THE SIGNIFICANCE OF THE CHEMICAL COMPOSITION AND CHARACTERISTICS OF LINSEED OIL IN RELATION TO DRYING BEHAVIOUR

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THE SIGNIFICANCE OF THE CHEMICAL COMPOSITION AND CHARACTERISTICS OF LINSEED OIL IN RELATION TO DRYING BEHAVIOUR

INTRODUCTION

Flaxseed is produced primarily for the manufacture of linseed oil which is one of the principal components in the manufacture of protective coatings, linoleum, patent leather, etc. The commercial value of flaxseed depends primarily on the quantity of oil yielded and on the drying properties of the extracted linseed oil.

The drying properties depend upon the extent and rate of oxygen absorption, both of which are associated with the total degree of unsaturation. The rate of oxidation of linolenic, linolic and oleic acids decreases in the order named, and hence is influenced in part by the relative proportions of these acids present as glycerides; the total degree of unsaturation, as measured by iodine value, is taken as giving a valuable and fairly reliable index of the drying quality of linseed oils.

Since the iodine value measures only total unsaturation of an oil and does not distinguish between the unsaturated fatty acids present, it may not be always the most reliable index of quality. Thus, an oil could contain a high percentage of linolenic acid, coupled with a high percentage of oleic acid, and yet possess an iodine value approximately equal to that of an oil composed of different proportions of oleic, linoleic and linolenic; it would follow that the latter oil would be the most valuable drying oil, since it would contain less soft material (olein) dispersed throughout the film.

Other tests which are at times employed for estimating the quality of linseed oil include refractive index of the raw oil, the bromine value, the elaidin test, the oxygen or ozone absorption value, the bromide or hexabromide value, acid value, etc. Many of these tests are of considerably less importance in estimating drying quality than the iodine value; however, refractive index and the bromide test respectively give results in accordance with the iodine value.

In addition to variations in the degree of unsaturation, the drying behaviour of linseed oil appears to be associated with the type and concentration of the natural pigments and also with phosphatides present in the oil.

It is well known that the quality of linseed oil varies not only with the source of the seed from which it has been extracted, but also from season to season with oils from seed grown in the same locality. In Canada the variation in iodine value may be from 168.5 to 197.9 Wijs' units in any one season.

REVIEW OF THE LITERATURE

(a) Composition of Linseed Oil.

Linseed oil is essentially composed of the mixed glycerides of linolenic, linoleic and oleic acids, together with the glycerides of saturated acids, such as palmitic, stearic and possibly myristic and arachidic. Many authors, in particular Fahrion (13), Coffey (8), Friend (14) and Eibner and Schmidinger (10), have published composition studies of linseed oil. Eibner and Schmidinger, in a study of Dutch linseed oil, separated the α and β isomers of linolenic and linoleic acids. The summarized data of these five investigators are tabulated below:-

TABLE I.

The Composition of Linseed Oil as determined by Fahrion (1910), Friend (1917), Coffey (1923) and Eibner and Schmidinger (1923).

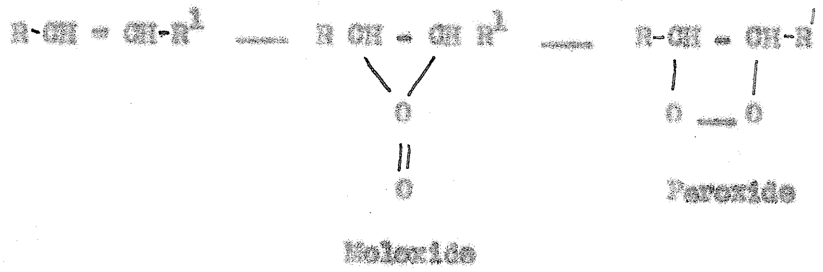
	Fahrion %	Friend %	Coffey %	Eibner and Schmidinger %
Unsaponifiable	0.6	-	-	1.0
Saturated Acids	9.3	10.0	8.1	8.8
Oleic acid	17.5	5.0	5.0	4.5
Linoleic acid	30.0	48.3 - 59.1	48.5	α 17.0 β 41.8
Linolenic acid	38.0	21.3 - 32.1	34.1	α 20.1 β 2.7
Glyceryl radicle	4.6	4.6	4.3	4.1

Morrell (30) examined the saturated acids of linseed oil, and found a yield of lead salts equal to 8% of saturated acids. The saturated acid fraction showed a composition of 64.4% stearic acid (actually separated plus eutectic mixture), 20.0% palmitic acid, 8.0% residual eutectic mixture and 4.0% oleic acid.

(b) The Mechanism of the Drying of Linseed Oil

It is generally recognized that the oxidation of linseed oil proceeds in stages and that oxygen is absorbed at the ethenoid linkages as peroxide. This oxidation continues through the induction period up to the tacky point.

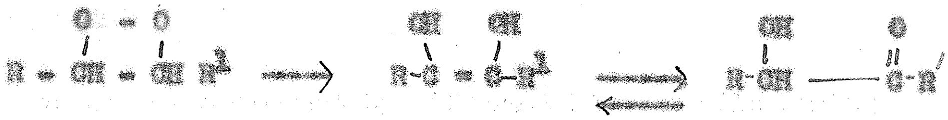
Staudinger (37) believes that peroxides are not the initial products of reaction, but that they are preceded by extremely unstable and highly reactive substances to which he assigns the term "moloxide", with the possible formula as given below:



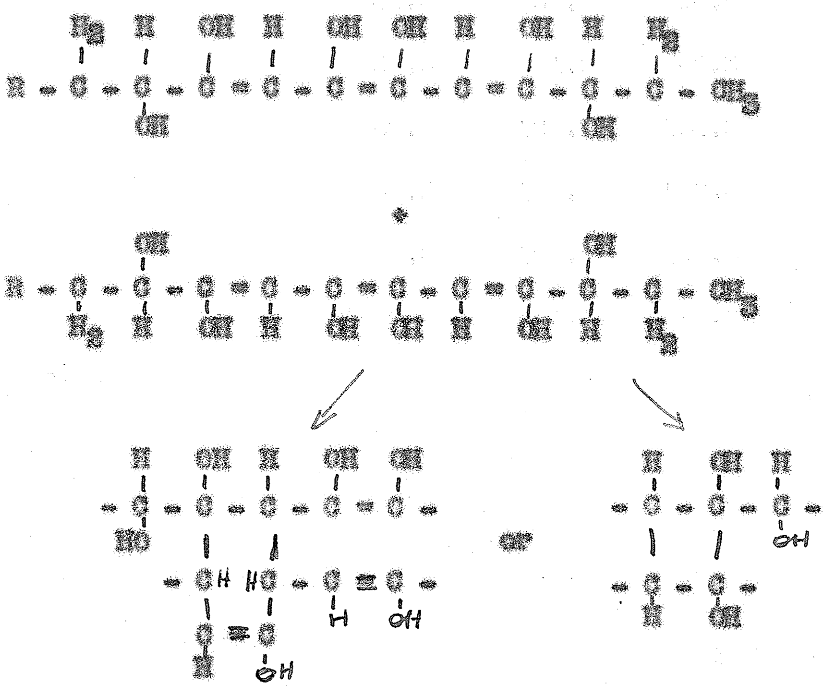
According to the chain-theory of Christiansen (6), an activated molecule of the autoxidisable substance and a molecule of oxygen unite with the production of a peroxide and the liberation of a considerable amount of energy. The freshly formed peroxide molecule is able to pass this energy on to another molecule of the substance, thus initiating a reaction chain (or chains) which may be many thousand molecules long.

Elm (12) has shown a definite relationship between peroxide and iodine value in the drying of trilinolenic glyceride. As oxygen is absorbed, the ethenoid linkages become blocked and there is consequently a definite decrease in iodine value. About the time the film is dry to touch, the peroxide value decreases gradually with the iodine number remaining practically constant.

The precise manner in which the peroxide decomposes is still largely a matter for conjecture. Ellis (11) postulated an intra-molecular re-arrangement of the peroxide to a ketohydroxy- dihyrdoxy system, and produced experimental evidence in support of this view by identification of considerable quantities of hydroxyl and keto groups in films of dried linseed oil.



There appears to be considerable divergence of opinion regarding the next step in the drying of the oil film. Ingle (21) considers that polymerization during oxidation rests on insufficient evidence. Morrell (31) has shown in the case of tung oil that polymerization subsequent to oxidation actually occurs. Rheineck (35) proposes the scheme of the reaction as follows:



Morrell and Marks (32) have shown that similar polymerization occurs but they prefer the six-membered ring. The polymerization reaction proceeds at a considerably slower rate than the primary oxidation; this reaction also gives rise to molecules of colloidal dimensions and properties which are readily coagulated into the form of the oil film.

(e) Determination of Drying Behaviour

Morrell (29) showed the changes in weight, density and volume of thin linseed oil films spread on glass and allowed to oxidize at 15°C.

Salin (36) found that a film of raw oil gave linoxyn of a density of 1.088 with a total gain in weight of 2%.

Morrell and Wood (33) compared the drying curves compiled from the weight increase of films of linseed, perilla and hempseed oils.

Numerous tests have been published, outlining methods for evaluating the drying time of oil films.

Cochran and Graham (7), in a study of insulating varnishes, used the swinging beam for determining drying time.

Wolff (42) recommended determining the dry point by spotting a drying film at suitable intervals of time with a 2% solution of Brilliant Scarlet. As drying proceeds, the spots first spread to a decreasing extent, passing through a minimum at the dust-free stage, after which the extent of spreading increases.

The Sanderson Drying Time Meter (8) is regarded as an excellent recording device for estimating drying time.

Harrison (19) describes a device similar in principle to that of Blom (5), in which the drying-film panel is placed under a weighted tip and gently drawn to the edge. The film is considered dry when no marring is observed under predetermined loads.

Problem:

A review of the literature indicates that little or no attention has been paid to the relationship which might exist between the composition and chemical characteristics of linseed oil and its actual drying behaviour.

It is of interest to note that the linseed oils of commerce vary very considerably in iodine value. The oil from Argentine and Indian seed seldom reaches 185 Wijs' iodine units, while the Baltic oil may exceed 200 units. It has been shown that the iodine value of Western Canadian flaxseed may range from 168 to 204 Wijs' iodine units.

The significance of the degree of unsaturation, as measured by iodine value, in the processing of linseed oil is not definitely clear. It is not known whether such properties as rapid thickening on heat treatment, rapid drying in both the raw and varnish state may be associated with any specific differences in composition and characteristics.

It is therefore the object of this investigation to ascertain the importance of differences in composition in relation to the drying behaviour of both the raw and treated oils.

It is possible that with a more thorough knowledge of the processing significance of certain chemical differences between oils, premiums might be established on flaxseed of definite quality standards, so that the low-yielding varieties which have consistently high iodine values might be recognized commercially for their intrinsic value and command a premium which would offset the low yield per acre.

MATERIALS AND METHODS

Samples Employed

The materials chosen for this investigation consisted of eleven samples of flaxseed of different origin. These included three composite commercial samples grown in Manitoba, Saskatchewan and Alberta respectively during 1938, a sample representing the 1936 and 1937 crops respectively (Ottawa grown), two samples of the 1934 crop representative of large and small seeded varieties (Ottawa grown), a Winnipeg average sample of the 1932-33 crop purported to possess poor quality, a sample of Cyprus flaxseed which is an unusually large-seeded low-iodine type, and an average Argentine and Indian cargo shipment.

Preparation of Oil Samples

The linseed oils used in these studies were prepared in the laboratory by a procedure developed to duplicate the more common commercial hydraulic process.

