

USE OF ADSORBENTS IN REFINING  
LINSEED OIL

A Thesis

by

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## I. GENERAL INTRODUCTION

Wartime shipping restrictions have resulted, during the past two years, in a scarcity of the edible oils ordinarily used in this country. The possibility of utilizing linseed oil for edible purposes is now under investigation.

Linseed oil has an objectionable odor and color. The ordinary refining procedures which are applicable to edible oils do not improve the color and odor to any extent. Edible oils must also have a low free fatty acid content and good stability during storage.

Deodorization removes the odor completely from raw linseed oil. However, on heating the refined and deodorized oil, off odors develop which are referred to as "reverted odors".

Attention was directed in this laboratory to the refining of linseed oil to produce the desired qualities of an edible oil. A study was also made of the "reverted odor" and stability of linseed oil insofar as they were affected by refining with adsorbents.

## II. HISTORICAL REVIEW

### 1. General

The experimental portion of this thesis deals with the production of a refined linseed oil suitable for edible purposes. Since the substances which are removed from most oils are similar, the literature will deal with refining processes of various edible oils, insofar as they can be applied to linseed oil.

Vegetable fats and oils as expressed by the ordinary methods, viz., boiling water treatment, pressing or extraction, are not usually in a suitable condition for use in industry. The oils must undergo various refining treatments to remove constituents which may prove harmful in subsequent processes. The choice of refining procedure depends upon:

- (1) - subsequent use of the oil, and
- (2) - seeds and extraction details.

In some cases, the products are sufficiently pure for immediate use in manufacturing, e.g., poorer grade oils can be used without refining for lubricants and leather polish. Some edible oils such as olive and nut oil have been used without purification of the expressed oil.

The removal of free fatty acids is not important if the oils are to be used in candle making and soap making. However, olive oil can not be used for lubricating purposes or rape oil for burning if the free fatty acids are not removed.

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Oils which are to be used for edible purposes require the most complete purification. G. McBride (57) has stated that "the general public believe that the important factor is flavor stability and removal of undesirable flavor; the presence of a suitable color and brilliance is secondary in importance."

Edible oils are not generally refined by chemicals with the exception of alkalis. Lewkowitch (50) states that "notwithstanding the large number of patents which claim effective purification by means of chemicals, no chemically treated oil can be looked upon as a product fit for human consumption."

The purity of the oil may depend partly upon the procedure used in expressing. It has been shown (50) that contact of oils and fats with organic matter from which they have been obtained leads to accelerated formation of free fatty acids, which in turn dissolve foreign substances. Hence rapidity of extraction is necessary. Oil extracted from seeds that are unripe also shows a higher content of free fatty acids than the oil from ripe seeds.

## 2. Substances Removed by Refining

In most vegetable oils, the impurities are of the same type and have been classified by Hilditch (34) as:

(1) Suspended and coarse material, mainly mucilaginous substances, resins and albuminoid matter.

(2) Fine suspensions of colloiddally dispersed particles of the above type.

(3) Natural coloring matters extracted from vegetable tissues and dissolved in the fat.

(4) Free fatty acids produced by hydrolysis of the natural fat.

(5) Semi-volatile compounds dissolved in the fat and conferring upon it undesirable odor and taste, e.g., aldehydes.

In addition to these, a small proportion of moisture may cause some turbidity in the oil. Furthermore, nitrogen compounds are removed during refining. G. Bourchard (15) asserts that nitrogen is a constituent of all oils and fats, being produced by a breakdown of remnants of vegetable tissues. However, Thornton and Kraybill (73) report that one-third of the nitrogen of soybean oil is not held by an aluminum silicate absorbent. They state that the unadsorbed nitrogen is not lecithin or cephalin since they are completely recovered from the absorbent.

When hydrogenated linseed oil is heated, a characteristic "reverted" odor develops even though the oil may have been previously refined and deodorized. The possibility of the reverted odor being due to odoriferous nitrogen compounds has been studied by several workers.

Voskrenski and Dobrumina (74) report the presence of an odoriferous constituent in soybean oil with a variable nitrogen content. Davies (18) has shown that fishiness in linseed oil is connected with peroxides, formaldehyde, and tertiary nitrogen compounds. The trimethylamine oxide, associated with decomposition products of lecithin and



and choline, acts as an oxygen carrier during oxidation of the fat producing trimethylamine which has a characteristic fishy odor and flavor. The more (12) highly unsaturated the oil, the greater the tendency to form formaldehyde and dimethyl and trimethyl amines from the amine oxides.

### 3. Refining Methods

A large number of refining procedures have been developed in the last 150 years and numerous patent specifications claiming varied results have appeared in the literature. This can easily be understood since the refining of each individual oil is a separate problem.

However, the methods of refining edible oils can be considered broadly under the headings: (a) tanking, (b) alkali refining, (c) acid refining, (d) general chemical methods and (e) adsorbent refining. Adsorbent refining will be discussed at some length since it is the main concern of this thesis.

#### (a) Tanking:

This method is not applied generally to edible oils but is used specifically for oils of fairly high quality which will subsequently be alkali refined. In tanking, moisture and mucilaginous material settle out, the early removal of the latter being important since they act as stabilizers of emulsions of oil and soapstock formed during alkali refining. Tanking is employed to a great extent in the preliminary refining of linseed oil which may also involve treatment with

water or steam and then settling of impurities. (8)

(b) Alkali Refining:

The main purpose of alkali refining is to neutralize the free fatty acids which poison the catalysts used in hydrogenation and which impart an undesirable flavor and possibly odor to the oil.

