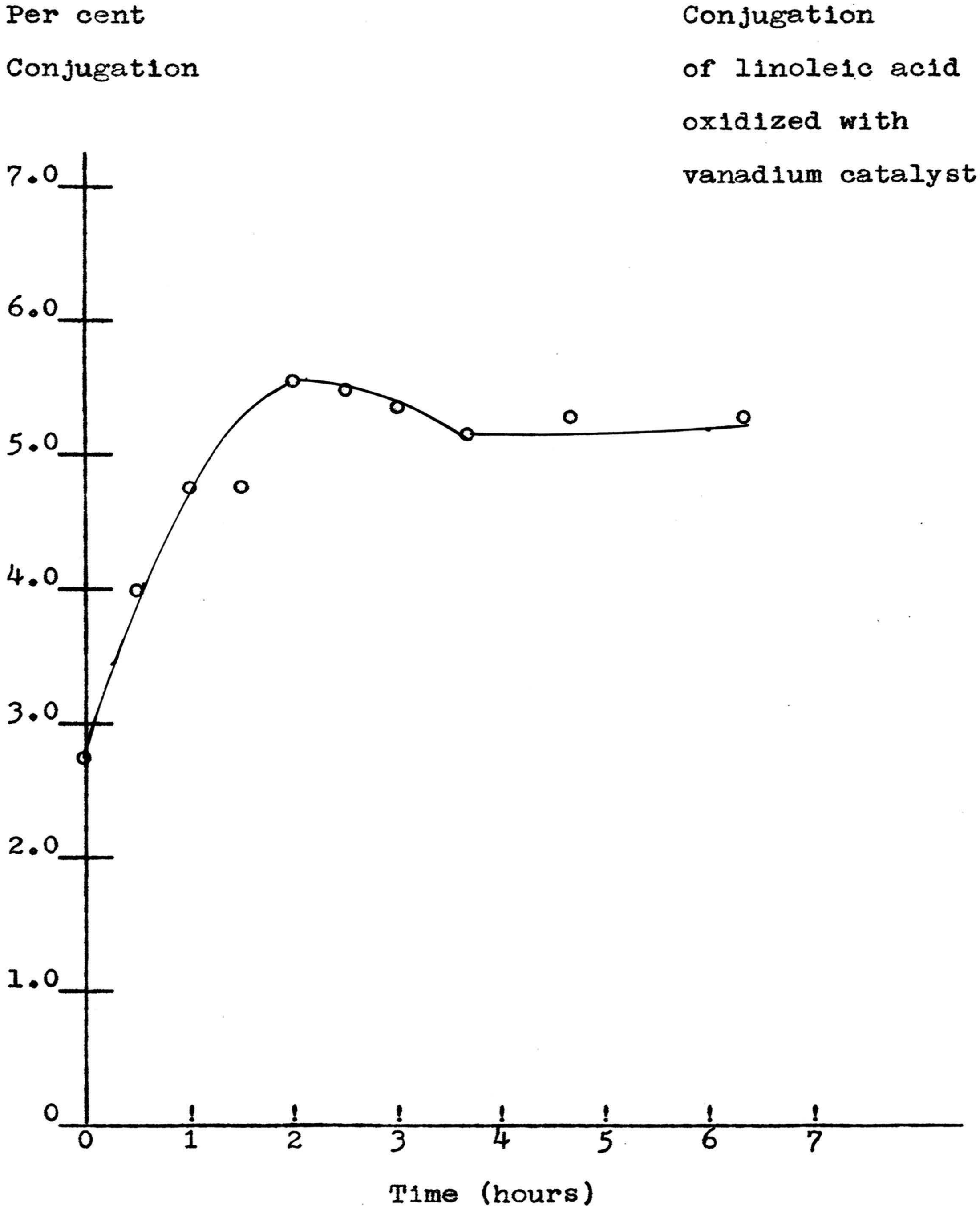


Figure 24



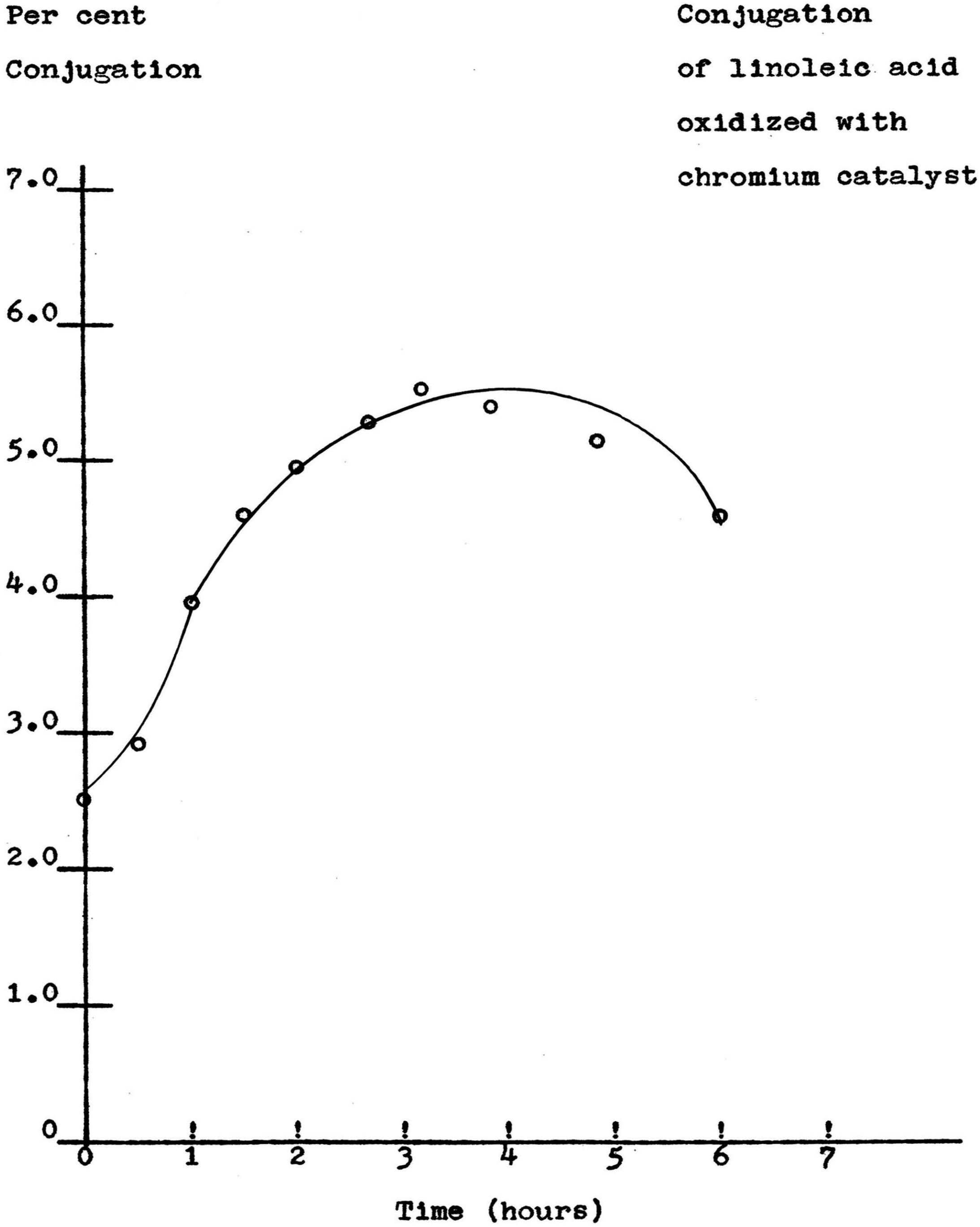
Conjugation
of linoleic
acid oxidized with
calcium catalyst