Approximately 3000 grams of seed was finely ground in a Hobart No. 6 Burr Mill and transferred in 600-gram lots to a pressure cooker where the meal was heated for 30 minutes at 10 pounds pressure. This pre-treatment facilitates the expression of the oil by rupturing the cells in which the oil is contained; moreover, the viscosity of the oil is reduced so that it flows more readily on pressing. The hot meal from the cooker was then transferred to the press cylinder and the oil expressed at 60 to 70° C. at a pressure not exceeding 10,000 pounds to the square inch. Since the pressure cylinder of the Carver laboratory hydraulic press conveniently holds no more than 600 grams, five separate pressing were conducted on each sample and the oils composited therefrom, filtered and stored in glass containers. Filtering was found to be most conveniently conducted by means of the Sharples Supercentrifuge, care being exercised to prevent oil losses.

The Estimation of Drying Time

One of the primary considerations of the present investigation has been to develop and standardize conditions whereby reliable data might be obtained relative to the measurement of the drying time of linseed-oil films.

There are a number of testing devices on the market specifically manufactured for the purpose of determining drying time. These may be summarized as the Gardner Drying Time Meter, the Sanderson Drying Time Meter, the Paraffine Companies Drying Time Machine, and the Parks Dry-o-graph.

The author was fortunate in having the last named device available for this study, and a brief description of the Parks Dry-o-graph is given below:

The Parks Dry-o-graph.[$]

The apparatus consists of a track in which strips containing the drying films are placed, a roller to press a strip of cotton flannel upon the drying film, and a Telechron motor to pull the roller over the film.

Films are carefully made on tin test strips (38" x 1") and if no induction drying period is necessary the filmed strip is placed in the drying track. The brass roller, covered with a rubber tire, is placed at the far end of the

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[$] Parks Equipment Company, Bourse Bldg., Philadelphia, U.S.A.

track from the telechron clock motor which draws it over the coatings at a rate of one inch per hour or 12 inches per hour, adjustable according to the type of coating to be tested. As the roller travels, an appropriately sized flannel or other suitable material is sandwiched between it and the film.

The "dry-point" time of a film is indicated by the absence of adhering lint; the print free time by the disappearance of the impression of the corrugations. Upon completion of the test, the flannel is detached from the test strip and the drying time or "dry point" is measured in inches of the adhering lint. In the tests discussed in these studies, only the "dry point" has been considered.

Method of Preparing Suitable Films

In preliminary tests, an endeavour was made to secure uniform filming by such methods as brushing, spraying, dipping and by the use of a doctor blade. These methods were discarded as unreliable. Bubbling occurred in the case of brushing, spraying was found too wasteful and uneven, and dipping gave satisfactory results, provided the oils were of uniform consistency, but was valueless when uniform films were desired from both raw and treated oils. The purchase of filming equipment in the form of a Parks Filmograph eliminated these primary difficulties. The Filmograph consists of a chromium plated bronze cylinder with a milled channel cut in the end, through which the coating material flows. A plunger for use with material of thick consistency is provided. This device produces films of two thicknesses, viz., 0.001 or 0.003 inch thick, the film thickness being controlled by the milled steps in the ends of the cylinder.

Further difficulties were encountered in filming, in particular the tendency of raw oils to "crawling", which corresponds to the retraction of the uniform film into droplets. This difficulty is apparently due to the presence of moisture, wax or foreign material on the surface to be filmed. After considerable experimentation, it was found that the most convenient method of avoiding these difficulties was to clean the tin test strip thoroughly with absolute alcohol, followed by ethyl ether and finally to dry the strip by heating gently without discoloring the surface. The drying may be conducted in a suitable air oven at 110° to 150°C.; however, it is essential that the strip remain unbent and that the surface be absolutely flat.

Determination of Physical and Chemical Characteristics

Specific gravity (15°C.) and refractive index (25°C.) were determined by the usual methods (22).

Iodine values were determined in duplicate by the Wijs' method according to the Official A.O.A.C. (3) method, chloroform being used as the solvent; this method calls for a sample weight of 0.1 to 0.2 gram oil and a contact time of 30 minutes in the dark.

Unsaponifiable matter was determined by a modification of the Kerr-Sorber procedure, and acid values (free-fatty acids) by the usual titrimetric method; both these procedures are fully described in Jamieson (22).

Colour was estimated by means of the Lovibond Tintometer in a 1 cm. cell.

Construction of Drying Cabinet

It was realized at the commencement of this investigation that a suitable drying cabinet would be essential in order to obtain reliable results. The critical factors in the drying of oil films appear to be temperature, rate of air flow, humidity and light intensity; therefore, it seemed essential that these factors be considered of primary importance in the construction of a cabinet destined for drying operations.

The cabinet was constructed from a dismantled bread-dough fermentation cabinet, the framework of which was complete. The general constructional details of the finished cabinet are illustrated in Fig. 1. The cabinet was divided into two chambers, each section measuring 54" x 17" x 17". The lower section was heavily insulated with asbestos board and so constructed as to form a heating or conditioning chamber. The heating system consisted of suitable elements controlled by a sensitive thermoregulator. The temperature of the cabinet was regulated for 40°C. ± 1°. The upper section ($16\frac{5}{8}$" x $54\frac{1}{2}$"), designated as the drying chamber, was also heavily insulated. A fan (8-inch blade, 800 r.p.m.), was firmly housed at the extreme end of the chamber, in order to draw a continuous stream of air through the cabinet, which could be controlled by the aperature at the entrance to the heating duct. The air flow through the cabinet was regulated at approximately 20 feet per minute at the base level of the drying chamber and at 42 feet per minute at the ceiling level. This air flow was very gentle and yet entirely adequate for continuous conditioning. Humidity was controlled by the method outlined by Gardner (16), which consists of drying the intake air over $CaCl_2$ and exposing a super-saturated solution of $Mg(Cl)_2$ 6 H_2O in a small tray to a continuous stream of air; in this manner the humidity could be maintained at 35-37% saturation. Accessibility to the interior of the drying chamber was arranged by four small doors measuring 8" x 15", while a glass panel, 15" x 17" finished the length construction. The use of the small doors served as a precaution to changes in temperature, etc, manipulation in the drying chamber being possible only by opening one door at a time.

In order to secure uniform light conditions within the drying chamber, all the glass construction was heavily enameled black and a 60-watt frosted lamp was placed in such a manner as to produce a uniform dispersed light.

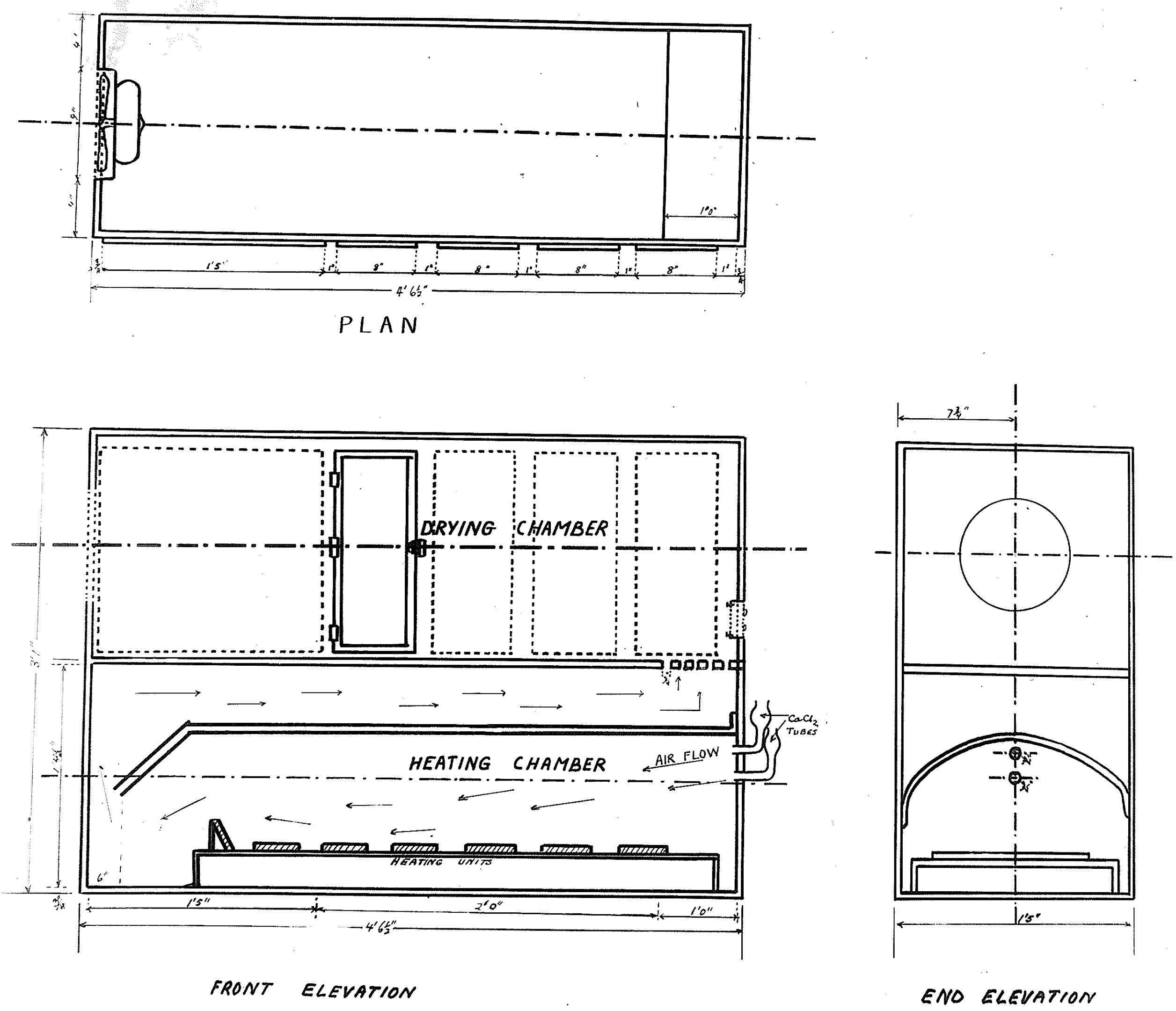

Fig. 1. Drying Cabinet. General working drawing showing main constructional features.

EXPERIMENTAL.

Preliminary Drying Tests

Tests conducted to determine optimum filming procedure, such as surface conditions and the uniform preparation of oil films have already been discussed. Tests were now conducted to determine the replicability which might be expected from such films as raw linseed oil, polymerized oil and rapid-drying varnish; the results of these tests are given in Table II.

TABLE II.

Drying Time Replicability of Linseed Oil Base Films

(Film thickness 0.002", temp. 40°C.)

Type of film	Replicates -- Time in hours.		
	a	b	c
Raw linseed. Sample A.	70	73	70 - 70.5
Raw linseed. Sample B.	108	109	108 - 109
Polymerized linseed (A)	26	28	25
Polymerized linseed (B)	31	31	30.5
Rapid linseed varnish (A)	0.58	0.60	0.61
Rapid linseed varnish (B)	0.75	0.70	0.75

From the results reported in the above table, it will be observed that under the drying conditions reported elsewhere in this paper the replicability is all that could be desired on the different types of films examined.

It is of interest to note the results obtained on two polymerized oils and a sample of raw oil when drying was conducted with and without admission of daylight to the cabinet. These are shown below:

TABLE III.

Effect of Daylight on Drying Time. (0.001" thick, 40°C.)