The common methods use sodium hydroxide, sodium carbonate and calcium hydroxide in various concentrations. These alkalis along with neutralizing fatty acids cause coagulation of colloidal impurities and effect some bleaching of colored materials. The merits of the various alkali reagents depends upon the results to be obtained. If, besides the removal of free fatty acids, decolorization of oil is desired, caustic soda is most efficient, though it causes a greater loss of neutral oil. Sodium carbonate gives a good yield of neutral oil but does not improve the color. Calcium hydroxide gives good decoloration but extensive emulsions are formed.

An important objection to the ordinary methods of neutralization is the loss due to excess of neutralizing agent, occlusion of neutral oil in the soapstock or "foots" and formation of extensive emulsions. The improved alkali refining methods give a well refined oil with minimum loss of neutral oil. Sodium carbonate has the advantage of not attacking neutral oil, but causes excessive foaming. The Clayton (16, 55) process using sodium carbonate is a continuous method which eliminates difficulties due to foaming and is superior

to others. The continuous (29) methods, which depend upon centrifugal separation of the foots, minimize losses due to occlusion and emulsions. Among the recent advances discussed by Rheublem (67) are methods in which salts are used to break the oil and soap emulsions. The separation of oils and foots by using solvents such as benzine has been proposed but is not successful.

In this section on neutralization or deacidification of oils and fats, it might be well to mention the process involving the distillation (54) of free fatty acids, first applied by Lever Bros. to the refining of vegetable oils. At temperatures above  $200^{\circ}\text{C}$ . and under reduced pressure the free fatty acids are removed. Although this process has not received the technical attention given to other methods, Manderstam (54) believes it is superior since it has a wide application and is continuous; no oil is lost and deodorization is simultaneously effected. Deacidification by means of carbodimides (69) and by adsorption (13) have recently been employed.

Numerous methods have been developed using alkalis in different concentrations and at different temperatures. The majority find a temperature of  $50^{\circ}\text{C}$ . most satisfactory.

### (c) Acid Refining:

This method (14) is very seldom used in edible oil refining. Purification with strong acids such as sulphuric acid causes the charring of impurities and their removal from the oil. Such rigid treatment leaves a disagreeable

flavor in the refined oil.

However, different refining procedures (43) use weak acids or weak solutions of strong acids to remove impurities. Corn oil, cottonseed oil, wheat germ oil and other vegetable oils are often treated with oxalic, boric or phosphoric acid to coagulate impurities. (7, 68) Dilute sulphurous (14) acid removes the acrid taste from soybean oil. Agitation of the oil with lactic, tartaric and citric acids removes heavy metals and improves the color of certain vegetable oils. (9) Refining with phosphoric (280) acid removes impurities and at the same time (26) preserves the odor and flavor of the oil. Proctor and Gamble have applied for patents on the use of phosphoric acid as an antioxidant. (21,22)

#### (d) General Chemical Methods:

Chemicals are not generally used in refining edible oils, since a disagreeable flavor is produced in the oil, which is very difficult to remove.

The most widely used methods apply oxidizing agents such as hydrogen peroxide, oxygen, ozone and bichromate which oxidize the colored pigments to colorless compounds.

However, certain methods employ chemicals for specific purposes. Polyhydroxy substances such as glycerol, diethylene glycol, mannitol and sorbitol are mixed with natural or hydrogenated soybean oil to inhibit the reversion of odor and to reduce the color. (23) Odor and color of oils are removed partially by such solvents as furfural, methyl furfural, ethylene, glycol and diethylene glycol. (71)

#### 4. Adsorbent Refining

Adsorbent refining involves the use of silicious clays, charcoals and hydrous oxides. It depends upon the property that these substances are able to fix colloiddally suspended materials or dissolved substances of relatively high molecular weight.

Adsorbent refining is essentially used to purify edible oils and fats. To deal with this subject more fully, the following topics will be discussed.

(a) Efficiency in Removing Impurities.

(b) Classes of Adsorbents.

(c) Theory of Adsorbents.

(d) Factors Effecting Adsorption.

(e) Qualities of a Good Adsorbent.

(f) Regeneration of Adsorbents.

##### (a) Efficiency in Removing Impurities:

Adsorbents remove a large proportion of the coloring matter as well as mucilaginous matter and colloiddally dispersed particles. They remove coloring matter completely from the oil, while chemical methods only decolorize the pigments but do not effect their removal from solution. Certain odoriferous constituents are also adsorbed.

The removal of free fatty acids is effected by certain adsorbents. In a mixture of neutral olive oil and 20% stearic acid, the free fatty acid value was reduced from 43.0 to 0.36% oleic acid after filtration through a column of alumina (44). Reports (59) of plant bleaches of various

refined oils with good adsorbent clays show a slight lowering of free fatty acids except in the case of cocoanut oil. The removal of free fatty acids must be due to preferential adsorption and not to neutralization since the adsorbents used were acid clays.

(b) Classes of Adsorbents:

Adsorbents are classified as colloidal earths, charcoals and hydrous oxides. These adsorbents will be discussed in order of their development.

(i) Colloidal Earths. Fuller's earth is the classical example of this type. It has been known since early times. At first, fuller's earth was used for clarifying oils, but later it acquired an additional use, that of decolorizing oils. Before the first Great War, colloidal earths of a different nature were developed, and German deposits of Frankonite, Siltonite and Tonsil were shown to have better refining effects upon vegetable oils than fuller's earth. (20,79) The Russians developed "askonite" and other natural deposits of colloidal clays.