Figure 25



Conjugation
of linoleic acid
oxidized with
vanadium catalyst

Figure 26



Conjugation
of linoleic acid
oxidized with
chromium catalyst

Figure 27

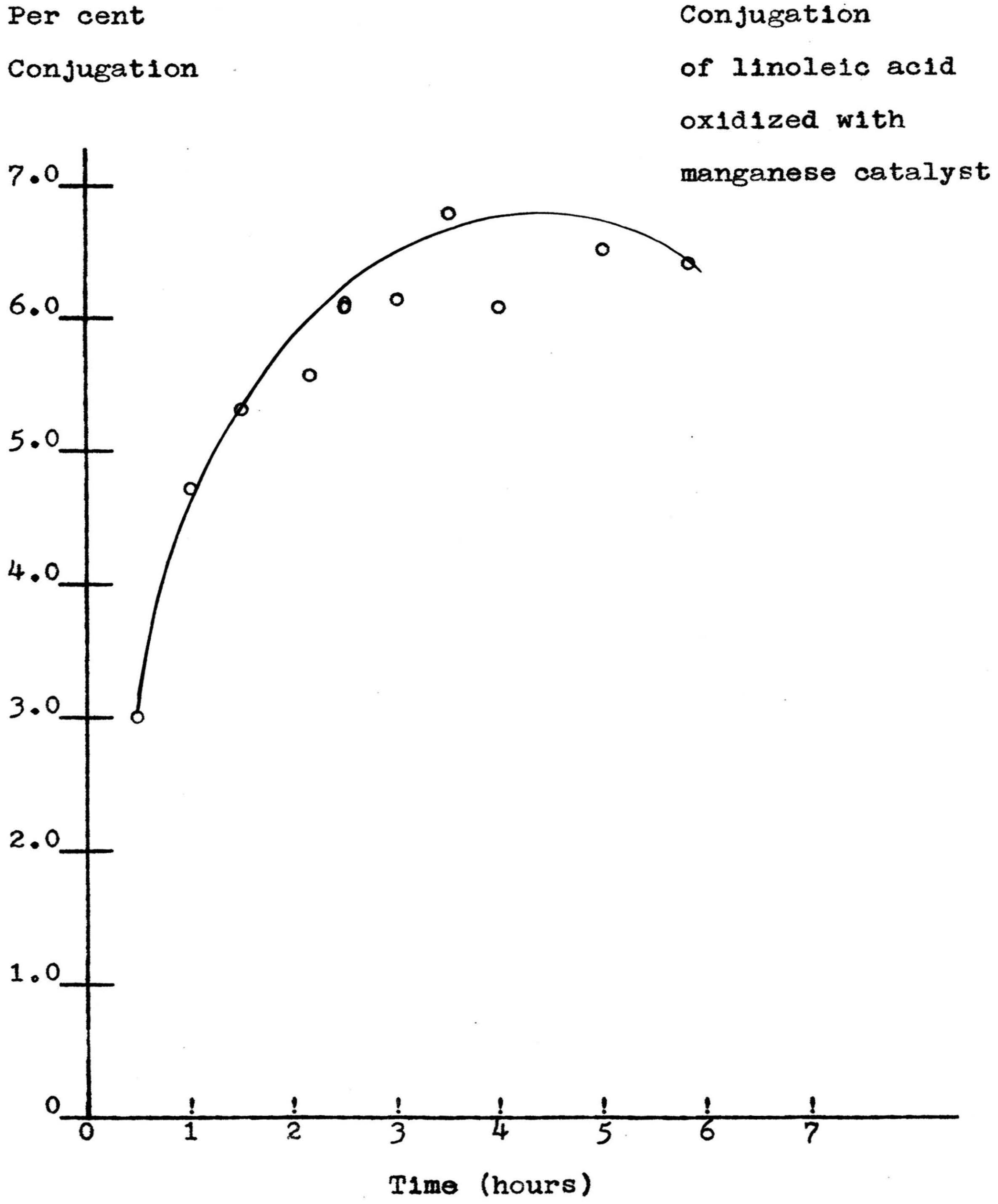

Per cent
Conjugation
Conjugation
of linoleic acid
oxidized with
manganese catalyst
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0
1
2
3
4
5
6
7
Time (hours)

