

Yeast and malt require special care on the part of the manufacturers in order to meet these standards.

The additive effect of rope spores when present in a number of ingredients is a condition which must be given consideration. Such a condition, although highly improbable, could easily cause development of rope in bread.

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Rate of Linseed Oil Oxidation with Driers

Measurements of the rate of absorption of oxygen at 98.5° C. by linseed oil containing oleates and linoleates of cobalt, manganese, and lead are reported. The concentration of drier used is, in general, 0.1 per cent of metal based on total weight of oil. The length of the induction period is used as a basis of comparison. The linoleates of cobalt and manganese have the same induction periods as the oleates of these metals. The linoleates of cobalt and manganese have shorter induction periods than the linoleate of lead. Lead salts of phenylpropionic, salicylic, and acetic acids are, in contrast to the lead

salts of linoleic and oleic acid, not appreciably soluble in linseed oil and have longer induction periods. Decrease of metal content in the cases of cobalt linoleate and lead acetate causes an increase in the length of the induction period. Induction periods for linoleic and oleic acid at a concentration of 1.0 per cent in linseed oil are practically the same as that for raw oil. In the case of linoleic acid alone, the induction period is very short with a high oxygen absorption; in the case of oleic acid there is no pronounced induction period and very little oxygen is absorbed.

FOR many years it has been known that the presence of certain substances in linseed oil accelerates the rate of oxidation or "drying" of the oil. Such substances, commonly known as "driers," apparently act as catalysts in the oxidation process. Many investigations have been made to determine the controlling factors and the effectiveness of driers. A survey of about twenty-five articles in the literature shows that three general lines of procedure have been followed:

1. Determination of the time required for a known weight of oil to reach a definite temperature, when absorbed on cotton (Mackey oil tester) (6).
2. Determination of the amount of oxygen absorbed as a function of time:
 - a. Volume or per cent of oxygen absorbed by a film of oil of known weight on cloth or paper (3, 9, 10).
 - b. Volume or per cent of oxygen absorbed by a known weight of oil (shown by change in iodine number) when "blown" in bulk by a stream of conditioned air (5, 11).
3. Tests on increase in weight, plasticity, or hardness of a film of oil spread upon a surface in contact with air or oxygen (4, 12).

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The present investigation deals with the rate of oxidation of linseed oil with various driers at the temperature of boiling

water. This temperature was chosen because the rapid rate of oxidation at this point makes it possible for a given experiment to be completed within 1.5 or 2 hours. Rhodes and Chen's measurements (9) were made at 30° C.; Long and Chataway (5) worked at 160° C.

Apparatus and Materials

The type of apparatus used (Figure 1) was somewhat similar to that used by Rhodes and Chen (9):

It consisted of two similar units in which two measurements of the rate of oxidation (absorption of oxygen) could be made simultaneously. Each unit was made up of a 250-cc., wide-mouth bottle containing a small frame of copper wire upon which a strip of cloth exactly 2 × 10 cm. was stretched. A known weight of linseed oil or oil containing the drier was absorbed upon this cloth. A known weight (5 grams) of soda lime was placed in the bottom of the bottle to absorb carbon dioxide, water, and volatile fatty acids formed during the oxidation of the oil (2). The wide-