The colloidal earths are composed of the inorganic colloidal material in the soil whose particles have a diameter between 20  $\mu$  and 100  $\mu$ . These earths are extracted from the soil with water and separated from the coarser particles by the centrifuge.

Colloidal clays contain a relatively constant composition of silica, alumina and iron oxide, and a variable content of alkali and alkaline earth metals. The most common adsorbent

clays have a montmorillonite structure ( $\text{MgO} - \text{Al}_2\text{O}_3 - 5\text{SiO}_2 - 2\text{H}_2\text{O}$ ).

The conversion of the colloidal earths to useful adsorbents is accomplished by the process of "activation".

Activation involves the leaching out of soluble material to enlarge the pores and capillaries in the clay with the subsequent increase in surface exposure. The extent of bleaching depends upon the interstices left in the minerals and upon the amount of exchangeable base.(45) The higher the amount of exchangeable base, the better the bleaching agent. Water, acids and electro-dialysis are used for activation of clays.(1,46,47) If water is present the clay hydrolyzes to some extent and hydrogen ions replace the alkali and alkaline earth cations. In electro-dialysis, hydrogen and aluminum ions replace calcium, magnesium, potassium and sodium ions. If the earth is treated with acid, the iron and aluminum are dissolved with an increase in surface and a gradual exchange of calcium and magnesium with hydrogen ions.

(ii) Charcoals. Charcoals have been used recently for refining purposes, their decolorising action and cheapness being their most favorable points. When charcoals or activated carbons are used, it is necessary that all mechanical impurities be removed first. Animal and bone charcoal are most economical but are not as advantageous as charcoal from selected sources.(3)

Conflicting reports (25,48) as to the efficiency of charcoals as compared with colloidal earths have appeared in

the literature. However, it has been well established that a mixture of a colloidal earth and an activated carbon give a better result than either adsorbent used alone.(25,70)

(iii) Hydrous Oxides. Although gels have been used for many years for the adsorption of gases, only recently did they become of value in removing solids from solution, and eventually in refining procedures. A drawback to their use in refining has been the cost.

Gels have been used where specific action is required. Phosphatides are removed from soybean oil by an aluminum silicate adsorbent (73). Lecithin can be removed from solutions containing it by calcium phosphate (10). In this laboratory a method has been developed for the concentration of Vitamin E from wheat germ oil with the use of an active mixture of silica gel and alumina (66). A more complete discussion of one of these gels will be given in a subsequent section.

Adsorbent methods have been combined with chemical methods. According to an American patent (78), cottonseed oil is bleached with a mixture of fuller's earth and an electrolyte such as ferric chloride or calcium chloride, the electrolytes effecting coagulation of the colored impurities. A German patent (78) describes a method of bleaching oils with zinc dust at 160°C.

Linseed oil is refined for edible purposes by askonite or silica gel; the askonite gives better decolorising action.



(c) Theories of Adsorption:

The adsorption system which is applied in the refining of vegetable oils is the removal of solutes from solutions. There are three actions which are possible:

(1) Positive adsorption where relatively more of the solute is adsorbed than of the solvent, (2) negative adsorption where the solvent is adsorbed more strongly than the solute and (3) where the solvent and solute are adsorbed in the same ratio as they exist in solution.

Odeen and Slosson (59) review the theories applicable to the bleaching of oils. Five common theories are given --

(i) Gibbs theory: This is stated: solutes which lower the surface tension of the solvent will be concentrated at the solid-liquid interface. McBain and Dubois (56), Bartel et al., (6) and others (66) applied this theory to different systems.

(ii) Gurwitsch's theory: Gurwitsch disagrees with Gibbs' theory and states that adsorption simply obeys Newton's law of gravitation. The concentration of dissolved substances at the adsorbent surface is due to a greater attraction between the adsorbent and solute particles than between the adsorbent and solvent particles.

(iii) The electrical theory is based upon the assumption that the adsorbent being positively charged attracts the negatively charged solute.

(iv) Haseman states that free di-silicic acid, formed from available H of the OH ions, is the active ingredient in

decolorization.

(v) Nutting suggests that during activation of a clay there is a removal of loosely held ions leaving free valences for preferential adsorption of coloring matter.

The modern concept is based on Langmuir's secondary valence forces. He states that the forces of adsorption are produced by the free cohesion forces on the fresh surface of the adsorbent which he denotes as residual or secondary valences. The substances which are adsorbed are held by virtue of their secondary valences produced by orientation and dispersion within the molecules.

Miller (5) states that the position of the hydroxyl and amino groups have an effect upon their readiness to be adsorbed. If these groups are in the ortho position, they will be more strongly adsorbed than if in the para position. This implies that adsorption depends largely on the nature and arrangement of the atoms or groups in the molecule, certain groups favoring and others opposing adsorption.

Linner & Gortner (51) showed that normal and iso-acids differ only slightly in adsorption values, which indicates that branching has little effect upon the number of molecules adsorbed.

#### (d) Factors Effecting Adsorption:

Purification of vegetable oils is industrially accomplished by either percolation through large beds of adsorbent or by agitation of large amounts of oil with a small proportion of adsorbent. The latter method is more commonly used for

economic reasons, while the first method is employed more generally in the petroleum industry. Fuller's earth is manufactured in two forms; coarse fuller's earth, suitable for filtration and very fine earth for the agitation process.

Efficiency of refining depends upon numerous variable conditions which will be discussed below.