Figure 28

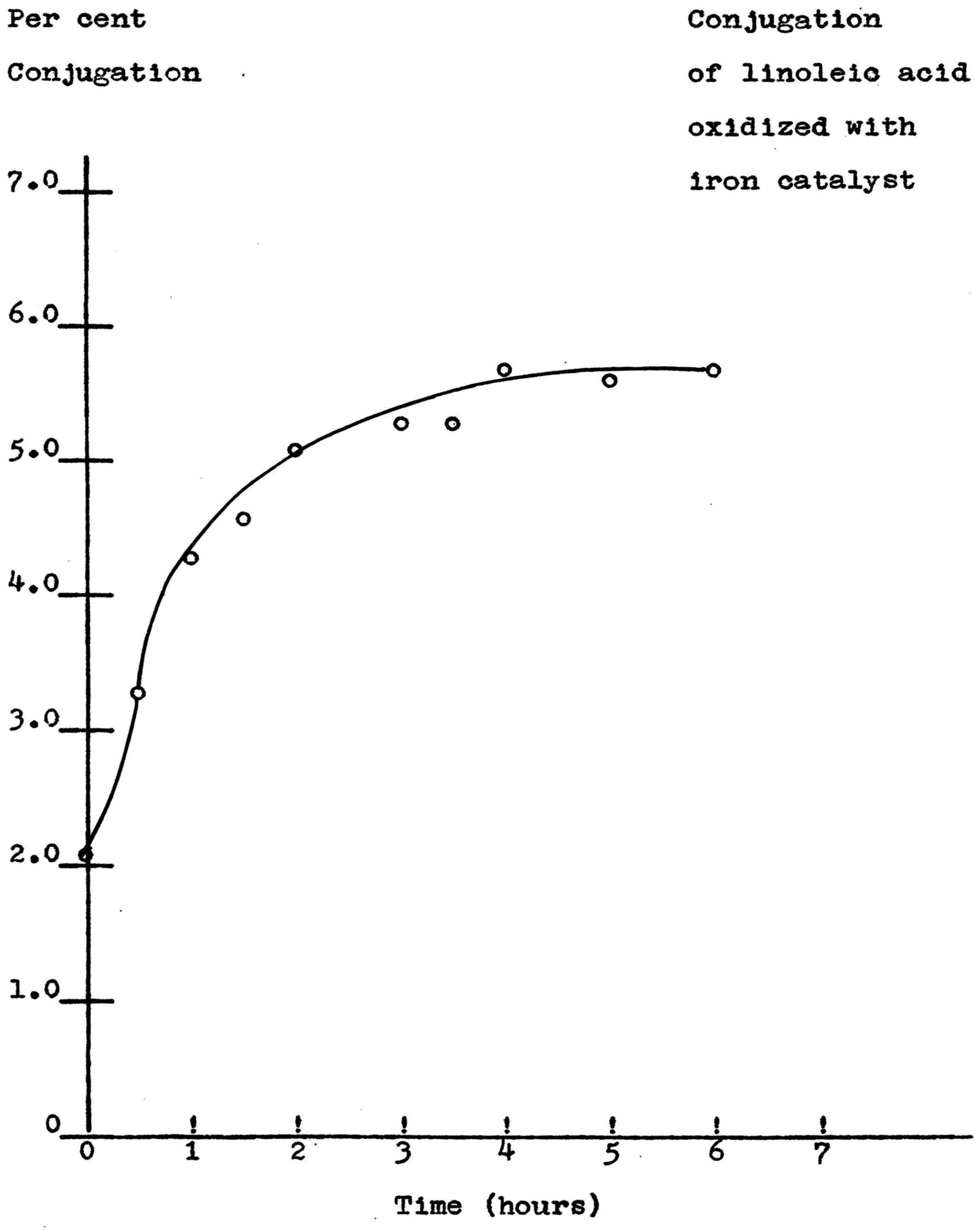
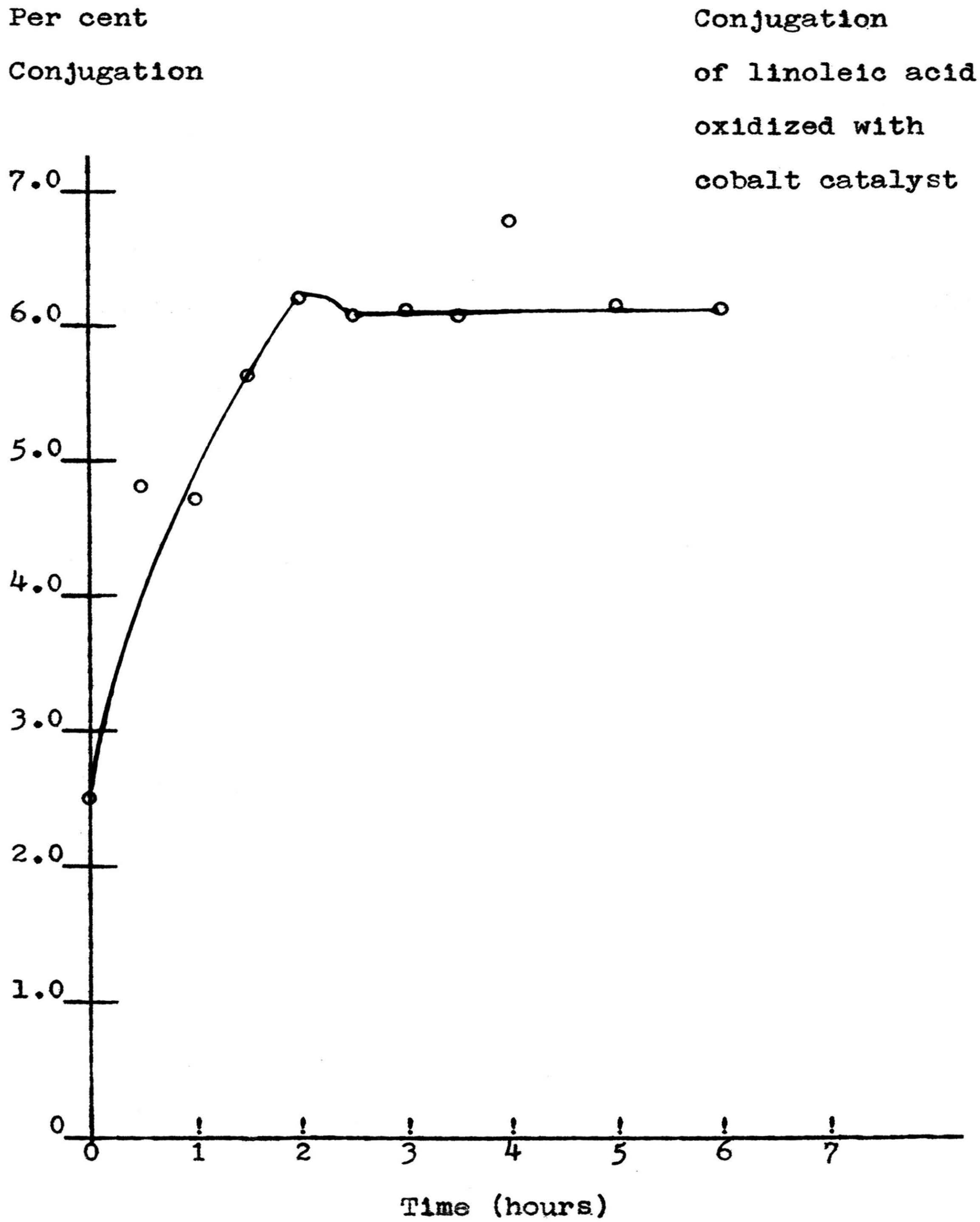
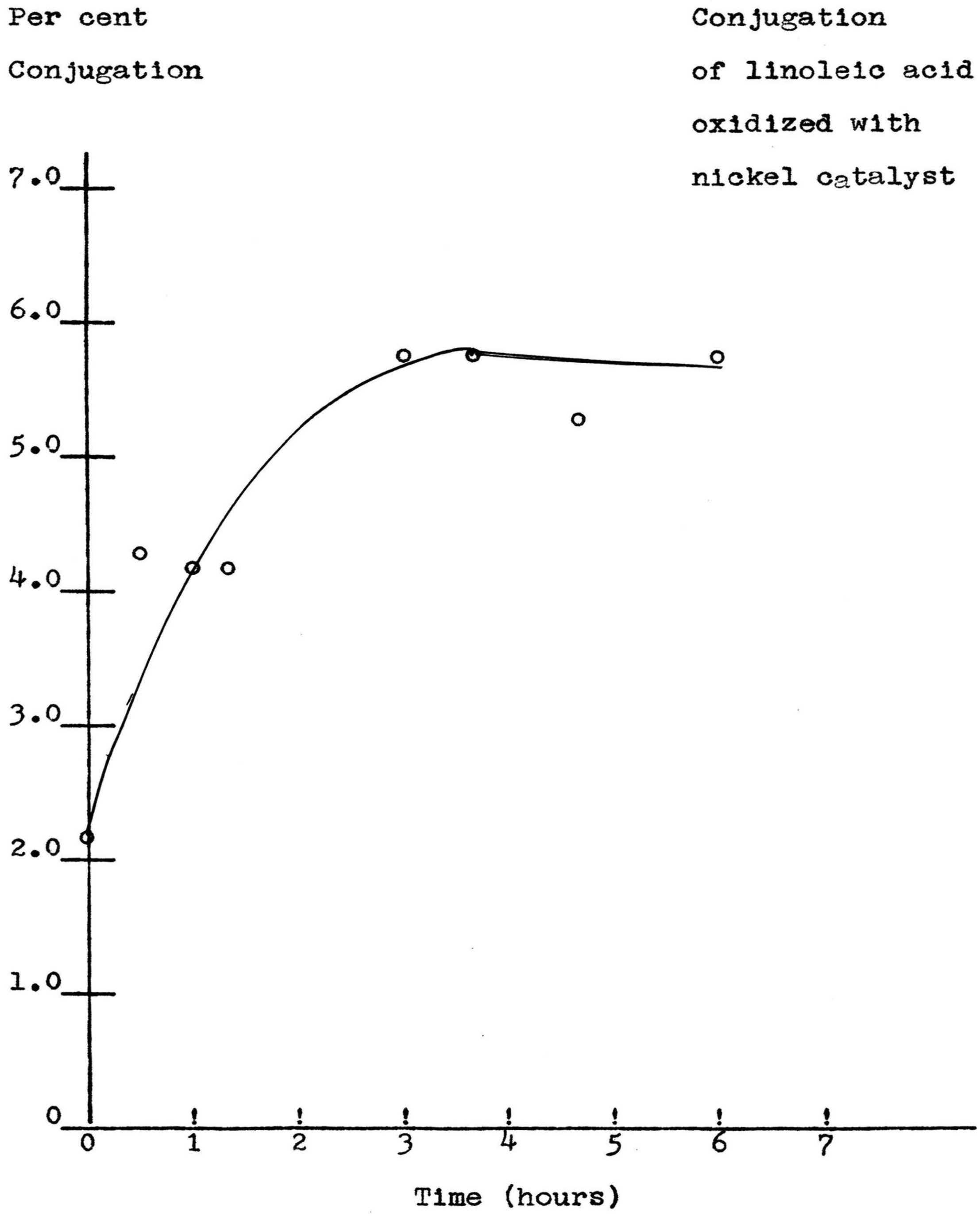