	Admission of daylight	Total darkness
	Time in hours.	
Polymerized oil	29	32
Drier polymerized oil	12 - 15	15
Raw oil	72	96

Physical and Chemical Characteristics as Related to Drying Time

The essential physical and chemical constants were now determined on the prepared linseed oil samples.

These various constants, together with drying time, are given in Table IV.

TABLE IV.

Physical and Chemical Characteristics and the Drying Time of Eleven Samples of Raw Linseed Oil.

Ref. No.	Grade	Origin of flaxseed from which oil was pressed	Specific gravity 15°C.	Refractive index 25°C.	Iodine value (Wijs')	Acid value	Unsaponi-fiable %	Colour: Lovibond units Orange	Colour: Lovibond units Yellow	Drying time hr.
1	1 C.W.	Composite, grown Alberta 1938.	0.9318	1.48044	193.8	0.22	0.75	1.0	20.0	55.5
2	1 C.W.	Composite, grown Saskatchewan 1938.	0.9314	1.47953	186.4	0.92	0.82	2.0	27.9	55.0
3	-	Indian (commercial) 1937-38.	0.9290	1.47959	184.6	0.36	0.80	0.9	19.1	60.0
4	1 C.W.	Composite Manitoba, Saskatchewan 1938.	0.9302	1.47915	185.0	0.94	0.91	1.0	19.0	65.5
5	1 C.W.	Winnipeg Average, 1932-33.	0.9298	1.47970	182.8	1.30	1.20	2.0	18.0	75.0
6	1 C.W.	Large-seeded varieties grown Ottawa 1934.	0.9306	1.47917	179.5	1.00	0.97	1.1	18.9	74 - 76
7	1 C.W.	1936, grown Ottawa.	0.9306	1.47959	183.8	1.06	0.88	1.2	18.8	67.0
8	1 C.W.	1937, grown Ottawa.	0.9307	1.47926	182.5	1.22	0.79	1.3	18.6	65.5
9	1 C.W.	Small-seeded varieties grown Ottawa 1934.	0.9314	1.48015	187.7	0.90	0.92	1.4	18.3	65.0
10	-	Cyprus variety (Ottawa)	0.9302	1.47850	176.5	0.54	1.22	1.3	19.7	> 100
11	-	Argentine (commercial) 1937-38	0.9309	1.47897	182.9	1.25	0.97	2.0	18.0	84.0

Although the oils were not cold expressed from the seed, there still existed a fairly good relationship between the refractive index and iodine value. The acid values of the different oils were very uniform and could not represent a variable in so far as drying is concerned. The percentage of unsaponifiable was also most constant. Cyprus, it is interesting to note, has the lowest acid value and the highest percentage of unsaponifiable.

There appeared to be a tendency for the higher iodine-value oils to dry more rapidly than those of lower iodine value. It will be observed, however, that four samples possessing approximately the same iodine value exhibited wide differences in drying time, viz., from 43.5 to 84.0 hours.

ESTIMATION OF FATTY ACID COMPOSITION

(a) Total Saturated Fatty Acids

The method of Bertram (4) is generally said to be more accurate than the older methods. It makes use of the oxidation of unsaturated fatty acids in alkaline permanganate solution under conditions which leave the saturated portions unchanged. The temperature during the oxidation must not be allowed to rise above 35°C. Gay (17) reported that the temperature used by Bertram was not sufficient to ensure complete oxidation, and he recommended two subsequent oxidations at 50 to 60°C. and 70 to 80°C. This investigator also suggested that a third oxidation may at times be necessary. Hilditch and Priestman (20) employed a single oxidation at 35 to 50°C., omitting the extraction of the unsaponifiable matter.

Pelikan and Von Mikusch (54), in a careful study of these different methods for the determination of saturated fatty acids, showed close agreement between the Bertram and Hilditch-Priestman procedures, while the Gay method gave entirely different results, all of them very considerably lower. These authors also reported that the Bertram method gave an almost theoretical result on a sample of known composition.

In view of the findings cited above, it was decided to follow a slightly modified Bertram method, the details of which are cited below:-

> Five grams of the sample are weighed and saponified in a 250 cc. Erlenmeyer flask by means of 75 cc. of approximately 0.5 N alcoholic KOH and refluxed for 30 minutes. The soap solution is transferred to a steam bath and evaporated until the alcohol is removed. The soap stock is then heated carefully over a flame until the remainder of the alcohol is volatilized.
>
> After cooling, 500 cc. of water is added and the solution is heated until the soaps have dissolved. These are transferred to a 2000-cc. flask, care being taken to rinse thoroughly and to ascertain that all the soap is dissolved. The solution is cooled to room temperature (25°C.) and 750 cc. of an aqueous solution containing 55 grams of MnO_4K added.
>
> After standing 12 to 18 hours with an occasional shaking, the solution must still show an excess of permanganate. If the solution is not violet coloured, a further addition of permanganate solution must be made. The solution is now acidified with 1:3 H_2SO_4 and sodium bisulfite added to decolorize the solution and to dissolve the precipitated manganese oxides when the solution is heated.

The fatty acid layer is separated from the aqueous solution by heating on a steam bath. After cooling, the solution is transferred to a separatory funnel of suitable size and extracted three or four times, using 200- to 250-cc. portions of petroleum ether. The petroleum ether extracts are combined and washed with water. Experience has shown that considerable losses may occur in the washing process if the solution is not allowed to stand for a considerable period between shakings (at least 1 hour). Apparently some emulsification takes place and considerable time elapses before the ether extract completely separates; results in this connection are to be found in Table V.

The petroleum ether extract is separated and the ether distilled off.

The fatty acids are heated with a few millilitres of ammonia and 200 ml. of hot distilled water added. When all the fatty acids have gone into solution, addition of 20 ml. of 10% NH_4Cl is made, and the solution heated to boiling, after which 20 ml. of 15% $MgSO_4$ solution is added. After again heating to boiling, the solution is cooled and filtered through a layer of absorbent cotton, lining a Buchner funnel. After washing, the cotton batting and precipitate are transferred back to the original flask and a few millilitres of 50% H_2SO_4 added. The solution is heated to boiling, swirled to disintegrate cotton fibres, cooled and the fatty acids allowed to form a clear layer.

An excess of ammonia is added and the solution warmed until all the fatty acids are dissolved. Precipitation and filtration are repeated as above. After decomposing the precipitate as previously outlined, the fatty acids are extracted in a separatory funnel, using petroleum ether to wash the flask. After two extractions with petroleum ether, the extract is washed three times with water, similar precautions being taken as above. The extract is filtered into a tared 250 ml. extraction flask, washing the funnel with petroleum ether. The solvent is distilled off and the flask containing the saturated fatty acids dried in an oven at 105°C to constant weight.

For the sake of convenience, the saturated fatty acids are not reported separately, the results being given in Table VII with the complete fatty acid composition.

TABLE V.

Effect of Method of Petroleum Ether Extraction on Yield of Fatty Acids by Bertram Method.

Sample No.	Percentage saturated fatty acids. Separation immediately after shaking	Separation after 60 mins. repose
1	10.57	10.85
2	9.01	9.24
3	9.28	9.47

(b) Total Unsaturated Fatty Acids

The methods available for the analysis of the unsaturated fatty acids of linseed oil or of any oil containing more than two unsaturated acids are still far from dependable. The recent work of Stillman and Andrews (33) indicates that none of the four methods generally employed for the separation of liquid and solid fatty acids, which depend upon the insolubility of lead salts of saturated fatty acids, is entirely satisfactory.

The bromination method was not considered satisfactory, since the solid bromination products obtained do not represent the total hexa and tetra bromides, and bromine determinations should actually be carried out on the various fractions of the liquid bromides.

Kaufmann and Keller (34) have shown that linseed oil dissolved in chloroform or carbon tetrachloride is partially saturated to a definite end point by the use of a thiocyanogen solution. Oleic acid is completely saturated and therefore has a theoretical thiocyanogen value of 90.1; linoleic acid absorbs thiocyanogen in only one of its centres of unsaturation and therefore its theoretical thiocyanogen value is 90.7; linolenic acid is acted upon by thiocyanogen at only two of its three double bonds and for this reason has a theoretical thiocyanogen value of 182.7. The thiocyanogen number is the number of grams of thiocyanogen absorbed by 100 grams of the oil calculated in iodine equivalents. Since iodine adds to all the double bonds in the fatty acid series, Kaufmann (35) has shown it is possible to calculate from the iodine and thiocyanogen values and the percentage of saturated fatty acids the percentages of the various unsaturated fatty acids in a mixture of fatty acids. Griffiths and

Hilditch (18) investigated the Kaufmann method and found it entirely satisfactory if sufficient care were taken to exclude all traces of moisture. The Committee on Analysis of Commercial Fats and Oils of the American Chemical Society (1) investigated this method and recommended its adoption by the Society.

The Kaufmann method for estimating fatty acids was selected for the present composition study, due to the simplicity and purported reliability of the procedure. The author experienced considerable difficulty with the thiocyanogen determination, in particular with regard to storage of the thiocyanogen solution. The test is a delicate one and cannot be recommended for routine work. As it requires scrupulous care and cleanliness, it is essential that all traces of moisture be eliminated. The lead thiocyanate should be dried in an Abderhalden apparatus prior to use and the temperature at which addition takes place should be very accurately controlled and should not exceed 21.1°C. (70°F.). Details of the test are not given here, but it is recommended that the monograph "Studien auf dem Fettgebiet" by H. P. Kaufmann (22) be consulted in this connection.

Iodine and thiocyanogen values were determined in duplicate on the prepared mixed fatty acids of the same linseed oils reported in Table IV; the mixed fatty acids were prepared in the manner reported below:

Preparation of Mixed Fatty Acids.

Approximately 25 grams of linseed oil were saponified with 0.75 N alcoholic KOH. The saponification was effected in a current of previously washed CO_2, in order that oxidation be inhibited during the 2 to 3 hours of refluxing necessary. After saponification the alcohol was distilled off and upon cooling, approximately 400 cc. of distilled water added. During the entire operation, the soap solution was maintained in a current of CO_2.

After complete solution of the soap, concentrated hydrochloric acid was added until the solution showed acid to litmus. The curds were heated on a steam bath (in a current of CO_2) until the fatty acids formed a liquid layer. These were then dissolved in ethyl ether and separated from the aqueous layer by means of a separatory funnel. The fatty acids were washed with water until the washings showed no trace of acidity with methyl orange.

After filtration of the ethereal mixture, the ether was distilled off in a current of CO_2. The fatty acids were later dried in an air oven at 100°C. until the weight remained constant. Precautions were taken to avoid oxidation by bubbling a rapid stream of CO_2 through the acids in each separate flask during the entire drying period.

The iodine and thiocyanogen values determined on the mixed fatty acids are reported in Table VI. The percentage of oleic, linoleic and linolenic acids, together with the total saturated acids, are given in Table VII.

TABLE VI.

Iodine and Thiocyanogen Values of Liberated Mixed Fatty Acids.

Sample No.	Iodine Value	Thiocyanogen Value
1	202.0	122.3
2	197.4	121.0
3	193.3	116.2
4	191.4	116.1
5	191.4	121.2
6	197.9	118.0
7	191.1	120.2
8	191.0	118.0
9	193.4	119.8
10	196.5	122.0
11	191.6	117.5

TABLE VII.

Composition of the Liberated Mixed Fatty Acids.