(i) Time and Temperature of Agitation. These factors vary with the refining procedure; it is necessary to predetermine the optimum conditions before actual refining. At high temperatures, the adsorption capacity of the adsorbent is decreased; however, the viscosity of the oil is decreased and better agitation of the oil with the adsorbent is effected. An optimum intermediate can be obtained whereby best agitation and refining are obtained.

(ii) Moisture Content. An excess of moisture in the oil deactivates the adsorbent. However, Odeen and Slosson (59) show that a small amount of moisture is actually beneficial to refining.

(iii) Soap. If an alkali-refined oil is further refined with adsorbent, an increase in free fatty acids might result owing to the presence of soaps. The soaps dissolve in the fat and split at elevated temperatures liberating free fatty acids.

(iv) Addition of the Adsorbent. If the adsorbent is added all at once, better bleaching is obtained than if added in increments.

(v) Multiple Bleaches. If the oil is bleached several

times with fresh batches of the same adsorbent, an increased refining does not result. It has been suggested that this is due to increased exposure to the air and polymerization.

(vi) Amount of Adsorbent. This will vary with the oil and the desired result.

(vii) Percentage of water in the Adsorbent. The last trace of water in the adsorbent earths and gels is very strongly held. Holmes and Elder (37) found that some gels retained that last 3.5% of water after heating at 900°C. Patrick (58) states that 4% moisture is necessary for full porosity properties and best refining.

(e) Requirements of a Good Adsorbent:

As a conclusion to a discussion of adsorbents, it might be well to state the necessary requirements of an adsorbent for refining edible oils. The following list has been compiled partially by Whitlatch (75).

1. Earth, gel or charcoal must not cause any chemical reaction with the fatty material.
2. The adsorbent should not increase the uptake of oxygen or increase the fatty acid content.
3. The clay taste must not linger with the oil.
4. A satisfactory color must be produced.
5. Earth must permit a fair rate of filtration.
6. A low ratio of adsorbent material to the oil is necessary for efficient operation.
7. Retention of oil should not be greater than 35%.

#### (f) Regeneration of Adsorbents:

Regeneration of bleaching clays is not economic if the original earth is very cheap. However, for expensive adsorbents, e.g., silica gel and alumina, their recovery is necessary.

The most common methods use hot water, hot salt solutions and organic solvents to release the fat from the adsorbent (49,27,31).

Erdheim (24) compared several methods and found extraction with benzine and drying at  $110^{\circ}$  gave the most active recovered earths.

Even after an adsorbent has done its work, it still has a reserve power for removing color from unbleached oil. Hassler (32) utilized this reserve power to partially bleach fresh oil, thus saving on fresh adsorbent.

#### 5. Manufacture of Silica Gel

The adsorptive power of silica gel has been known since 1861. However, the first important work on the properties of silica gel was studied by Van Bemmelen (11). He found that dried silicic acid adsorbs various vapors and removes some materials from solution. Later in 1919, Patrick (61) prepared a highly adsorbent gel by mixing hot solutions of hydrochloric acid with sodium silicate. After washing and drying slowly, a hard transparent silica gel is produced.

Holmes and Anderson (36) prepared an adsorbent gel by treatment of sodium silicate with ferric chloride. After

incineration, the soluble ferric oxides were leached out with hydrochloric acid. This adsorbent was more active than that prepared by Patrick's method. Since capillary size and extent of inner surface of the adsorbent has a great deal to do with its capacity, it would follow that Holmes' adsorbent is more active owing to the increase in capillary space. Holmes' silica gel was found to have a good decolorizing effect upon lima oil while Patrick's silica gel had no such effect.

Since these first methods, variations in the preparation of active silica gels have been put forward. Sulphuric acid, acetic acid ethanol and methanol have been used to precipitate the gel substances (39,40,76); the last two increase the velocity of precipitation. Hurd et al. (38,39,40,41,42) and other workers (64,65,72) have studied the effect of temperature, pH, and precipitant on the time of set. Increase of temperature increases the time of set; a pH between 3-6 is optimum; hydrochloric acid-precipitated gels are most active. Heating beyond 750°C. resulted in a loss of activity.

Gordon, Martin and Synge (30) prepared silica gels by Patrick's method varying the conditions of temperature, pH and time of set. They found that the adsorbent properties of silica gel vary greatly with changes in the above conditions.

## 6. Stability of Raw and Refined Oils

The stability of most oils is lessened by alkali and adsorbent refining due to the removal of natural antioxidants (33). The nature of the antioxidant of linseed oil has not been well established. It has been suggested (17) that the natural antioxidants in linseed oil are carotenoid pigments, xanthophyl and phosphatides, since these substances inhibit the oxidation of linseed oil in the dark. Dean isolated an antioxidant concentrate from the foots of an alkali-refined linseed oil. Hilditch also obtained a concentrate having antioxidant properties from soybean oil (35).

Olcott and Mattill (60) affirm the presence of natural antioxidants in cottonseed and wheat germ oils which they refer to as inhibitols. They were obtained in the methyl alcohol extract of the unsaponifiable matter after crystallizing out the sterols from the petrol ether extract.

### III EXPERIMENTAL

#### 1. Methods

##### (a) Refining Procedures:

(i) Alkali -- The amount of free fatty acids was first determined. Then a 30% solution of caustic soda was added to the oil, about 2% in excess of that required to neutralize the free fatty acids. The mixture was agitated rapidly at room temperature for 45 minutes. The temperature was then raised quickly to 65-70° and agitation decreased. These conditions were held for 30 minutes. The mixture was allowed to stand overnight and then was filtered with suction. By this method the free fatty acid value was lowered to 0.03% oleic acid.