Per cent
Conjugation
Conjugation
of linoleic acid
oxidized with
iron catalyst
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
0
1
2
3
4
5
6
7
Time (hours)

Figure 29



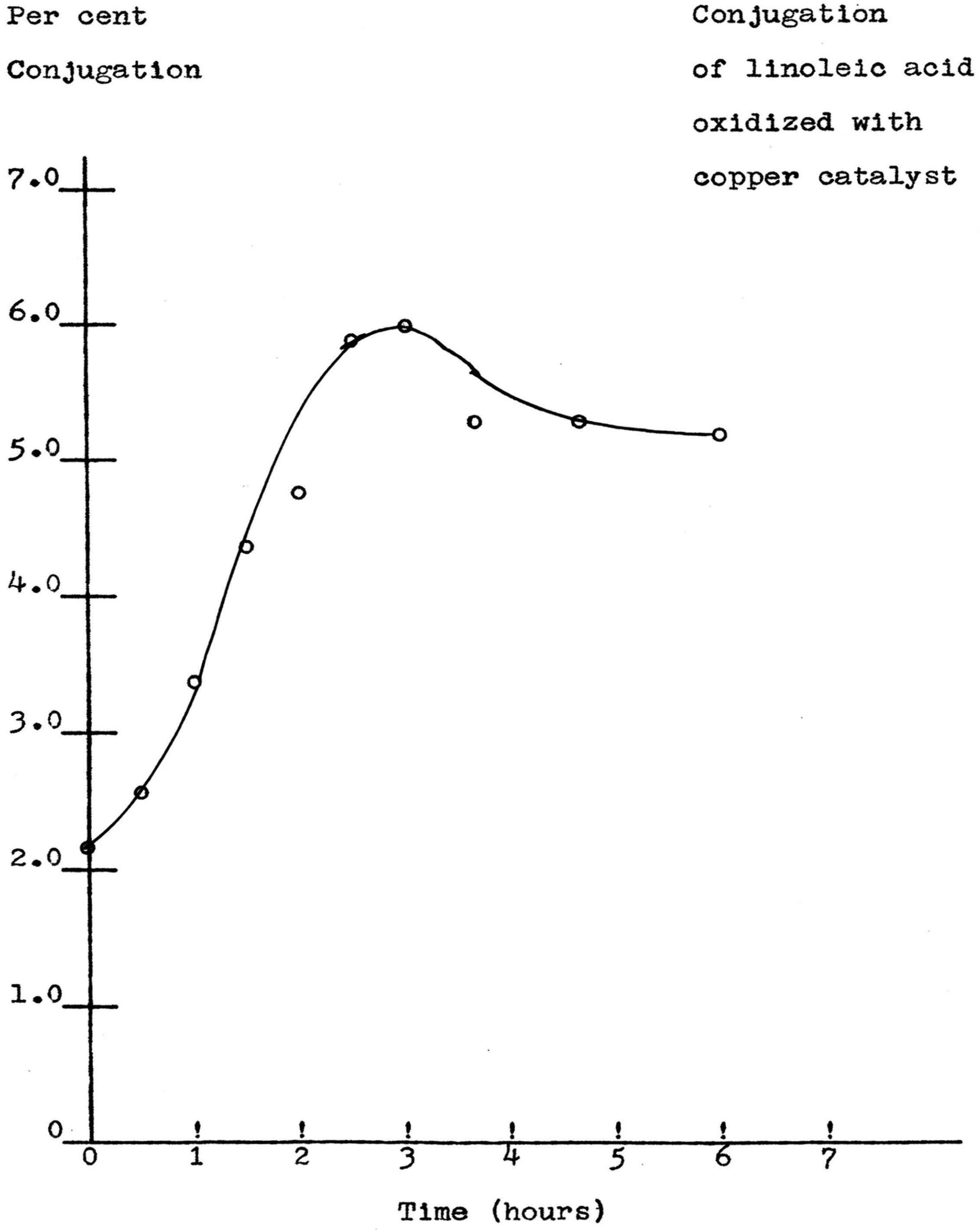
Conjugation
of linoleic acid
oxidized with
cobalt catalyst

Figure 30



Conjugation
of linoleic acid
oxidized with
nickel catalyst

Figure 31



Conjugation of linoleic acid oxidized with copper catalyst

Figure 32

A Comparison of the Maximum Peroxide Numbers of Linoleic Acid Oxidized with Various Catalysts.

```
Catalyst

  None XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

  Ca   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

  V    XXXXXXXXXXX

  Cr   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

  Mn   XXXXXX

  Fe   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

  Co   XXXXXX

  Ni   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

  Cu   XXXXXXXXXXXXXXXXXXXXXXX

  Zn   XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

       !         !         !         !         !
  -------------------------------------------------------
       0         40        80       120       160

                Peroxide Number
```

Figure 33

A Comparison of the Iodine Value Decrease of Linoleic Acid Oxidized with Various Catalysts.