Sample No.	Description of sample	Total saturated %	Total unsaturated %	Oleic %	Linoleic %	Linolenic %
1	Composite, grown Alberta 1938.	10.85	89.15	1.38	41.68	46.09
2	Composite, grown Saskatchewan 1938.	9.24	90.76	6.41	41.53	42.82
3	Indian (commercial) 1937-38	9.15	90.85	5.73	47.68	37.44
4	Composite, Man. } Sask. } 1938.	10.59	89.41	6.28	44.37	38.76
5	Winnipeg Average, 1932-33	9.47	90.53	13.05	34.23	43.27
6	Large-seeded varieties, grown Ottawa, 1934.	10.79	89.21	12.27	35.88	41.06
7	Composite, grown Ottawa, 1936	12.63	87.37	9.10	32.04	46.23
8	Composite, grown Ottawa, 1937.	13.10	86.90	4.10	41.64	41.16
9	Small-seeded varieties, grown Ottawa, 1934.	15.37	84.63	2.07	38.94	44.62
10	Cyprus variety. (Ottawa)	16.20	83.80	12.60	20.32	50.88
11	Argentine (commercial) 1937-38.	9.32	90.68	8.96	42.66	39.06

The results reported in the above table indicate the factors responsible for the inferior drying quality always associated with the Cyprus variety (No. 10). It would appear that the high percentage (28.8) of saturated and oleic acids be conducive to the production of soft tacky films.

The total saturated fatty acid content varied from 9.15 to 16.20%, the samples of highest saturated fatty acid content all originating at Ottawa, Ontario.

Oleic acid varied from 1.38 to 13.05%, linoleic acid from 20.32 to 47.66%, linolenic from 37.44 to 50.86%.

If the drying time of the raw oils is compared with the corresponding fatty acid composition, it will be observed that the sum of the percentages of total saturated fatty acids and oleic acid appears to be a function of drying time. This trend is shown graphically in Fig. 8; the actual data as calculated from Table VII are given in Table VIII.

TABLE VIII.

Sum of Percentages of Total Saturated Fatty Acids and Oleic Acid compared with Drying Time.

Sample No.	Total saturated F.A. plus oleic acid (per cent)	Drying time, raw oil (0.001", 40°C.) hours
1	12.23	53.5
2	15.65	55.0
3	14.62	60.0
4	16.87	62.3
5	22.50	75.0
6	23.06	74.0 - 76.0
7	21.73	67.0
8	17.20	65.5
9	17.44	65.0
10	25.60	> 100.0
11	18.30	84.0

Samples Nos. 4, 5, 7, 8 and 11 possess iodine values which ranged from 182.5 to 185.0, indicating the same degree of total unsaturation. However, the drying time of these five samples varied from 62.3 hours to 84 hours, while the sums of total saturated acids and oleic acid ranged from 16.87% to 23.06%, which is a clear indication that in these particular cases iodine value failed to indicate "drying quality".

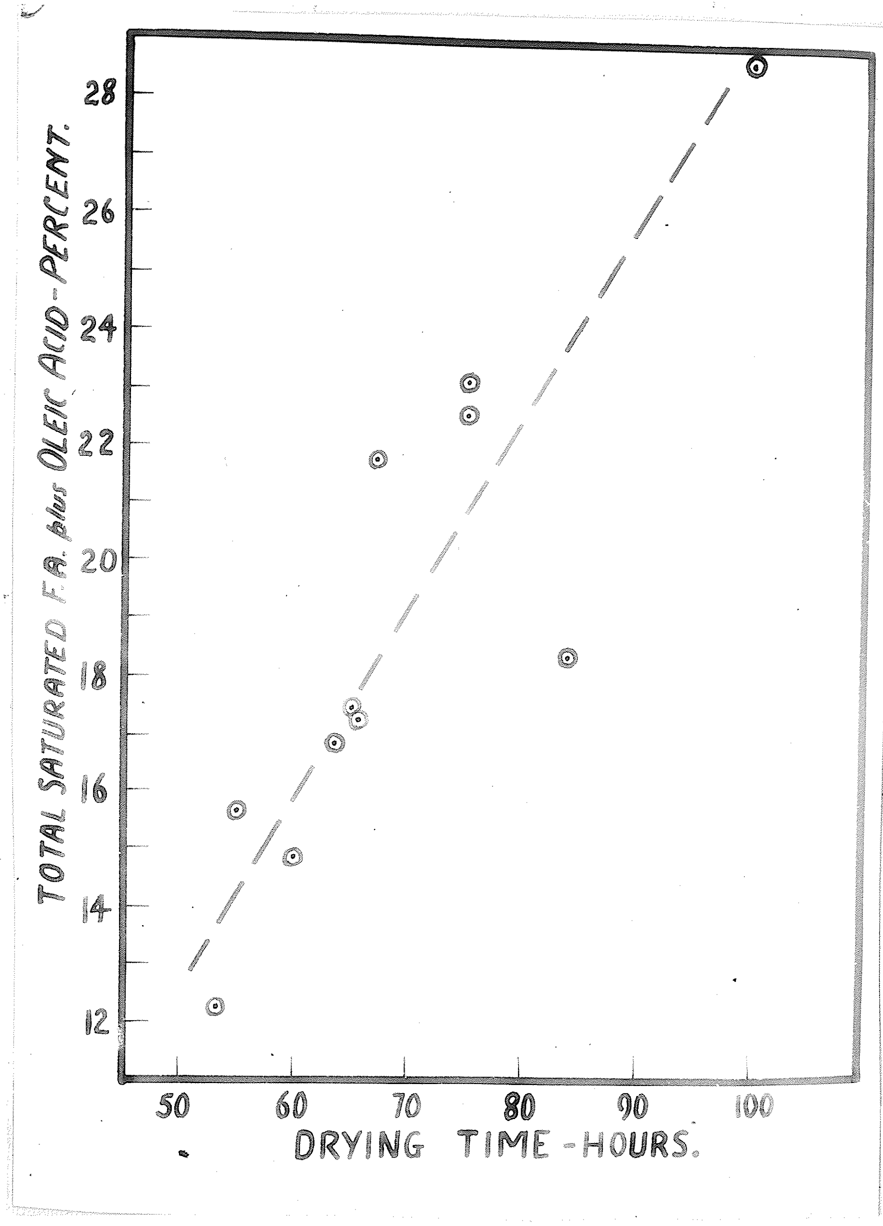

Fig. 2. Sum of the percentages of total saturated fatty acids plus oleic acid as a function of drying time.

It was considered advisable to ascertain by statistical method the fatty acid or acids primarily responsible for differences in rate of drying. Accordingly, multiple correlations of the data presented in Table VII were conducted; these statistical data are given below:-

TABLE IX.

Correlation Coefficients for Drying Time, Total Saturated, Oleic, Linoleic and Linolenic Acids.

	Drying time	Total saturated acids	Oleic acid	Linoleic acid
Total saturated acids	.417	-	-	-
Oleic acid	.789	-.066	-	-
Linoleic acid	-.745	-.044	-.686	-
Linolenic acid	.378	.700	.150	.825

(5% Point = 0.602).

Multiple Correlation

	Drying time	
Total saturated acids plus oleic acid	0.880	(5% Point = 0.692)

The correlations of .789 and .745 between drying time / oleic and linoleic acids respectively are significant. There is also a significant correlation between total saturated acids and linoleic acid, and between linoleic acid and oleic acid.

In so far as linolenic acid is concerned, there appears to be no significant correlation between this acid and drying time. However, there is a very significant correlation between linolenic and linoleic acid; there is also a significant correlation between linolenic and the total saturated fatty acids. The multiple correlation of .893, involving total saturated acids plus oleic acid and drying time, is very significant. This indicates that variations in the sum of these acids may account for 80% of the differences in drying time.

WEIGHT BEHAVIOUR DURING DRYING OF LINSEED OIL FILMS

As previously outlined, the Parks Dry-o-graph registers the so-called "dry point" which is indicated when no further lint from the roller adheres to the film. In order to obtain more definite information on the secondary changes taking place during drying, it was considered advisable to follow the change in weight behaviour of the different samples under investigation.

The raw linseed oil was spread by means of the filmo/graph on a microscope slide in a layer 0.001 inch thick, the total weight of oil varying from approximately 20 mg. to 30 mg. The slides were dried under identical conditions already cited for the drying studies.

The quantitative relations between increase in weight of film, volume of oxygen absorbed and time, etc., have been investigated by a number of workers including Friend (18), Coffey (9) and Lippert (27). The author is not aware, however, that any effort has previously been made to associate weight behaviour of different linseed oil films with drying quality.

The change in weight behaviour of the samples under investigation is reproduced graphically in Fig. 3 to Fig. 6 inclusive.

Figure 3 shows the different drying behaviour between sample No. 1 (drying time 55.5 hours), and sample No. 6 (74 to 76 hours). It will be observed that in the case of the oil of rapid drying time the weight decrease was greater and occurred sooner than that of the slower drying oil. Maximum weight was attained by the third day for sample No. 1, while sample No. 6 only attained maximum weight by the seventh day. After maximum weight is reached, loss in weight ensues. In the case of sample No. 1, this loss is very considerable, decreasing from + 7.6% calculated from the original film weight, to -4.3%. Sample No. 6 decreased from a maximum of + 9.6% to a minimum of + 5.5%.

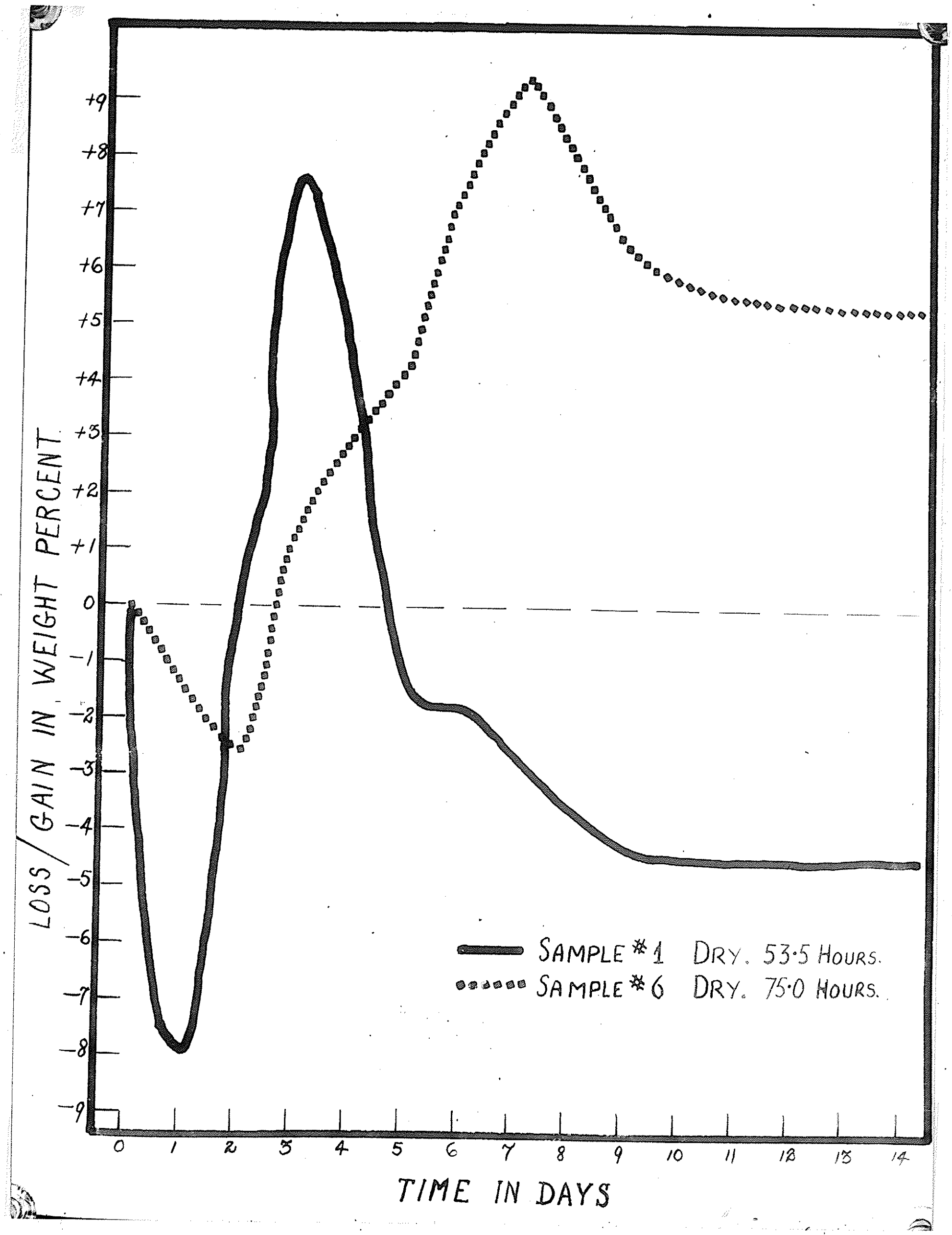

Fig. 3. Relation of film weight to time dried for a rapid- and slow-drying linseed oil respectively.