(ii) Bisulphite -- A 10% solution of sodium bisulphite was mixed with 100 grams of oil. The mixture was agitated slowly in order to avoid an emulsion. These conditions were maintained for one-half hour. The aqueous layer was removed and the oil was filtered. A large portion of the odor was removed by this treatment.

##### (b) Analytical Tests:

(i) Acid Value. The A.O.A.C. method was followed in this determination. 5 grams of sample were used and N/100 alkali was necessary in the titration, since the amount of free fatty acids determined was low. The results were expressed as percent oleic acid, based upon the factor: 1cc. of 0.1N sodium hydroxide = 0.0282g. oleic acid.



(ii) Peroxide Value. The ferric thiocyanate method as developed by Lips et al. (52) was employed. The peroxide value was expressed as milliequivalents per kilogram of oil.

(iii) Stability. An oven test was used to measure the stability of oils. A three gram portion of the oil was placed in the oven on a wide surface, a petri dish being found most suitable. The temperature of the oven was controlled at 100°C. At various intervals the peroxide content of a sample of the oil was determined. The oxygen uptake of the oil then could be measured against the time of heating.

(iv) Nitrogen Determination. The nitrogen content of various oils was found using the method of Gunning and Arnold (A.O.A.C.) with some modifications.

I. Digestion. Two grams of oil were used. Ten cc. of sulphuric acid were added and the mixture was heated slowly. After considerable charring, fifty cc. of sulphuric acid, ten grams of potassium sulphate and 0.5 grams of mercury were added. Heating for three hours then caused complete digestion. The above method prevents excessive foaming and gives most efficient digestion.

II. Aspiration. Aspiration of the ammonia, from the digested oil made alkaline with sodium hydroxide, into standard acid (0.0025N) for three hours, was used instead of distillation. The air was purified by previously bubbling it through solutions of potassium permanganate, sulphuric acid and sodium hydroxide. The hydrochloric acid was backtitrated with 0.0025N base. In distillation it was found that a

large volume was obtained in the standard acid obscuring the end point.

(c) Columns in Filtration:

Although these varied in the course of the work, three main types of columns were used.

(i) For small amounts of adsorbents a glass tube with a diameter of 2.3 cm. was employed. (Fig.1)

(ii) To obtain more efficient filtering with only slightly more adsorbent a column, 3.5 cm. in diameter, was found satisfactory. (Fig.2)

(iii) The best yield of oil per gram of adsorbent was obtained with a Buchner funnel, 8.5 cm. in diameter. This column was used when comparing various clays and gels. (Fig.3)

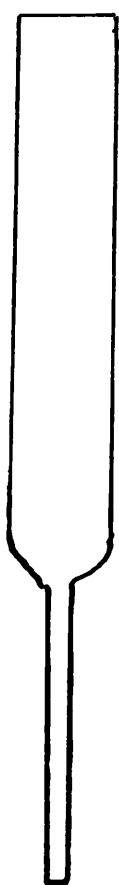


Fig 1

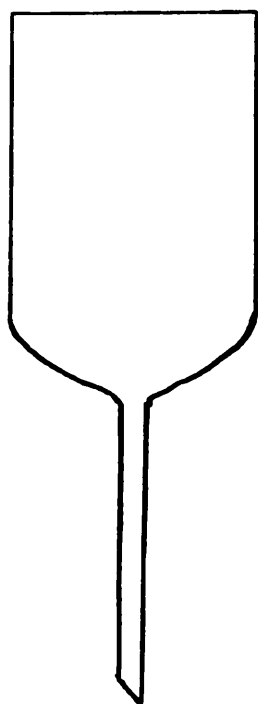


Fig2

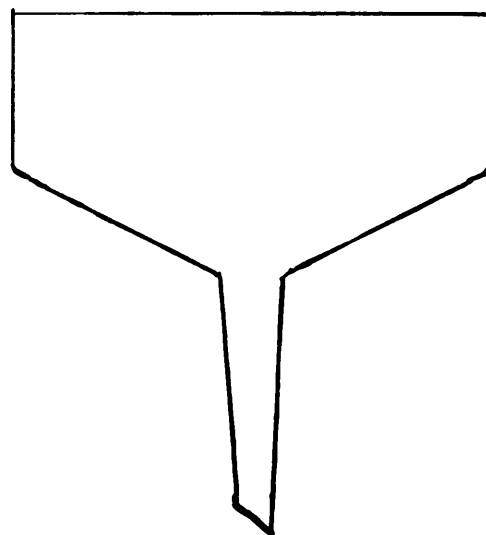


Fig 3.

## 2. Preparation of a Silica Gel-Alumina Adsorbent.

Preliminary work (53) in this laboratory showed that the usual adsorbents have little effect on refining. Fuller's earth, cellite, Hyflo supercell, wood charcoal, Carbox E, magnesium oxide, Brockman's alumina and silica gel removed very little color.

An active mixture of magnesia or alumina with silica gel gave a very active adsorbent. The following procedure was used in the preparation of this combination. Magnesium nitrate or aluminum nitrate in alcohol solution was added to the silica gel and with constant stirring the alcohol was evaporated off on a steam bath. The resulting mixture was heated for several hours in a muffle furnace to change the nitrates to oxides. Mechanical mixtures of alumina or magnesia with silica gel did not produce any better results than each adsorbent used individually.