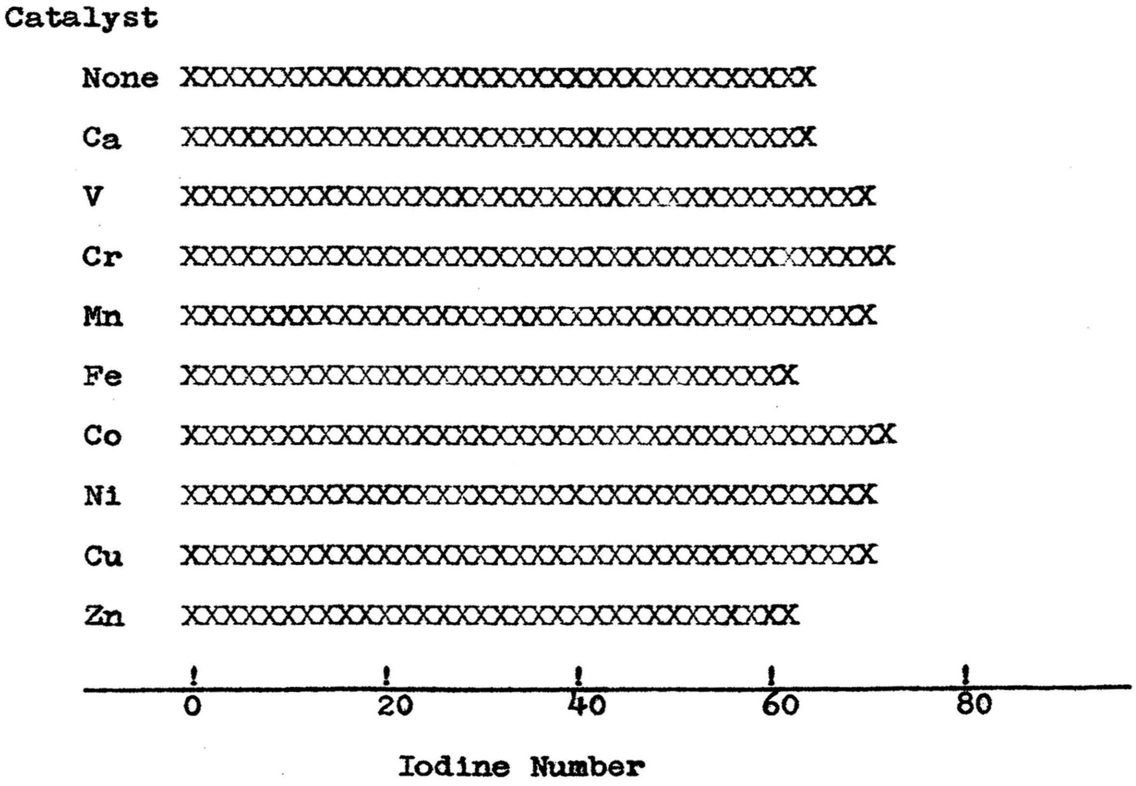


Figure 34

A Comparison of the Saponification Numbers of Linoleic Acid Oxidized with Various Catalysts.

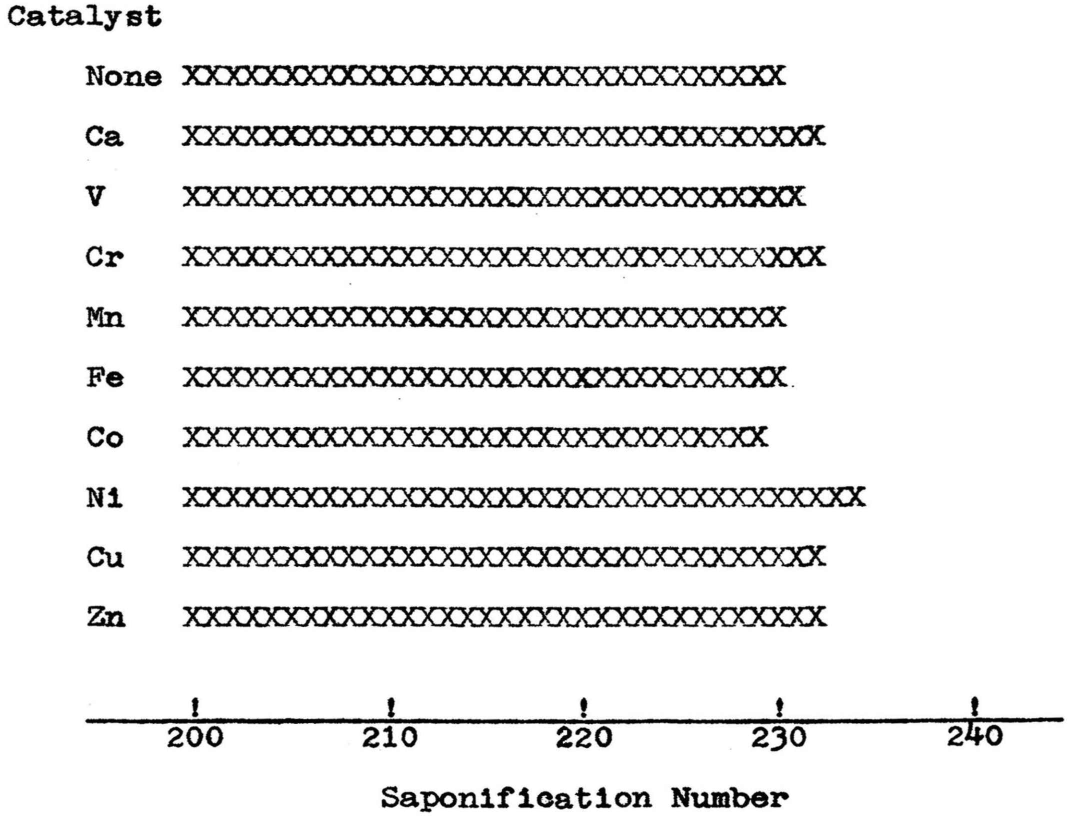


Figure 35

A Comparison of the Ester Numbers of Linoleic Acid Oxidized with Various Catalysts.