TABLE I. OXYGEN ABSORPTION BY VARIOUS DRIERS

Time, Min.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R
5	0.2	40.1	11.6	0.0	38.3	35.2	27.8	14.0	1.9	0.2	12.6	0.0	0.7	0.7	0.0	0.2	35.7	0.0
10	0.8	25.7	15.2	1.2	32.1	15.3	23.8	18.4	6.0	1.0	14.1	1.8	2.0	2.8	0.0	0.9	28.7	0.0
15	1.3	16.4	13.5	2.7	28.5	14.2	18.0	13.2	10.4	1.3	11.5	8.4	4.6	3.5	0.9	1.4	15.7	0.0
20	1.8	10.0	12.1	6.2	14.2	8.9	12.7	12.1	12.5	2.1	8.1	9.4	5.5	2.6	2.7	2.9	12.1	0.4
25	3.4	6.7	9.4	12.2	12.2	6.4	10.8	10.0	13.2	3.7	7.7	9.8	8.2	4.6	3.9	1.4	9.8	0.4
30	3.7	6.7	8.9	17.1	8.2	6.4	8.9	10.0	11.1	4.7	7.2	8.6	9.1	6.8	4.5	1.7	8.4	1.2
35	5.0	5.1	7.2	17.6	6.1	6.6	7.8	8.6	11.1	5.0	6.4	8.4	11.6	8.1	5.1	3.5	6.4	2.1
40	6.8	5.7	4.0	15.4	6.1	4.0	6.0	6.7	11.1	7.1	5.1	7.4	10.6	9.0	7.5	4.6	6.4	2.1
45	6.6	4.3	4.0	10.9	5.6	5.0	6.8	7.4	9.0	7.3	4.9	6.5	9.8	10.2	8.1	5.1	6.4	2.1
50	8.4	4.6	2.7	11.6	5.6	4.2	4.4	5.8	8.6	8.6	3.9	5.9	9.1	10.2	10.5	7.1	4.2	1.2
55	9.7	4.3	3.5	11.4	4.8	2.3	4.4	5.6	8.1	8.9	4.3	5.9	8.7	9.2	11.4	7.6	3.6	1.6
60	11.0	4.0	3.2	7.2	3.3	2.3	3.7	4.4	6.9	10.2	3.0	4.7	7.8	8.1	10.2	9.3	3.6	2.1
65	10.2	3.2	3.5	7.9	4.8	3.0	3.1	3.3	5.8	10.2	3.8	4.1	7.5	7.2	9.9	8.1	3.3	2.1
70	10.5	3.7	2.0	6.4	4.6	3.3	3.1	4.4	5.3	8.4	2.8	4.9	6.8	7.2	9.6	9.1	2.8	2.1
75	9.2	4.5	2.5	6.9	2.3	3.3	3.1	4.2	6.2	8.6	4.1	6.1	5.5	6.6	8.1	8.8	3.6	3.3
80	8.9	2.8	2.2	0.9	2.8	1.9	3.1	4.4	3.2	8.4	2.4	3.3	5.2	5.2	7.8	8.6	2.8	2.1
85	8.7	2.8	2.0	4.9	3.5	1.9	2.9	2.8	4.4	8.1	2.8	3.3	5.0	6.1	7.2	7.8	2.5	1.2
90	7.4	2.8	1.7	4.7	2.5	1.9	2.0	2.8	4.2	8.1	2.6	2.9	4.6	4.4	6.9	7.4	2.3	0.8

^a A, raw oil; B, cobalt linoleate (0.1% Co); C, cobalt linoleate (0.01% Co); D, cobalt linoleate (0.001% Co); E, cobalt oleate (0.1% Co); F, manganese linoleate (0.1% Mn); G, manganese oleate (0.1% Mn); H, lead linoleate (0.1% Pb); I, lead oleate (0.1% Pb); J, raw oil; K, lead acetate (1.0% Pb); L, lead acetate (0.1% Pb); M, lead salicylate (0.1% Pb); N, lead phenylpropionate (0.1% Pb); O, linoleic acid in oil (1.0%); P, oleic acid in oil (1.0%); Q, linoleic acid (pure); R, oleic acid (pure).

mouth bottle was connected by means of a rubber stopper and capillary tubing to a Bunte buret enclosed in a water jacket and to a leveling bulb containing mercury. The rubber stoppers and connections were sealed with de Khotinsky cement. The two units assembled side by side were connected in parallel to a storage bottle containing oxygen. Two flasks were placed in the oxygen feed line. The first flask was empty and served as a trap; the second flask contained concentrated sulfuric acid which was used to dry the oxygen.

A metal hot water bath fitted with a constant leveling device surrounded the two bottles and could be raised or lowered by chains and pulleys (5). The temperature could be maintained fairly constant at 98.5° C. (maximum 99°, minimum 98° on different days) by allowing a very small stream of water to flow through the bath. In order to ensure uniform heating, the bottles were not allowed to come in contact with the bottom of the water bath.

The linseed oil used was a fresh (unboiled) commercial product. The oleic acid used was taken from a Kahlbaum sample. The "linoleic acid" used was of the best quality available. The iodine number of this sample was 183.9. It was found to contain linolenic acid by a qualitative colorimetric method proposed by Martin (7). Since the purpose of these experiments was to prepare driers of a high degree of unsaturation, this material was used, although other more saturated acids may have been present in the sample. The difficulties involved in preparing linoleic acid of high purity (more than 81 per cent) were shown recently by Brown and Stoner (1). The oxygen used was 99.5 per cent pure and was taken from the laboratory supply of compressed oxygen.