The mixtures of silica gel with alumina or magnesia were compared at different concentrations of the silica gel to the magnesium or aluminum nitrates. Thirty cc. of raw hot-pressed linseed oil was passed through ten grams of the adsorbent in a column, 3.5 cm. in diameter. The extent of refining was determined by the color of the refined oil. The readings of color were based on 100 for mineral oil, using the 440 filter in the Evelyn colorimeter to measure the yellow color and the 520 filter to measure the red color.

Table I  
Effect of Concentrations of Silica to Alumina  
or Magnesia on the Adsorbent Properties

	Ratio of Components	Galvanometer (440 filter)	Reading (520 filter)
I Silica Gel- Alumina	25:75	8.1	82.0
	50:50	8.8	84.0
	75:25	25.5	96.0
II Silica Gel- Magnesia	25:75	8.2	40.2
	50:50	8.0	61.5
	75:25	8.2	73.0
III Raw Hot- pressed Oil			39.0

The best refining was obtained with silica gel-alumina prepared from 75 grams of silica gel and 25 grams of aluminum nitrate. In the following work silica gel-alumina was used in preference to silica gel-magnesia, and the 440 filter was used to give the color of the refined oil since it measures the upper limit of refining from yellow to colorless.

The various factors in the preparation of the silica gel-alumina adsorbent were investigated in the following order: (a) concentration of components, (b) temperature of heating and (c) time of heating in the muffle furnace.

(a) Concentration of Components:

This has already been investigated above. However, the optimum concentration of the components of the mixture was found within smaller limits. The mixture was prepared in the usual manner, and the oil was passed through 15 grams of the adsorbent in a column, 3.5 cm. in diameter.

Table II

Effect of the Ratio of Silica to Alumina on the Adsorbent Properties

Ratio $\text{SiO}_2$ to $\text{Al}(\text{NO}_3)_3$ (g.)	Galvanometer Reading (440 filter)
65:35	90.6
75:25	88.1
85:15	82.0

The best results were obtained when the adsorbent was prepared from 65 grams of silica gel and 35 grams of aluminum nitrate.

(b) Temperature of Heating in the Muffle Furnace:

Silica gel-alumina (concentration 65:35) was heated at various temperatures for a three and one-half hour periods.

Table III  
Effect of Temperature of Heating on the Adsorbent Properties

Temperature (°C)	Colorimeter Reading (440 filter)
250 - 450	60.5
600 - 750	72.2
900 - 1000	40.2

The silica gel-alumina which was heated in the muffle at 600-750°C. removed the largest amount of color from the linseed oil.

(c) Time of Heating:

Finally, the time of heating in the muffle was varied, keeping the other conditions constant.

Table IV  
Effect of Time of Heating on the Adsorbent Properties

Time of Heating (Hrs.)	Galvanometer Reading (440 filter)
3	92.0
6	73.5
9	52.0
24	30.0

The optimum time of heating is three hours.

Thus the preparation of a silica gel-alumina adsorbent, which refines linseed oil to a colorimetric reading with the 440 filter as high as 92, can be described specifically.

It was found advantageous to use 400 cc. of ethanol for 35 grams of aluminum nitrate. This volume allowed the formation of a homogenous mixture of silica gel and aluminum nitrate and fairly rapid evaporation of the ethanol on the steam bath.

### 3. Use of the Silica Gel-Alumina in Agitation and Filtration

#### (a) Agitation

In industry the method of fat refining is almost exclusively the agitation of batches of oil with a small proportion of the adsorbent. The effect of the contact of the oil with the adsorbent is demonstrated in the following experiment. The ordinary type of malted milk machine, No. 22 Gilchrist Model, and the Waring Blendor effected good agitation of the oil with the adsorbent. Stirring by hand was also employed.

Table V  
Effect of Agitation on Refining

Agitator	Weight of Adsorbent (g.)	Weight of Oil (g.)	Time (min.)	Galvanometer Reading (440 filter)
Agitation by hand	10	30	5	16
Gilchrist Agitator	10	40	5	28
Gilchrist Agitator	10	40	20	42
Waring Blendor	20	80	20	58
Waring Blendor	20	80	45	62
Waring Blendor	30	60	30	70

Increase in agitation, time of agitation and concentration of adsorbent to the oil caused increased removal of color. Previous filtration methods gave a much lighter colored oil.

#### (b) Filtration

The use of a column of adsorbent for refining oils requires the control of several factors such as height of column, surface area and time of contact of the oil with the adsorbent. These conditions vary with the adsorbent and the material to be filtered.

In the following experiments, the optimum values for the above-mentioned factors were found. The column was not



packed with the adsorbent but was tapped several times to settle the adsorbent.

(i) Height of Oil above the Column. The time of contact of the oil with the adsorbent should theoretically have some effect. This could be determined either by the degree of packing or by the height of the oil above the column. The latter was varied since it is less difficult to ascertain than the former. The column was 2.3 cm. in diameter and the height of the adsorbent was 6 cm. The color of the first ten cc. was obtained.

Table VI  
Effect of Varying the Height of Oil above the  
Column on Refining

Height of Oil (cm.)	Galvanometer Reading (440 filter)
2	85
6	85
8	80
8 (with suction)	60

The rate of filtration is sufficiently slow such that the difference of time of contact of the oil with the adsorbent due to different heights of oil above the column is only slight. When suction was applied the time of contact was greatly decreased and the resulting oil was darkest in color.

(ii) Height of Column. The height of adsorbent in the

column was varied keeping a constant width of 2.3 cm. The color on both the first and second ten cc. portions was obtained.