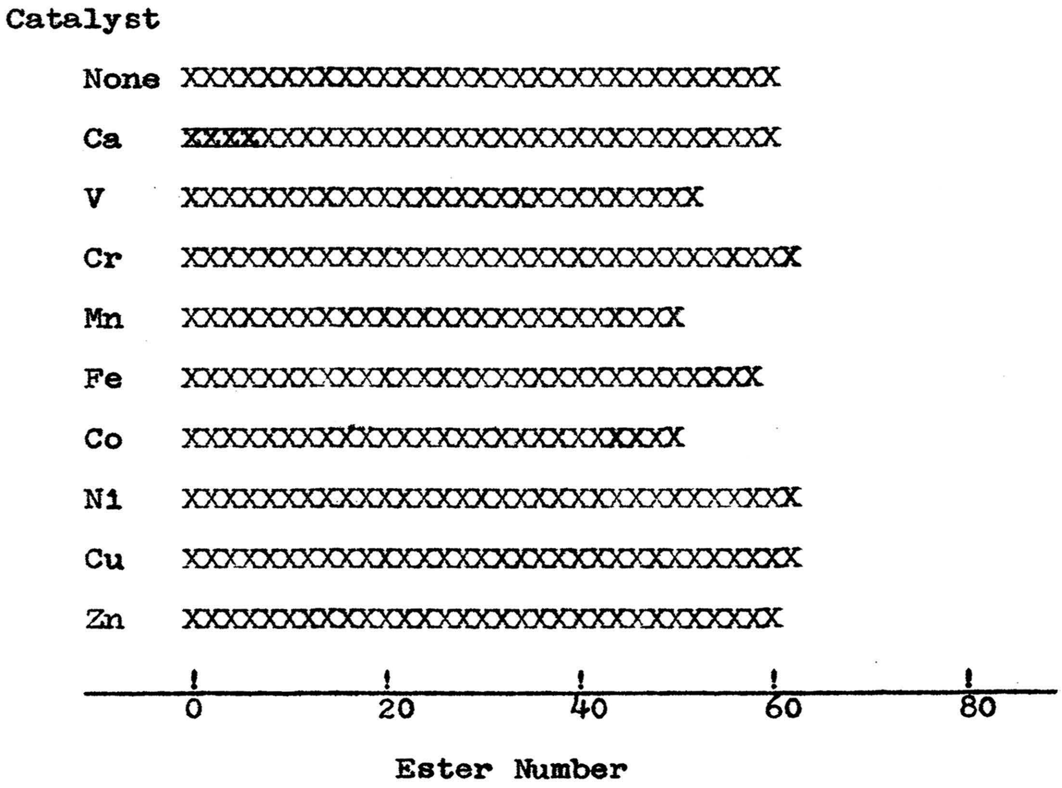


Figure 36

A Comparison of the Molecular Weights of Linoleic Acid Oxidized with Various Catalysts.

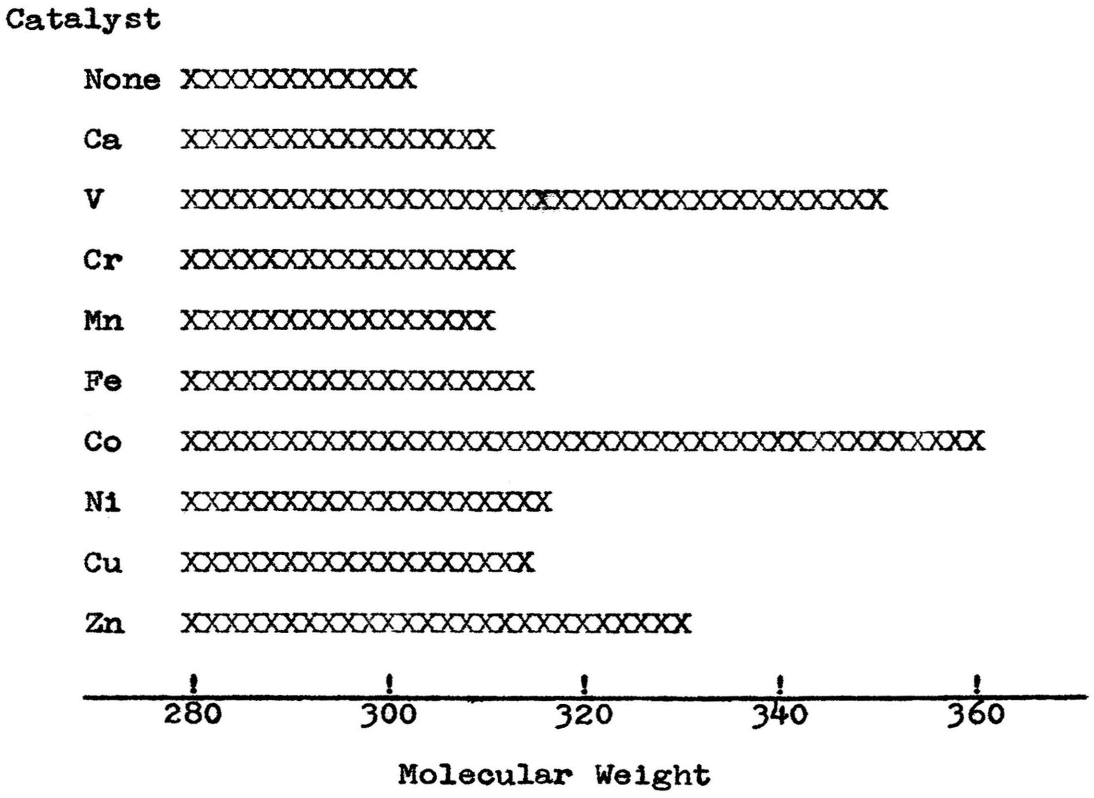


Figure 37

A Comparison of the Viscosities of Linoleic Acid Oxidized with Various Catalysts.