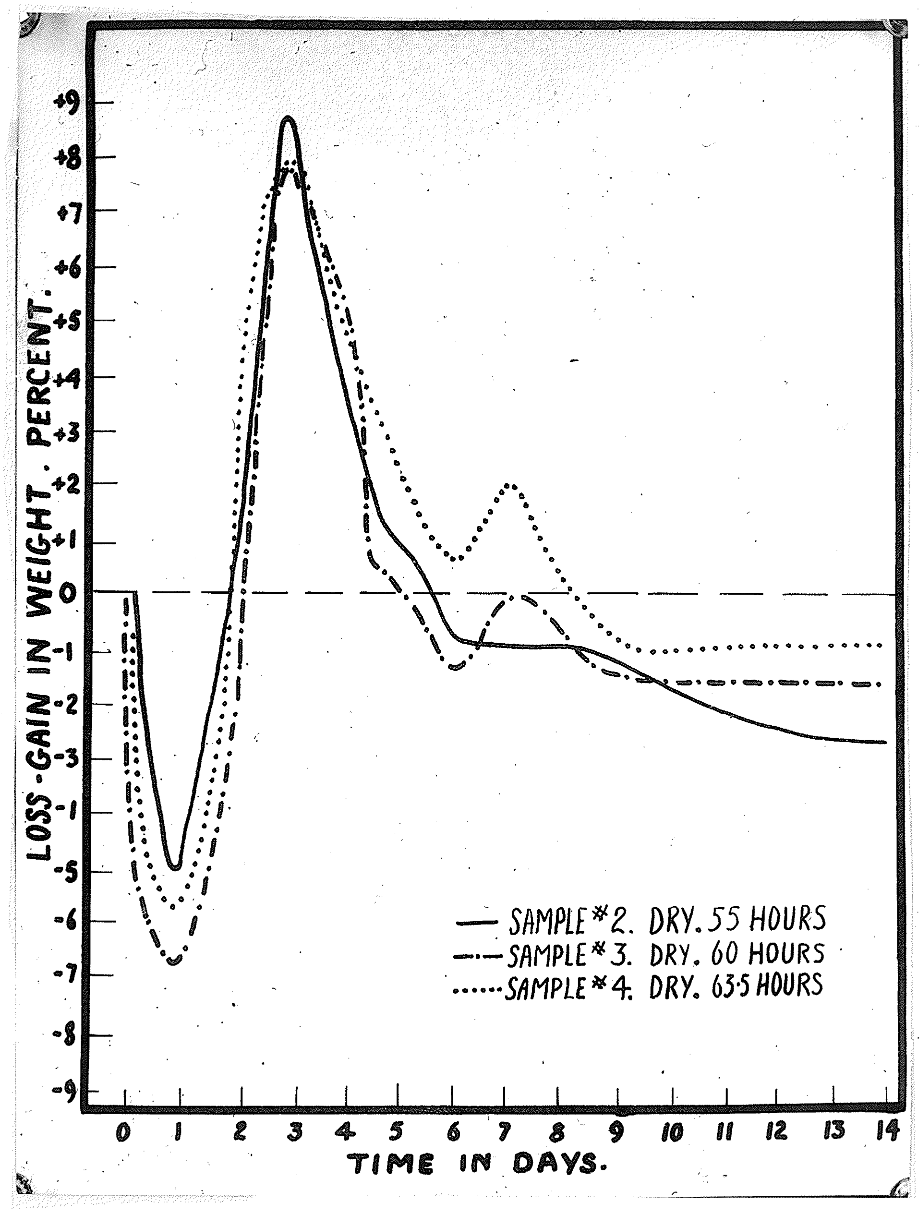

Fig. 4. Relation of film weight to time dried for three different linseed oils of good quality.

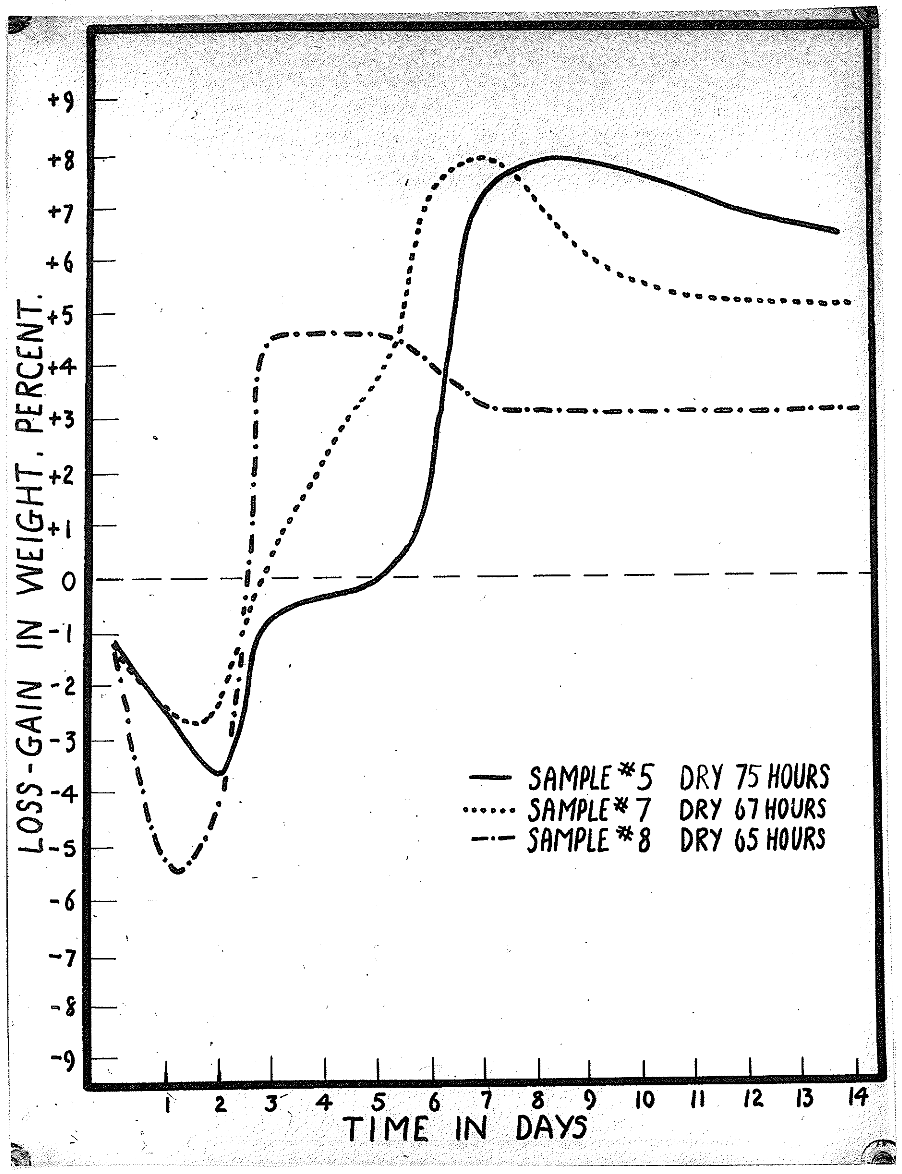

Fig. 5. Relation of film weight to time dried for slow-drying linseed oils.

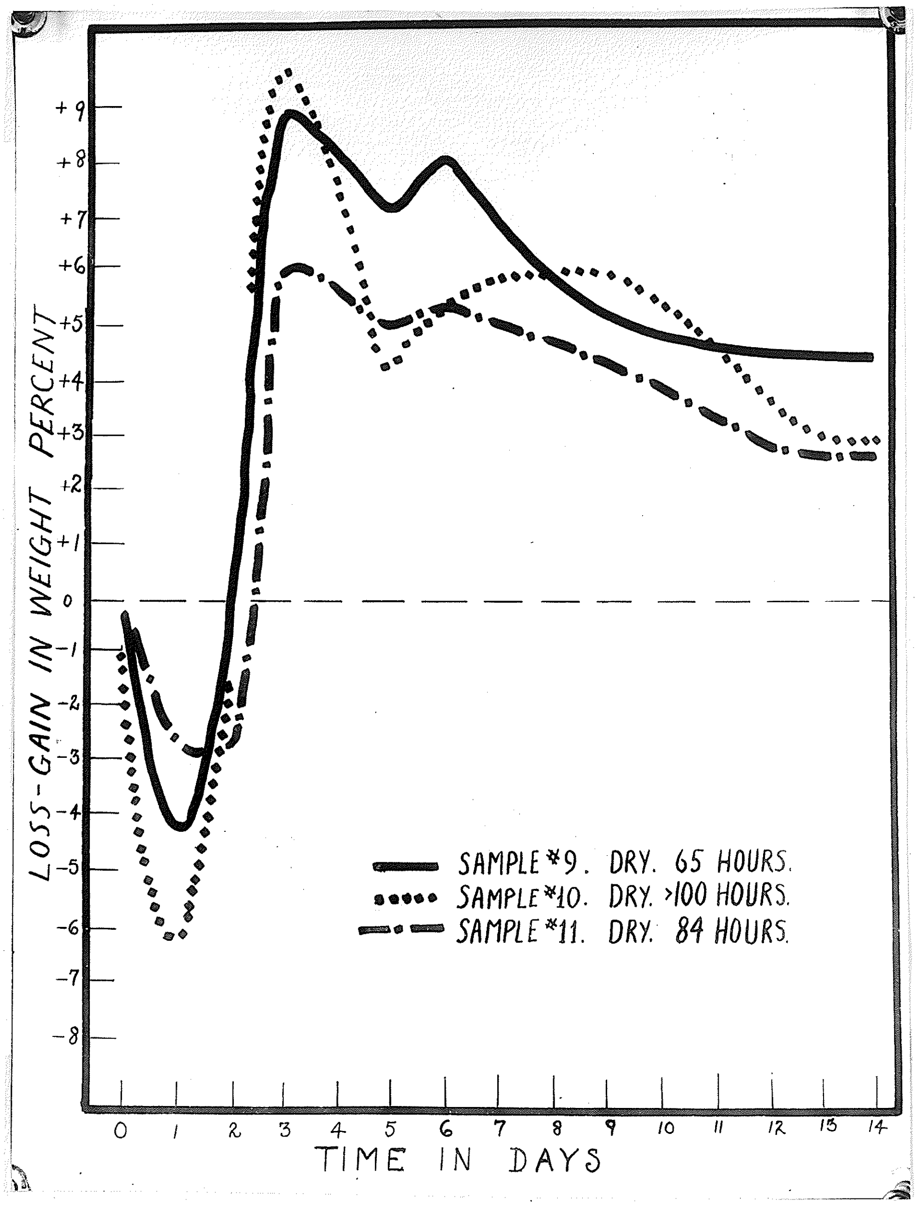

Fig. 6. Relation of film weight to time dried for three different linseed oils representing very slow and slow drying oils.