Table VII  
Effect of Various Heights of Adsorbent on Refining

Height of Column (cm.)	Galvanometer Reading (440 filter)	
	1st portion	2nd portion
3	65	39
6	90	72
9	91	85
12	87	72
21	65	--

The optimum height of adsorbent is 9 cm. for a diameter of 2.3 cm.

The silica gel-alumina adsorbs most of the coloring matter and mucilaginous material at the top, forming a dark zone. On addition of further oil a clear yellow zone is formed immediately below the dark portion. Instead of increased height of adsorbent refining more oil, a yellow colored oil gradually spreads down the column and the raw oil is only partially refined.

(iii) Surface Area. The height of column was kept constant at 4 cm. and the surface area was varied. The color of the first ten cc. was recorded.

Table VIII  
Effect of Surface Area of the Column on Refining

Area of Column (sq.cm.)	Galvanometer Reading (440 filter)
8.5	62
20	65
80	100

The height and area seem to be closely connected since different optimum heights were found for an area of 10 sq.cm. (Table VII -- column of diameter of 2.3cm.) and for an area of 80 sq.cm. (Table VIII). The most efficient refining was obtained using a short, wide column.

#### 4. Adsorbent Refining of Variously Treated Linseed Oils.

The adsorbent refining was applied to samples of cold-pressed as well as hot-pressed oil. Also various pretreated oils were passed through the adsorbent to be further refined. The linseed oil was treated with water, acids and alkalis; the required amount of acid and water being agitated with the oil in the Waring Blendor. The alkali treatment was accomplished according to the procedure described in the section on Methods. The pretreated oils were washed, dried and then passed through columns of silica gel-alumina.

Table IX

## Adsorbent Refining of the Pretreated Oil

Pretreatment of Oil (Volume of Reagent per 100g. of oil)	Galvanometer Reading (440 filter)
Raw Hot-pressed Oil	84
Raw Cold-pressed Oil	75
Alkali-refined Linseed Oil	75
25cc. Distilled Water	72
7cc. 25% Phosphoric Acid	70
14 cc. 25% Phosphoric Acid	78
5 cc. 3% Sulphuric Acid	74
6 cc. 3% Sulphuric Acid and Alkali Refining	79
5 cc. 1% Sulphuric Acid and Alkali Refining	56
7 cc. 25% Phosphoric Acid and Alkali Refining	52

The cold-pressed oil when refined with silica gel-alumina had a fluorescence which interfered with the reading of the color. The same amount of colored materials appeared to be removed from the cold-pressed oil as from the hot-pressed oil.

The combination of pretreatment and adsorbent refining did not give as efficient removal of color as did the adsorbent refining alone. The pretreatment of the oil coagulated impurities and produced an oil which was lighter in color than the raw oil.

## 5. Preparation of an Active Silica Gel

Gordon, Martin and Synge (30) found that by varying factors in the preparation of the silica gel, an adsorbent could be produced which had quite different adsorbent capacities.

The commercial silica gel, which was used in the previous experiments has a disadvantage of adsorbing only at the top and not completely over the column. In subsequent experiments, the variable conditions as suggested by Gordon, Martin and Synge were investigated, in order that a more active silica gel might be obtained.

The silica gel was prepared according to the method proposed by the above-mentioned workers. The following factors were varied: precipitants, pH of precipitation, aging of the precipitate, temperature and time of drying.

### (a) Precipitants.

Ten normal hydrochloric acid, 25% phosphoric acid and alcohol were each added to a solution of sodium silicate to precipitate the silicic acid. A pH of 3.5 was maintained in the solutions precipitated by the acids. The precipitate after setting was washed and dried. The silica gels were combined with alumina (section 2.), and their efficiency in refining was compared with that of the commercial silica gel.

Table X  
Effect of Precipitants on the Adsorbent Properties  
of Silica Gel

Method of Preparation	Galvanometer Reading (440 filter)
Alcohol Precipitation	8.1
Phosphoric Acid Precipitation	17.2
Hydrochloric Acid Precipitation	23.1
Commercial Silica Gel	90.0

The silica gels prepared as above were poor. However, the hydrochloric acid-precipitated silica gel has the best adsorbent properties of the three precipitated gels.

(b) Hydrogen Ion Concentration.

The pH of precipitation was varied by the use of indicators in the solution of sodium silicate. The 10 N hydrochloric acid was added with constant stirring until the indicator changed color. The silica gels were washed, dried and combined with alumina.

Table XI  
Effect of pH on the Adsorbent Properties of Silica Gel

pH of Precipitation	Galvanometer Reading (440 filter)
2.5	16
3.5	70
5.5	35
8.0	4
10.0	11

The optimum pH of precipitation of the silicic acid with hydrochloric acid was found to be 3.5. The hydrogen ion concentration must be carefully controlled to obtain a gel with best adsorbent properties.

(c) Temperature and Drying of Precipitate:

The precipitate of silicic acid was dried at different time and temperatures. The following table shows the optimum conditions.

Table XII

Effect of Temperature and Time of Drying on the  
Adsorbent Properties of Silica Gel

Temperature 23°C.	Time of Drying (hrs.)		Temperature 350°C.	Galv. Reading (440)
	Temperature 100°C.	Temperature 250°C.		
24				23
17	17			33
24	3			57
24	9			59
24	26			17
24	26	3		17
24	26	3	1	8
24			3	11

Heating gradually during drying is advantageous to produce a good silica gel. With quicker drying the structure of silica gel apparently is altered and a less active adsorbent is obtained.