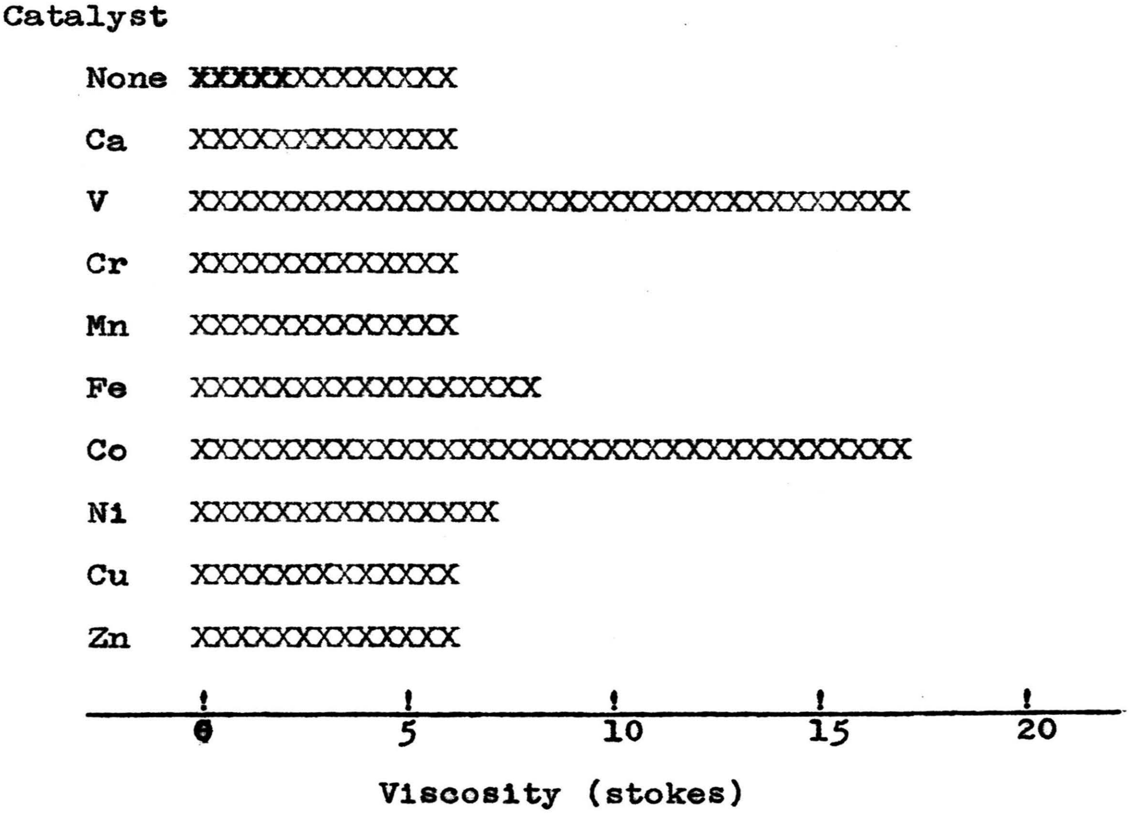


Figure 38

A Comparison of the Drying Times of Linseed Oil with Various Catalysts.

Catalysts

None XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Cs XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
V XXX
Cr XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
Mn XXX
Fe XXXXX
Co XX
Ni XXXXXXXXXXXXXXXXXXXXXXXXX
Cu XXXXX
Zn XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX

0 2 4 6 8

Drying Time (days)

DISCUSSION

The apparatus used in the oxidation of linoleic acid was designed in such a way that oxygen pressure, oxygen flow, agitation, and temperature could be kept constant. This was desirable in order that any differences in oxidation which might be found could be attributed to the metallic soaps rather than to some flaw in the experimental procedure.

Metallic soaps of uniform composition were chosen as catalysts. Several metallic linoleates were prepared in the laboratory and their activity compared with that of commercial metallic napthenates. The commercial soaps were more effective as catalysts and were chosen for that reason. Chromium and vanadium napthenates were prepared in the laboratory, so that their activity may not compare with that of commercial chromium and vanadium napthenates. However, since the soaps used for oxidation and for the drying time test were samples of the same batch of soap, comparisons between the effect of chromium and vanadium on drying time and on oxidation should be valid.

Linoleic acid was chosen as the material to be oxidized for several reasons. Oils which are chiefly esters of oleic acid dry very slowly (35), which means that studies of the oxidation of oleic acid would be of little value when compared with the drying time of linseed oil. Oils containing esters of linoleic or linolenic acid are the drying oils, and from that standpoint either would have been suitable. However, linolenic acid was unavailable commercially, so that linoleic acid was chosen. All of the oxidations were made on samples from the same bottle to prevent any errors due to differences in linoleic acid.

A careful study of the work done by Gunstone and Hilditch (36) on the oxidation of methyl linoleate was made before conditions for oxidation were chosen. It was considered undesirable to prolong the oxidation for more than 6 or 7 hours, and conditions were desired under which any peaks in peroxide content or conjugation could be noted within this time. Gunstone and Hilditch found that at 80°C. these peaks would be reached at approximately four hours. There was a drop in iodine number of 50 after 5.9 hours. In an attempt to duplicate these conditions, 80°C. was chosen as the temperature for oxidation. Their work also indicated that the mechanism of the oxidation of methyl linoleate was independent of temperature, so that comparisons between oxidation at 80°C. and drying times at room temperature had some meaning..

The analytical methods are those found in general analytical chemistry texts and in paint technology texts. There are more precise methods of analysis, but most of these methods are time consuming. As the time available for carrying out the work was limited, it was considered more valuable to make several determinations with less precise methods than to make only a few determinations very precisely. For the same reason, oxidations and analyses have not been made in duplicate. Making oxidations in duplicate would have meant that fewer metallic soaps could have been studied.

The results of the analysis of the products of oxidation have been presented in Tables 3-12 and Figures 3-38. The results of the oxidation indicate that polymerization is preceeding according to the mechanism suggested by O'Neill (37). The peroxide value rose to a maximum and then dropped. The conjugation built up to a small maximum, then dropped slowly and stayed nearly constant. The iodine number decreased rapidly for about three hours, and then at a slower rate for the remainder of the oxidation period. Acid number decreased, and saponification number, ester number, viscosity, and molecular weight increased.

With a few exceptions which will be discussed later, the driers could be divided into three groups on the basis of their effect on the oxidation of linoleic acid.

V, Mn, and Co	Low peroxide peaks, 70 units iodine number decrease, acid number-180, saponification number-230, ester number-50, conjugation peak-5.5-6.5%, viscosity-17, molecular weight-350.
Cu and Fe	Intermediate peroxide peaks, iodine number decrease-68, acid number-170, saponification number-230, ester number-60, viscosity-6 to 7, conjugation peak-5.5 to 6.0%, molecular wt., 315.

Ca, Cr, Ni, and Zn	High peroxide peaks, wide variation in iodine number decreases, acid number-170, saponification number-230, ester number-60, conjugation peak-5.5 to 6.0%, viscosity-6, molecular weight-310.

There were two metals which fail to fall in the group to which they were assigned in some respects. Manganese showed a viscosity and molecular weight which would place it in the third group. Zn showed a molecular weight which would place it in the first group, and also a very low conjugation peak. A white polymerized material which settled to the bottoms of tubes containing oxidized linoleic acid and zinc may explain the high molecular weight for zinc. This material was insoluble in methyl alcohol which may account for the low measured conjugation. No apparent explanation is available for the low molecular weight and viscosity of linoleic acid oxidized with manganese.

The results of the drying time test are shown in Figure 38. The results of this test indicate that the metals can be assigned to the same groups listed above.

The comparison of the results of oxidation of linoleic acid and the drying time tests indicates that the driers which decrease the drying time and increase the polymerization of linoleic acid to the greatest extent are those which allow the smallest buildup of peroxide content. This suggests, but is not proof, that the driers function by catalysing peroxide decomposition. The low peroxide content could also be caused by the drier catalysing both formation and decomposition of the peroxides.

If this were true, however, conjugation would be expected to increase to a greater extent than with no drier or with a poor drier. Following conjugation, the iodine number would be expected to decrease more rapidly. As the conjugated double bonds would then be oxidized to free acids or aldehydes, the saponification number would be expected to increase. This was not found to be true for the oxidation as carried out in this work. The increase in conjugation, increase in saponification number, and decrease in iodine number were nearly the same for all driers used. Thus, it seems that the driers must be catalysing the decomposition of peroxides.