It is interesting to observe that the final weight of sample No. 1, after 14 days' drying, was 4.2% below the original oil film weight, while after the same period, sample No. 6 was 5.5% above the original weight.

In Fig. 4 are grouped samples Nos. 2, 3 and 4 which represent the more rapid drying oils of the series. The general trend of these curves is similar to that of sample No. 1, showing a decrease below the original oil film weight after prolonged drying.

Figures 5 and 6 show the poorer drying oils, the curves of which are somewhat different in general character from the above, their final film weight being considerably higher than the original. If these graphs are compared with the fatty acid composition data given in Table VII, it will be seen that the samples having the highest sum of saturated fatty acids and oleic acid do not dry as rapidly or decrease in weight upon prolonged drying to the same extent as would samples containing a lesser amount of these fatty acids.

According to Lippert (27), an oil may be considered dry when maximum weight is reached. The "dry point" as measured by the Dry-o-graph varied somewhat with the type of sample, in most cases occurring before maximum weight was attained.

PEROXIDE FORMATION AS A MEASURE OF INDUCTION DRYING.

Earlier in this study, it has been shown that peroxides are formed as the initial step in the drying process. It was considered therefore that a relative measurement of peroxide formation might possibly be an index of induction drying.

It is acknowledged that the fatty acids in general tend to become more reactive towards oxygen as the number of double bonds increases. Linoleic acid has been shown (Taufel and Suess (40) to oxidize much more rapidly than oleic acid under the same conditions. However, the stability of natural oils and fats is only partly accounted for by differences in the proportion and degree of unsaturation. Susceptibility to oxidation would also depend on natural antioxidants present and to some extent on molecular structure. Ellis (loc cit), Long et al (28) have indicated that drying oils take up at least two atoms of oxygen per double bond, but that in the majority of the experiments a considerable amount of secondary decomposition and further oxidation must certainly occur.

Since time is a factor in producing decomposition, it was decided to conduct experimental tests using an accelerated method such as is employed in the estimations of rancidity in edible oils and fats. The method employed was essentially that of Lea (25, 26).

The tests were conducted in a thermostatically controlled oil bath maintained at 100°C., with the rate of aeration controlled at 2.33 cc. per second.

Lea's method of estimation is given in detail below:-

One gram of the oil is weighed into a numbered and tared pyrex test tube, approximately 17 mm. in diameter. Approximately 1 gram of powdered KI is added, followed by 20 ml. of a mixture of glacial acetic acid and chloroform or carbon tetrachloride (2:1 by volume). A rubber stopper, bored with one hole, is fitted and nitrogen or carbon dioxide passed into the air space above the liquid for about 1 minute to displace most of the air. The tube is then heated in an inclined position over a small flame applied to its lower end, a finger resting lightly over the hole in the stopper.

As soon as the solution is bubbling fairly freely, the tube is plunged into a boiling water bath. The liquid boils smoothly, chloroform vapour expelling any remaining traces of air. When vapour begins to issue from the tube, a glass plug is forced in, and the tube immediately cooled under the tap. The contents are then poured into a titrating vessel and the tube washed with 30 ml. of distilled water and the free iodine titrated with 0.002 N sodium thiosulphate, adding starch solution as the end point is approached. 1 ml. of 0.002 N thiosulphate per gram is equivalent to 1 millimole or 2 mill. equivalents of peroxide. Peroxide values are usually reported as millilitres of 0.002 N $Na_2S_2O_3$ per 1 gram of oil.

The results of the tests conducted on the eleven oil samples used in this investigation are given in Table X. These are also shown graphically in Figure 7.

TABLE X.

Peroxide Development by Different Linseed Oils during Aeration at 100°C.

Sample No.	Time in hours:	Peroxide, ml. 0.002 N thio per g.			
		1	2	3	4
1		68.2	120.0	165.9	211.0
2		72.0	121.3	172.0	213.0
3		66.0	131.9	200.8	230.0
4		70.0	113.4	181.0	230.0
5		42.8	60.5	90.0	121.2
6		33.5	51.0	62.3	87.6
7		66.0	138.6	194.0	226.0
8		64.3	124.0	187.0	221.0
9		58.0	160.0	184.6	241.0
10		40.0	54.0	65.0	120.0
11		40.5	66.1	95.2	126.0

The general trend of these data indicates that rapid induction development, as recorded by weight behaviour graphically represented in Figures 3 to 6, is associated with the higher peroxide values. It will also be observed that the samples of poor drying quality, viz., samples Nos. 5, 6, 10 and 11, had a low rate of peroxide formation and gave low final values.

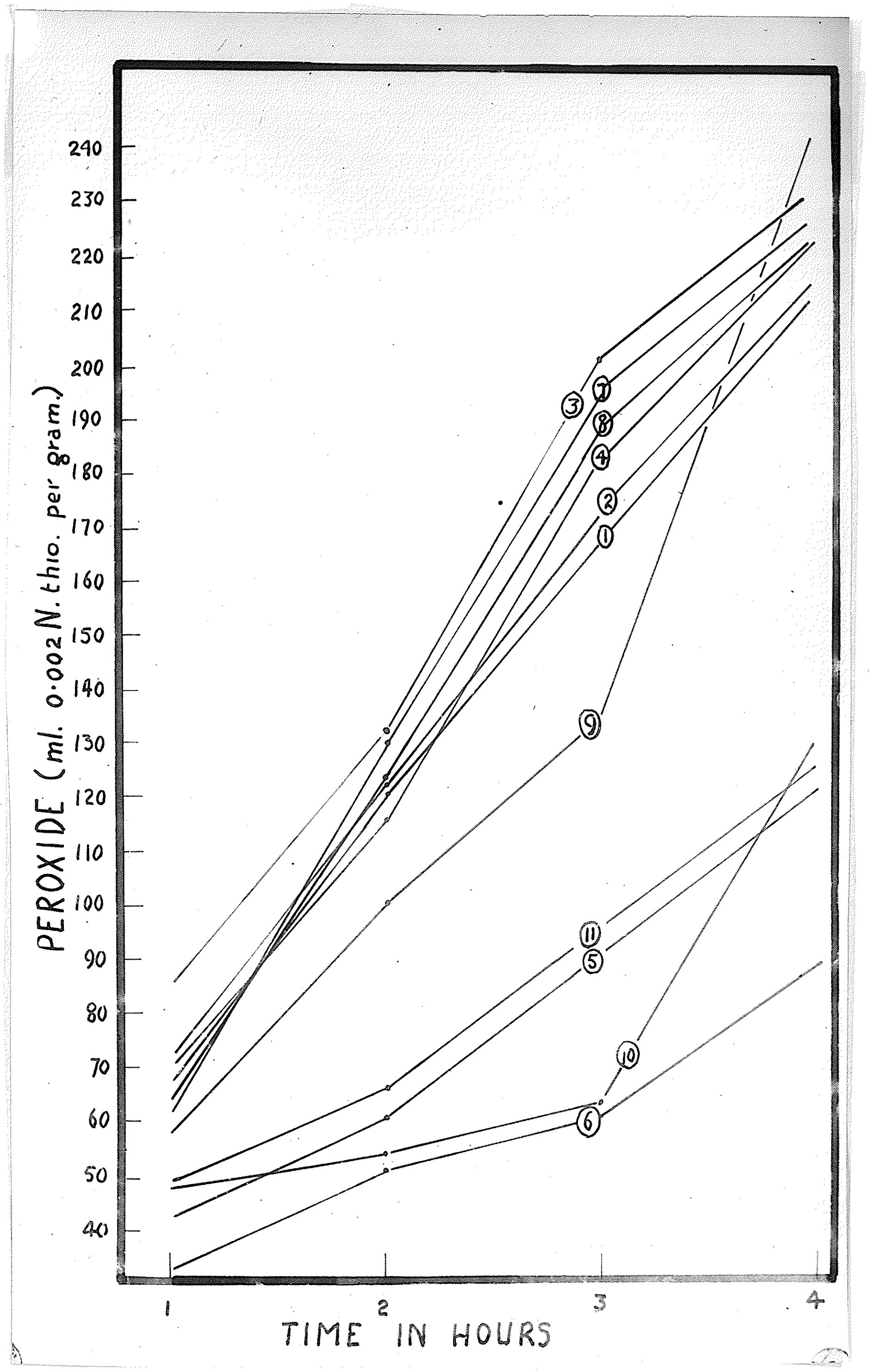

Fig. 7. Peroxide formation as a function of induction time.

POLYMERIZATION BEHAVIOUR

Untreated raw or refined linseed oils are seldom employed as such for the preparation of protective coatings. Usually, the oil receives a suitable pre-treatment which corresponds to polymerization. It seemed essential therefore that any study concerned with the significance of composition in relation to drying should also include a study of the polymerization behaviour.

Considerable variation in industrial processing exist, but the methods of pre-treatment generally consist of heat bodying or blowing with air or oxygen. The heat bodying of an oil results in polymerization, whereas blowing causes an initial auto-oxidation and subsequent condensation.

Polymerization increases viscosity, specific gravity and refractive index, while iodine value is decreased. Polymerized oils are known commercially as "Stand oil" or "lithographic oil". Industrially, polymerization is achieved by heating the oil in a kettle (enameled, silvered, but preferably of nickel). If the heating be performed out of contact with the air, the kettle is provided with a form of special lid. Otherwise, a lid of the usual hood form may be employed, connected with a flue or suitable condensing system. The kettle may be heated over a fire or by superheated steam. Operation temperature is between 260 to 280°C.

Among the many advantages of heat-treated oils are their better sealing properties, decreased yellowing tendencies, greater resistance to excessive oxidation, better levelling properties, quicker setting and improved water resistance.

The laboratory technique adopted for this study consisted of following the refractive index changes of the oils during heat treatment at 270°C.

Refractive index changes were considered preferable to changes in iodine value, since many investigators have been unsuccessful in this respect. Steger and Van Loon (39) have shown that iodine values of polymerized oils are only apparent and not actual, and that under certain conditions iodine value may show even a temporary increase during polymerization.

For this purpose an oil bath containing suitable oil of high flash point (540°F.) was so arranged as to function at 270°C. (± .5°C.). Both an electrically heated, thermostatically controlled bath and an adjusted gas-flame heated bath were used, the gas-heated bath proving more desirable and giving a more satisfactory temperature regulation. In both cases it was essential to have a stirring device.

Preliminary tests were conducted on 10 cc. portions of oil placed in a 17 mm. test tube and fully immersed in the bath at the appropriate temperature. Refractive index readings were made at different time intervals over a period of 14 hours, care being taken that cooling of the main body of oil was at a minimum during the reading interruption.

It was observed that after a number of hours of heat treatment, considerable condensate was collecting on the walls of the tube. Therefore, in the final tests, 25 cc. of the oil was placed in a 125 cc. round-bottom long-necked Florence flask, in order that the oil might be rotated from time to time during the reading intervals; however, this did eliminate the condensate formation.