Preparation of Driers

Lead, manganese, and cobalt oleates and linoleates were prepared as follows: An alcoholic solution of the acid was neutralized by means of an alcoholic solution of potassium

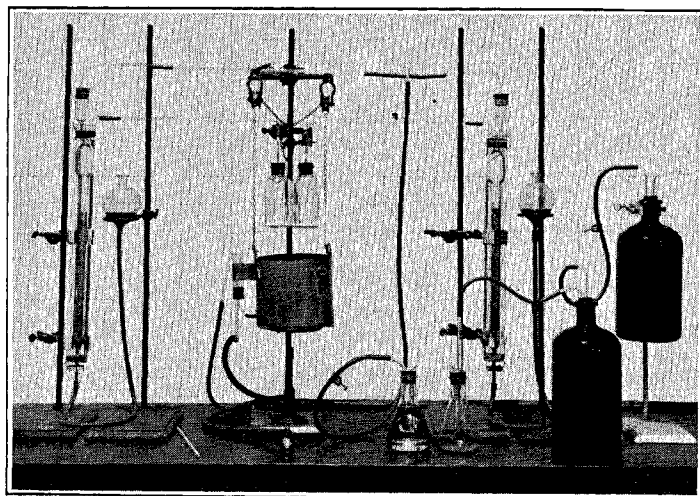


FIGURE 1. PHOTOGRAPH OF APPARATUS

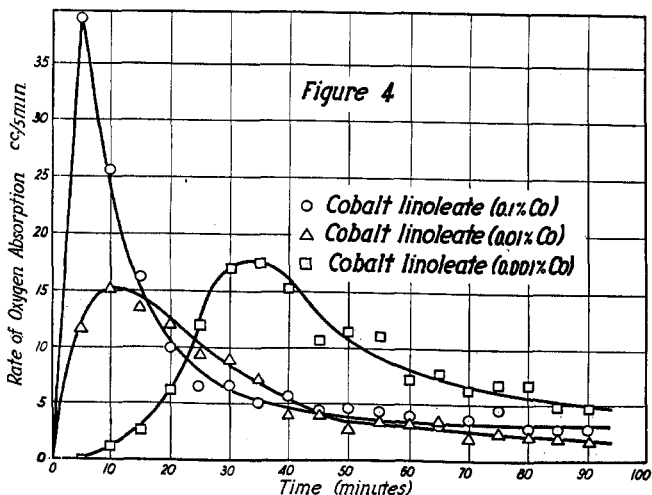
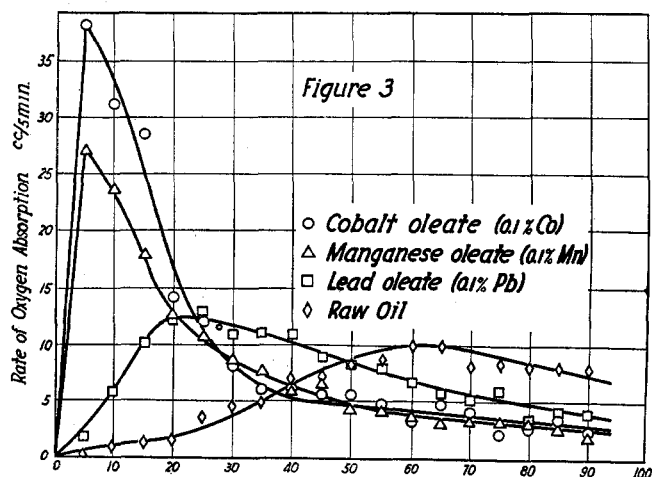
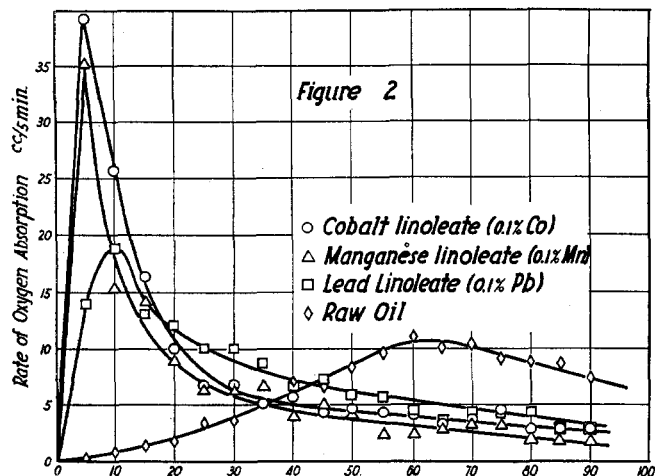
TABLE II. DATA ON INDUCTION PERIOD

Drier	Induction Period Min.	O ₂ Absorbed Cc.	Av. Vol. O ₂ Absorbed per Min. Cc.
Cobalt linoleate (0.1% Co)	5	40.1	8.0
Cobalt oleate (0.1% Co)	5	38.3	7.6
Manganese linoleate (0.1% Mn)	5	35.2	7.0
Manganese oleate (0.1% Mn)	5	27.8	5.5
Lead linoleate (0.1% Pb)	10	32.4	3.2
Cobalt linoleate (0.01% Co)	10	26.8	2.6
Lead acetate (1.0% Pb)	10	26.7	2.6
Lead oleate (0.1% Pb)	25	44.0	1.7
Cobalt linoleate (0.001% Co)	35	57.0	1.6
Lead acetate (0.1% Pb)	25	30.4	1.2
Lead salicylate (0.1% Pb)	35	40.7	1.1
Lead phenylpropionate (0.1% Pb)	45	48.3	1.0
Linoleic acid (1.0%)	55	54.6	1.0
Oleic acid (1.0%)	60	45.7	0.8
Raw oil	60	60.0	1.0