Two possible mechanisms for the catalysis of peroxide decomposition of driers have already been presented. The overall result of the decomposition may be represented by the following equation:

$$ROOH + RH + RH \longrightarrow ROH + R\text{-}R + H_2O$$

This suggests that an increase in peroxide decomposition would lead to a greater hydroxyl formation, and, as a consequence, a greater ester number. The opposite was found to be true. Linoleic acid oxidized in the presence of metals which were good driers showed a smaller ester number.

The explanation for this may lie in the different intermediate products formed by the two mechanisms. In that proposed by Williamson (38),

$$ROOH + Co^{++} \longrightarrow Co^{+++} + RO* + OH^-$$

$$OH^- + Co^{+++} \longrightarrow *OH + Co^{++}$$

$$RO* + RH \longrightarrow ROH + R*$$

$$OH* + RH \longrightarrow H_2O + R*$$

with the possibility of the side reactions

$$RO* + R* \longrightarrow ROR$$

$$RO* + RO* \longrightarrow ROOR.$$

Thus, the decomposition of one ROOH is necessary to initiate the polymerization reaction. This ROOH is converted to ROH unless one of the side reactions takes place. From this mechanism it may be seen that the number of hydroxyl groups depends both on the number of peroxides which decompose and the possible side reactions these peroxides may undergo.

The mechanism suggested by Meuller (39) is

$$ROOH + Co^{++} \longrightarrow RO* + OH^- + Co^{+++}$$

$$ROOH \rightleftharpoons ROO^- + H^+$$

$$ROO^- + Co^{+++} \longrightarrow ROO* + Co^{++}$$

$$RO* + RH \longrightarrow ROH + R*$$

$$ROO* + RH \longrightarrow ROOH + R*$$

with the possibility of side reactions

$$RO* + R* \longrightarrow ROR$$

$$RO* + RO* \longrightarrow ROOR$$

and in this case

$$ROO* + R* \longrightarrow ROOR$$

Thus if this mechanism is the one by which catalysis is taking place, there is a greater probability of side reactions taking place and the number of hydroxyl groups formed might be expected to be smaller.

Films which contain driers are known to dry faster than films without driers, to have a lower oxygen content at any stage of polymerization, and to dry with a lower final oxygen content. These facts may also be explained by the peroxide decomposition theory. If polymerization is initiated by peroxide decomposition, the driers should then catalyse that polymerization. The decomposition of peroxides would also lead to drying at a lower oxygen content.

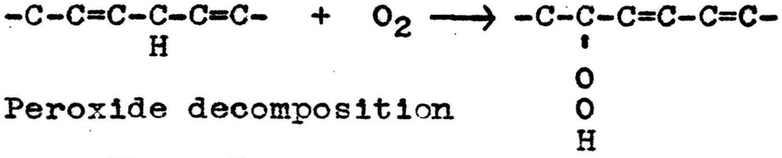
The fact that all the films with driers dried in a shorter time than films with no driers indicates that there may be some other way in which driers hasten film drying. They may exert some sort of orienting influence on the oil molecules, causing the film to dry in a shorter time. The data collected from these experiments is insufficient to make such a conclusion, however.

One of the aims of this work was to find the correlation between the effect of metals on driers and their electronic structure. The metals which acted as driers were those which exist in two or more oxidation states. However, chromium and nickel which also exist in two or more oxidation states did not catalyse drying. Also, certain aluminum compounds have been reported to greatly accelerate drying (40). No conclusions concerning the correlation of drying activity and electronic structure can be made at this time.

CONCLUSIONS

The mechanism of drying and drying catalysis which best agrees with data collected in this work and in other published work is that of peroxide formation followed by peroxide decomposition to form polymers. The function of the drier is to catalyse the peroxide decomposition. The mechanism can be represented by the following equations.

Peroxide formation



$$-C-C{=}C-\underset{H}{C}-C{=}C- \;+\; O_2 \longrightarrow -C-\underset{\underset{\underset{H}{O}}{O}}{C}-C{=}C-C{=}C-$$

Peroxide decomposition

Thermal

$ROOH \longrightarrow RO^{*} + {}^{*}OH$

Catalytic

$ROOH + Co^{++} \longrightarrow Co^{+++} + RO^{*} + OH^{-}$

$ROOH + Co^{+++} \longrightarrow Co^{++} + ROO^{*} + H^{+}$

Polymerization

$RO^{*} + RH \longrightarrow ROH + R^{*}$

$ROO^{*} + RH \longrightarrow ROOH + R^{*}$

${}^{*}OH + RH \longrightarrow H_2O + R^{*}$

$R^{*} + R^{*} \longrightarrow R-R$

with these side reactions possible

$RO^{*} + RO^{*} \longrightarrow ROOR$

$ROO^{*} + R^{*} \longrightarrow ROOR$

$RO^{*} + R^{*} \longrightarrow ROR$

$R^{*} + {}^{*}OH \longrightarrow ROH$

In addition there are other reactions which result in the scission of double bonds with the formation of aldehydes, acids, esters, and other oxygen containing compounds.

The metals which catalysed drying were metals which exist in two or more oxidation states. No conclusions can be drawn with respect to the correlation of their electronic structure with their drying activity.

SUGGESTIONS FOR FURTHER WORK

The results of this work have suggested several other research problems concerning this reaction. A few of these problems are listed in the following paragraphs.

1. An investigation of this type might be repeated under different conditions. One possibility would be the oxidation of linoleic acid or methyl linoleate in the presence of driers at room temperature. A second would be the thermal polymerization of methyl linoleate in the presence of driers. Finally, a similar series of oxidations might be made with the congeners of the driers used in this work.
2. An attempt might be made to follow the drying of linseed oil films at room temperature in the presence of the driers. Both chemical analysis and ultraviolet and infra-red absorption methods should be utilized to determine the kind and amounts of the different functional groups in the drying film.
3. An investigation of the structure of the drying film would be informative. This author is unfamiliar with the methods which might be used, but such a study could give an indication of any possible orienting influence the driers might have on the oil molecules of the film.

SUMMARY

1. Linoleic acid has been oxidized in the presence of a series of metallic soaps. These metals were those of the first transition series.
2. The drying time of linseed oil in the presence of these driers has been measured.
3. A comparison of the results of the oxidation of linoleic acid and the drying time of linseed oil was made. From this comparison, a mechanism for the catalysis of drying by driers has been suggested.
4. No conclusion could be made concerning the correlation of the electronic structure of the driers and their drying activity.
5. Suggestions for further work on this reaction have been made.

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VITA

The author was born October 11, 1929 at Eolia, Missouri. He was educated in the public schools of that city. He received an A. B. degree with a major in chemistry from Washington University, St. Louis, Missouri in 1952. After graduation, he served two years with the Army Chemical Corps. He entered the Missouri School of Mines as a graduate student in chemistry in 1954. During the school year 1954-55 he was employed as a graduate assistant, and was appointed Instructor in Chemistry in September, 1955. He was married to the former Sue Pollard Tucker in August, 1955.