Polymerization data as measured by increase in refractive index of the oil are given in Table XI. and graphically represented in Figs. 8 and 9.

TABLE XI.

Refractive Index Changes of Different Linseed Oils during Heat Treatment at 270°C.

Refractive Index 25°C.

Sample No.	Time in Hours.															
	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	
1	1.4804	1.4822	1.4832	1.4842	1.4850	1.4857	1.4867	1.4873	1.4883	1.4895	1.4907	ø 1.4920	ø 1.4925	1.4926	1.4940	ø gel 11-12 hr
2	1.4799	1.4818	1.4828	1.4838	1.4847	1.4853	1.4860	1.4867	1.4877	1.4887	1.4897	1.4907	ø 1.4914	1.4920	1.4930	gel 12 hrs.
3	1.4794	1.4809	1.4820	1.4832	1.4842	1.4847	1.4853	1.4858	1.4869	1.4888	1.4897	1.4906	1.4915	1.4919	1.4927	gel 12 hrs.
4	1.4792	1.4808	1.4818	1.4827	1.4833	1.4838	1.4845	1.4850	1.4860	1.4875	1.4884	1.4895	1.4904	1.4910	1.4910	gel 12½ hrs
5	1.4797	1.4809	1.4817	1.4824	1.4831	1.4839	1.4846	1.4855	1.4865	1.4875	1.4886	1.4897	1.4907	1.4913	1.4910	Not quite gelled on gel point at 14 hr
6	1.4796	1.4805	1.4815	1.4822	1.4829	1.4834	1.4838	1.4843	1.4853	1.4864	1.4874	1.4884	1.4905	1.4901	1.4908	idem.
7	1.4794	1.4812	1.4825	1.4833	1.4843	1.4848	1.4854	1.4860	1.4875	1.4889	1.4898	1.4907	1.4914	1.4920	1.4920	gel 12½ hrs.
8	1.4793	1.4808	1.4817	1.4825	1.4832	1.4842	1.4852	1.4859	1.4870	1.4882	1.4890	1.4895	1.4904	1.4920	1.4920	gel 12½ hrs.
9	1.4802	1.4815	1.4821	1.4835	1.4844	1.4851	1.4859	1.4869	1.4879	1.4898	1.4901	1.4909	1.4917	1.4930	1.4937	gel 12½ hrs.
10	1.4785	1.4806	1.4812	1.4817	1.4822	1.4827	1.4834	1.4842	1.4853	1.4865	1.4877	1.4888	1.4898	1.4910	1.4908	On gel point at 14 hours.
11	1.4790	1.4806	1.4815	1.4825	1.4831	1.4838	1.4845	1.4854	1.4865	1.4880	1.4889	1.4898	1.4895	1.4915	1.4910	gel 13 hrs.

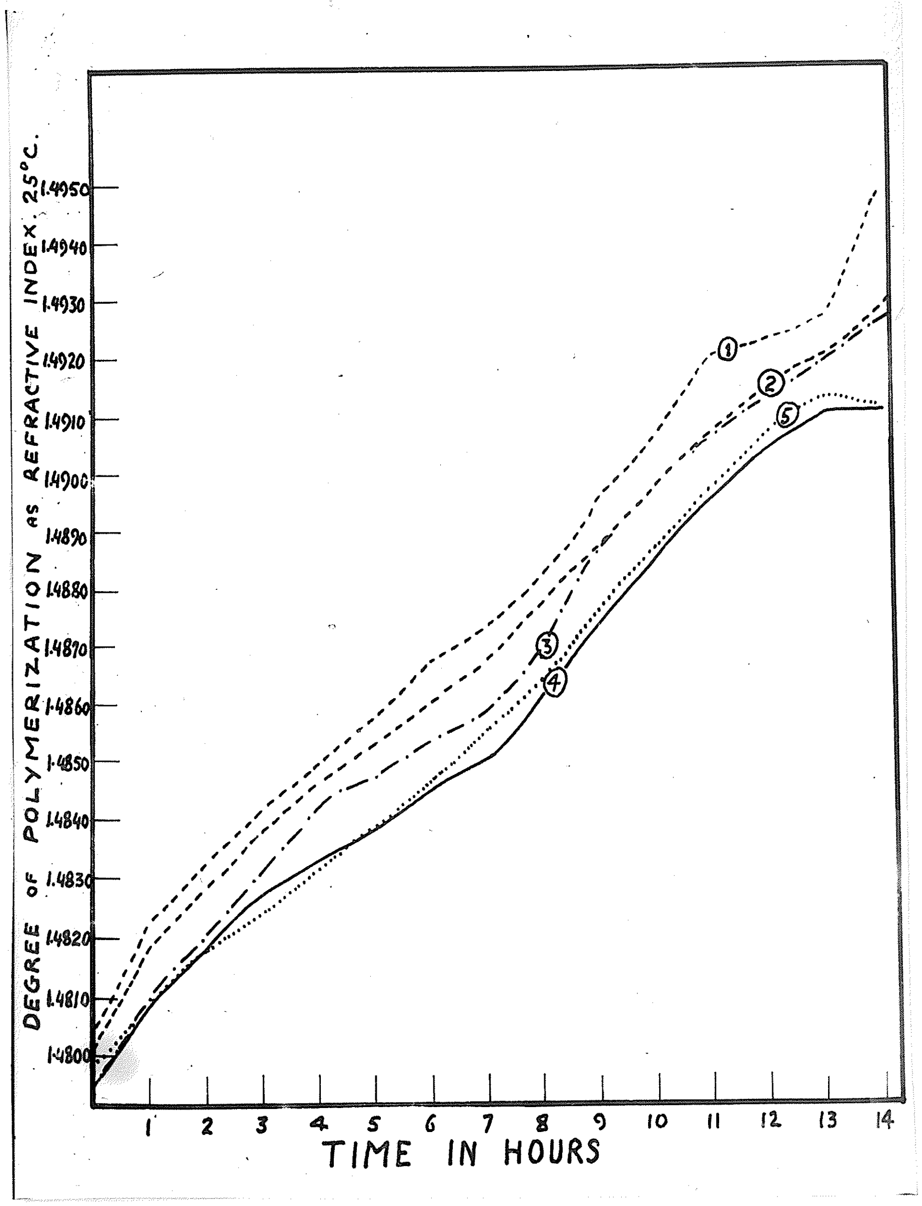

Fig. 8. Degree of polymerization of different linseed oils. Refractive index as a function of time of heat treatment in air at 270°C.

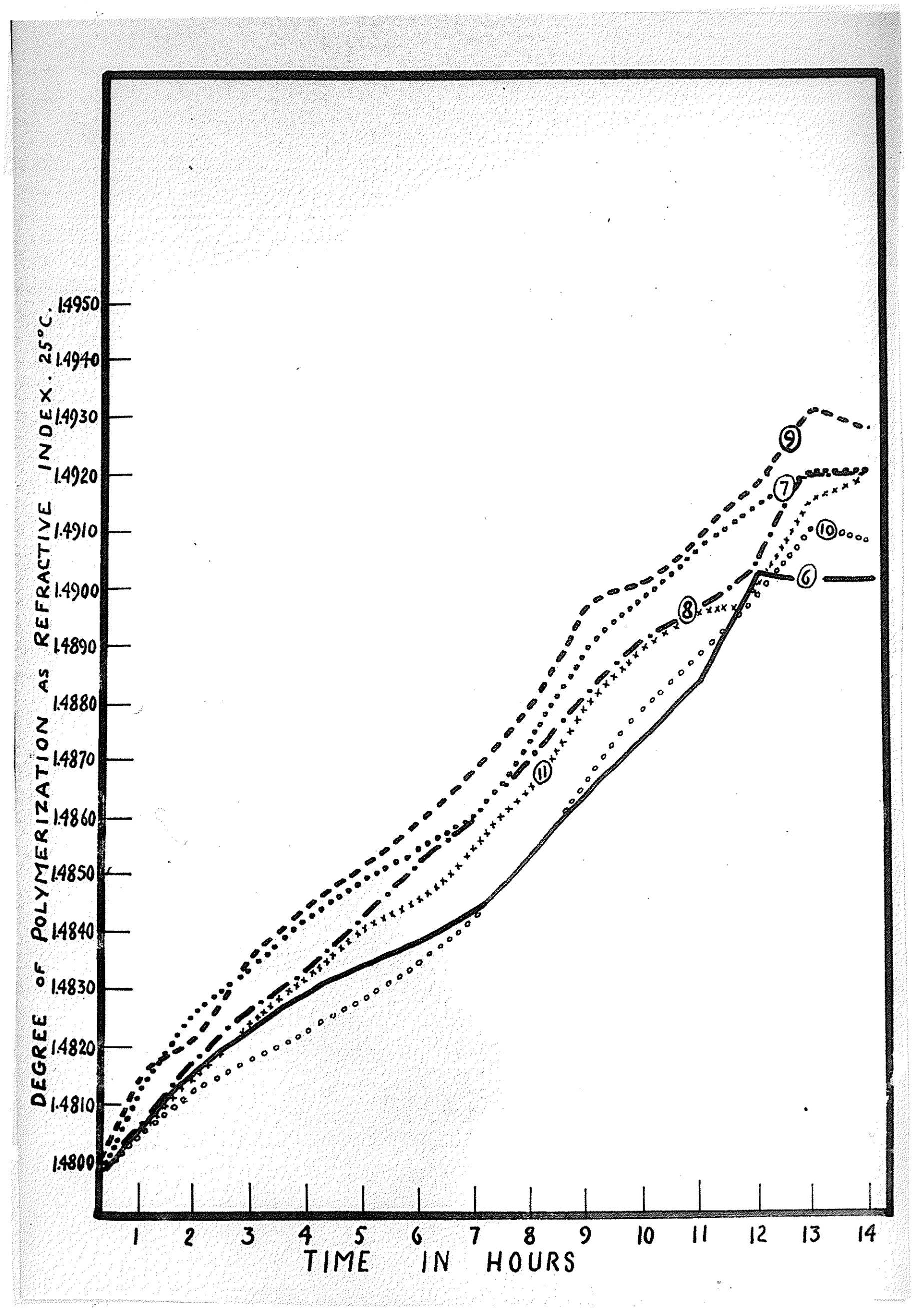

Fig. 9. Degree of polymerization of different linseed oils. Refractive index as a function of time of heat treatment in air at 270°C.

The general trend of the polymerization curves appears to correspond to the total degree of unsaturation. Initial high refractive index is an indication of final high refractive index after polymerization.

It would appear from these data that original differences in refractive index between samples are magnified by heat treatment. For example, samples Nos. 6 and 7 possessed an original n/D_{25} of 1.4782 and 1.4784 respectively; after 15 hours of heat treatment at 270°, this difference had increased the respective indices to 1.4901 and 1.4920 or from an original raw oil difference of n/D_{25} 0.0002 to a difference of n/D 0.0019 for the highly polymerized oils.

Further comparison of the individual curves showed that those samples giving poorer development curves (viz., samples Nos. 5, 6 and 10) also possessed a poorer original drying quality in the raw state. In the case of the samples investigated, there appeared to be a relationship between time of gel formation and oil quality. Samples Nos. 1 and 2, which have been shown to possess good drying quality, commenced to gel at 11½ and 12 hours respectively, while samples Nos. 5, 6 and 10 (poor quality) were not quite gelled at 14 hours.

This study would also indicate that the degree of total unsaturation may not be taken as a true index of polymerization behaviour, since it will be seen that samples of approximately the same degree of unsaturation show considerable differences in polymerization curves.