hydroxide, using phenolphthalein as an indicator. Aqueous solutions of lead, manganese, or cobalt nitrate were added to the solution of the potassium salt until no further precipitation was observed. The precipitated salts were filtered, washed, and dried in a desiccator. These compounds were generally soluble in linseed oil in the concentrations used—viz., 0.001 to 1.0 per cent of metal content in the oil. The linseed oil, fatty acids, and driers were all stored in a dark closet. The lead salt of phenylpropionic acid was prepared in a similar manner from a sample of the acid previously prepared for other work in this laboratory. Attention was directed to this compound because it contains the highly unsaturated (acetylenic) group. The cobalt and manganese salts of this acid could not be prepared successfully by the method outlined because of their greater solubility in water. The lead salt is not appreciably soluble in linseed oil and was therefore worked into the oil in the form of a suspension by grinding in a mortar. Similar conditions were met with in the use of the lead salts of acetic and salicylic acids.

Procedure

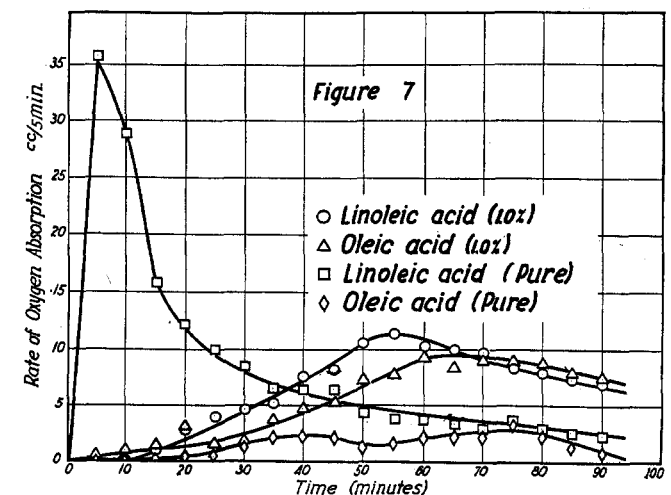
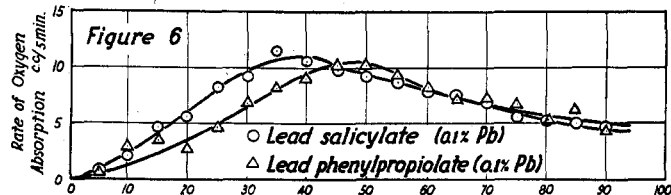
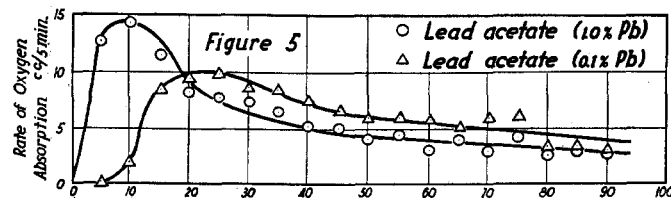
The air was displaced from the bottle by means of oxygen. The frame holding the cloth strip with a known weight (0.75 to 1.0 gram) of oil absorbed upon it was placed within the bottle which was connected by sealed joints to the buret. The bath of boiling water was quickly raised so as to surround the bottle up to the stopper, and the stopcock was opened. The oxygen quickly expanded to a maximum point and at this point readings were taken at 5-minute intervals over a period of 90 minutes. Burets were refilled with oxygen as needed. Atmospheric pressure was maintained as closely as possible by frequently adjusting the leveling



bulbs. This uniform procedure was followed in all of the measurements. Blank measurements in which no oil was used showed that no appreciable volume of oxygen was absorbed by the rubber stoppers and soda lime under these conditions.

Results

Table I gives the volumes of oxygen absorbed per gram of oil by eighteen different samples. Calculations showed that the temperatures and pressures existing during all of the experiments were sufficiently constant to justify the use of the observed volumes without correction to standard conditions.



The most extreme variations recorded correspond to a correction value of not more than 2.3 per cent. Experiments that were run in duplicate showed reproducible results. The driers used are listed in the footnotes. These data are plotted in Figures 2, 3, 4, 5, 6, and 7.

Table II shows the time of the induction period, the volume of oxygen absorbed, and the average volume of oxygen absorbed per minute during the induction period. The induction period is defined by Milas (8) as "the time necessary for the reaction to reach its maximum velocity."

Acknowledgment

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