OIL VARNISH TESTS

A simple type of oil varnish was now prepared, in order that the varnish drying time of the samples under investigation might be evaluated.

The varnish was prepared without the addition of resins, since it is known that oils of different composition react variously with different resins. It was considered advisable therefore to eliminate this variable. The linseed oils were polymerized for 7 hours at 270°C., after which the viscous stand oils were suitably thinned with varnish makers' naphtha in the oil : naphtha ratio of 1:0.7 by weight. The driers employed were cobalt and lead naphthenates[ø] which are oil-soluble without any preliminary treatment. This type of drier was selected because of its uniformity and its extensive use in the industry where it is replacing the so-called cooked driers. The drier was added in the proportion of 0.2% Pb and 0.03% Co, this combination being considered the most satisfactory for polymerized linseed oil.

After the addition of the drier, the oils were allowed to stand for 24 hours prior to conducting drying tests, as the ultimate effect is not obtained immediately. It is known that a certain amount of induction oxidation takes place, which stabilizes the oil varnish and that drying tests should not be made simultaneously with drier addition.

The oils changed colour considerably after the addition of the drier, and upon standing the oils containing the higher percentages of saturated fatty acids became quite cloudy with some precipitate formation. It is quite possible that the cloudiness might be attributed to insoluble lead salts of the saturated acids.

[ø] The drier employed was manufactured by the Nuodex Products Corp., Elizabeth, N. J., U.S.A.

Table XII shows the drying times of the various samples, together with remarks on appearance. This table also includes for comparison purposes the drying time of the corresponding raw oils and drying time calculated to a percentage basis, using the 1938 Manitoba - Saskatchewan composite sample (No. 4) as the standard.

TABLE XII.

Drying Times of Raw and Varnish Oils.

Sample No.	Description of sample	Drying time Raw Oil Actual hr.	 As % of Standard hr.	 Varnish Oil Actual min.	 As % of Standard min.	Varnish oil Appearance
1	1 C.W. Composite, grown Alberta, 1938.	53.5	84.3	35	77.8	Clear
2	1 C.W. Composite, grown Saskatchewan, 1938.	55.0	86.6	35	77.8	Clear
3	- Indian, (commercial) 1937-38.	60.0	94.5	45	100.0	Cloudy
4	1 C.W. Composite, Man.-Sask. 1938.	63.5	100.0	45	100.0	Clear
5	1 C.W. Winnipeg Average, 1932-33	75.0	118.1	60-62	133.3-137.8	Clear
6	1 C.W. Large-seeded varieties, grown Ottawa, 1934.	74.0- 76.0	116.5-119.7	57-60	126.7-133.3	Clear
7	1 C.W. Composite, grown Ottawa, 1936.	67.0	105.5	40	88.9	Very cloudy.
8	1 C.W. Composite, grown Ottawa, 1937.	65.5	103.1	45	100.0	Very cloudy.
9	1 C.W. Small-seed varieties, grown Ottawa, 1934.	65.0	102.2	40	88.9	Very cloudy.
10	- Cyprus variety (Ottawa)	> 100.0	> 157.5	75	166.7	Very cloudy.
11	- Argentine (commercial) 1937-38.	84.0	132.3	52	115.5	Cloudy.

The preparation of varnish, as is well known, phenomenally reduces the drying time of the raw oils, and this was true of the samples under investigation.

The series was compared with sample No. 4 which was considered as representative of oil typical of Western Canadian production. Using this method of comparison, it may be observed from the above table that the five oils of good or fairly good drying quality, viz., Nos. 1, 2, 7, 8 and 9, improved relative to the standard when dried as varnishes.

The Argentine sample, however, which was regarded as of poor quality in the raw state, requiring 32% longer to dry than the standard, required only 15.5% longer as a varnish, which must be regarded as a marked improvement.

The three oils of poor drying quality in the raw state, viz., 5, 6 and 10, showed a relative and increased impairment when dried as varnishes. These oils are particularly high in total saturated and oleic acids (Table VIII) and this is offered as an explanation of this behaviour, since the oils would not polymerise as readily.

It should be pointed out that sample No. 3, which exhibited good drying quality as a raw oil, showed a slight relative impairment as a varnish. It is of interest to note here that this oil contained the highest percentage of linoleic acid and a relatively lower linolenic acid content (Table VII).

INFLUENCE OF NATURAL PIGMENTS ON DRYING TIME

Numerous investigators have drawn attention to the fact that plant pigments, such as chlorophyll, xanthophyll and carotene, act as antioxidants. An unpublished study conducted by the author showed that carotene and xanthophyll represented a considerable percentage of ripe flax carotinoids; therefore, it seems of importance to determine whether pigment concentration would affect drying time of raw or drier additioned oils.

The samples under investigation were bleached by means of 6% of A.O.C.S. standard fuller's earth. Twenty-five grams of oil were stirred slowly for 5 minutes at a temperature of 100 to 105°C., after which the oil was filtered and colour readings were immediately made on the clear oil.

Table XIII shows the colour concentration before and after bleaching, together with the respective drying times of the raw oils.

TABLE XIII.

Influence of Pigment Concentration on Drying Time.

Sample No.	Raw Oil Colour Orange	Raw Oil Colour Yellow	Raw Oil Drying time hr.	Bleached Oil Colour Orange	Bleached Oil Colour Yellow	Bleached Oil Drying time hr.
1	1.0	28.9	53.5	1.0	19.0	54
2	2.0	27.9	55.0	1.2	18.8	54
3	0.9	19.1	60.0	0.6	7.2	58
4	1.0	19.0	65.5	0.8	9.2	59 - 60
5	2.0	18.0	75.0	1.4	18.0	75 - 77
6	1.1	18.9	74.75	1.1	18.9	74 - 76
7	1.2	18.8	67.0	-	-	-
8	1.2	18.8	65.5	1.2	18.8	65
9	1.5	18.5	63.0	1.5	18.5	62 - 65
10	1.3	18.7	> 100.0	1.0	19.0	> 100
11	2.0	18.0	84.0	1.2	18.8	82 - 84

The bleaching method employed was not effective in all cases, and when effective, the degree of decoloration varied considerably between samples. The effect on drying time of a reduction in pigment concentration is not particularly marked, and only in one case, namely sample No. 4, was the drying time reduced to any appreciable degree.

It will be observed that the degree of pigment reduction by the bleaching method employed was not very considerable; it should be explained, therefore, that it was regarded as inadvisable to induce bleaching by more stringent methods, in view of the possibility of inducing other changes.

PHOTOMICROGRAPHIC REPRESENTATION OF OIL FILMS

Recently, some interest has been shown in the so-called crystal formation in drying-oil films. Van Hoek (41) indicates that the crystals observed by the various investigators were probably solid fatty acid crystals and not soaps as thought by earlier observers.

The author draws attention to two photomicrographs of crystal-like formation observed in the various oil films referred to in this study. While no comment can be made in this connection, it is interesting to note that the lattice-like formation represented in Fig. 10 was produced by the rapid drying oils, while the star and/or needle-like forms (Fig. 11) were usually associated with the slower drying films.

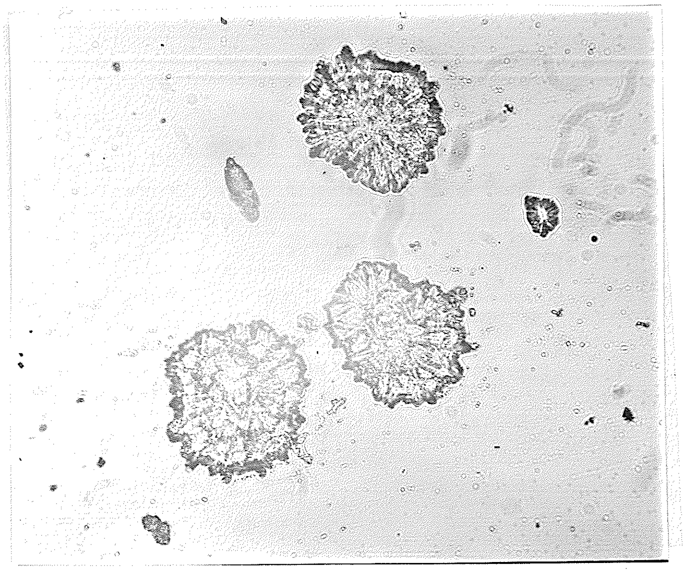

Fig. 10. Photomicrograph of crystal-like formation typical of good drying linseed oil (X 200).

Fig. 11. Photomicrograph of crystal-like formation typical of poor drying linseed oil (X 200).

SUMMARY

The construction and operation of a suitable drying cabinet, equipment and appropriate technique for conducting controlled drying tests of oil films is described.

The oil from eleven samples of flax of different origin was expressed by a laboratory procedure developed to duplicate as nearly as possible commercial practice. Various physical and chemical characteristics were determined on the expressed oils, which were correlated to drying time. Oils of high iodine value dried more rapidly than those of lower iodine value. Four samples possessing approximately the same iodine value exhibited differences in drying time, ranging from 63.5 to 84.0 hours.

Total saturated fatty acids were determined by a modification of the Bertram method, details of the method being given. It was shown that adequate settling of the fatty-acid layer increases yields as much as 0.27%. Total saturated fatty acids varied from 9.15 to 15.37%. Total unsaturated fatty acids were determined by the Kaufmann iodine value - thiocyanogen value method, which involved the preparation of the mixed fatty acids in an unaltered form; details of their preparation are given.

The three unsaturated fatty acids varied in the samples tested as follows: oleic acid from 1.88 to 13.08%, linoleic acid from 20.52 to 47.08%, and linolenic acid from 37.44 to 50.88%.

In correlating drying time to composition, it was shown that there was a distinct tendency for slow drying of raw oil to be associated with a high sum of the percentages of total saturated acids plus oleic acid.

Weight behaviour of oil films during and after drying was studied. It was graphically shown that weight development curves were relatively specific for fast- and slow-drying linseed oils respectively.

Peroxide tests were conducted as an index of induction drying. Samples of poor drying quality possessed a slow rate of peroxide formation and gave low final values.

The polymerization behaviour of the oils was followed for 14 hours at 270°C. These data indicate that original differences in unsaturation are magnified by heat treatment, and that oils of good drying quality reach the gel point sooner than slower drying oils. It was shown that samples possessing the same degree of gross unsaturation behaved differently during polymerization.

Varnishes were prepared and the series compared with a selected standard. Oils of good quality in the raw state improved relative to this standard. On the other hand, raw oils of poor drying quality were further impaired as varnishes, which may be attributed to the high percentage of saturated and oleic acids present.

The reduction of pigment concentration by fuller's earth bleaching had no marked effect on drying time, indicating that the antioxidant role of the adsorbed pigments is a minor factor in drying quality.

Attention is drawn to a micro-crystal-like formation occurring in dried linseed oil films, which appears specific for rate of drying.

CONCLUSIONS

The results of this investigation indicate that the higher the iodine value of linseed oil the greater is the probability that the oil will dry readily. It is also indicated that linseed oils of approximately the same iodine value may exhibit considerable variation in drying behaviour.

Impaired drying quality of linseed oil has been shown to be due primarily to a high percentage of the sum of total saturated fatty acids and oleic acid. A significantly high correlation was shown to exist between linoleic and linolenic acids.

Raw oils of good quality improved relative to a given standard when made into oil varnish, while oils of inferior drying quality were further impaired as varnishes.

This study also shows that the drying weight behaviour of linseed-oil films appears to be a specific quality characteristic, and that rapid induction development is associated with high peroxide values.

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