#### Aging of the Precipitate:

The precipitate of silicic acid was aged for several days in N/5 hydrochloric acid.



Table XIII

Effect of Time of Aging of the Precipitate on the  
Adsorbent Properties of Silica Gel

Time of Aging (days)	Galvanometer Reading (440 filter)
0	8
1	19
3	24
4	68
5	92

An increase in adsorbent capacity with an increase in time of aging was noted.

These above conditions were all controlled and a comparison was made between the commercial silica gel and the silica gel prepared as above.

Table XIV

Comparison of Sterne's Silica with the Silica Gel  
Prepared as Above

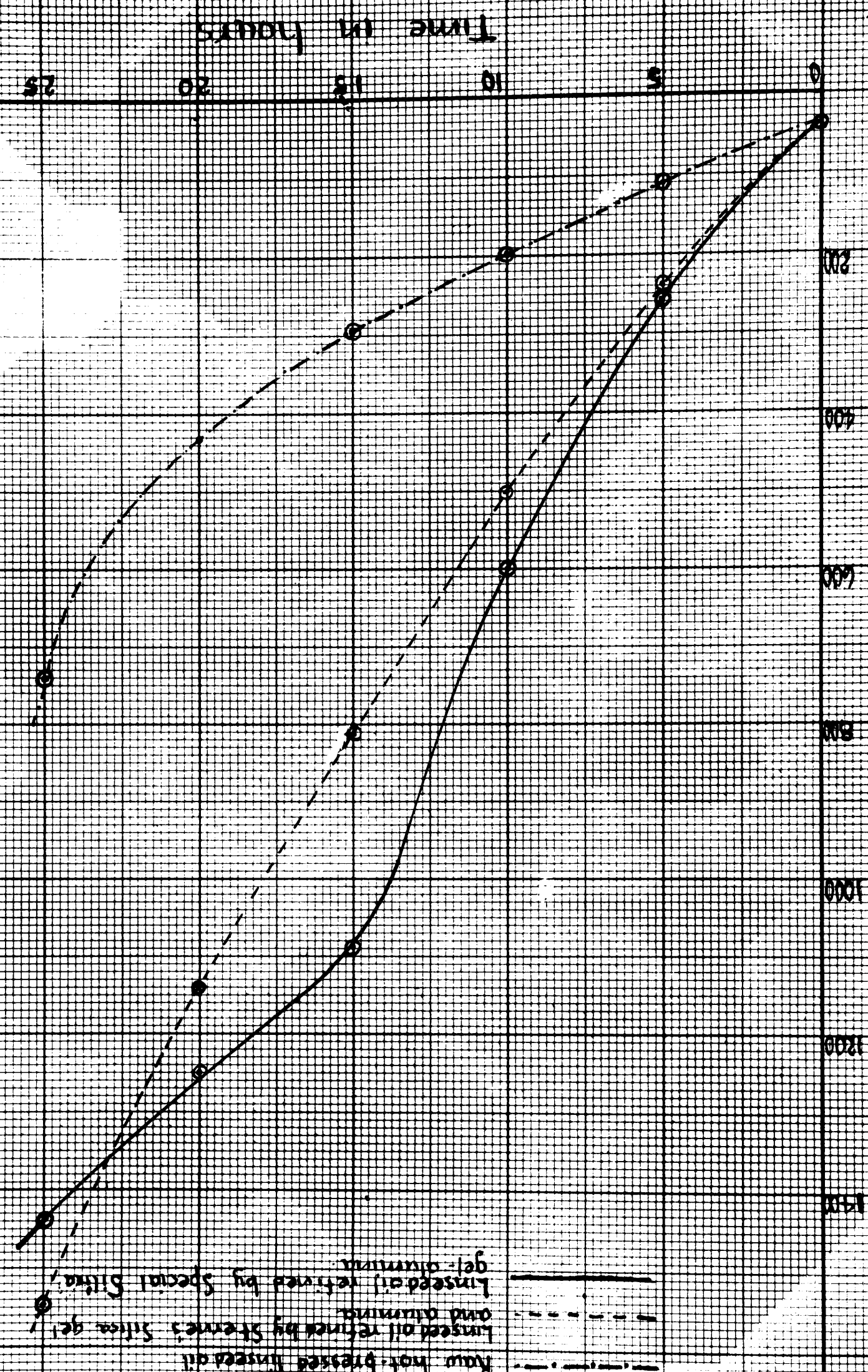
Adsorbent	Galvanometer Reading (440 filter)	Yield of Oil (color-90) per Gram of Adsorbent
Silica Gel- Alumina (Sterne's)	90	1.2
Silica Gel- Alumina	96	3.0

The stability of the two oils were compared. The oxygen uptake was slightly greater in the case of the silica gel prepared in this laboratory; however both refined oils were much less stable than the raw oil.

The silica gel prepared in this laboratory had different adsorbent properties than the commercial silica. The former allowed adsorbing to take place completely down the column rather than just at the top, giving a greater yield of light colored oil (Table XIV).

Different methods of preparing the silica gel-alumina during precipitation of the gel were attempted. The sodium silicate was precipitated by an alcoholic solution of aluminum nitrate. Also precipitation of the gel with hydrochloric acid, after diluting with a water solution of aluminum nitrate was tried. The precipitates were heated in the muffle furnace, glass-like gels being obtained. These were ground and used as adsorbents; they gave poor results in removing color.

# Milliequivalents of Peroxide oxygen per kilogram



Graph I

## 6. Comparison of Silica Gel-Alumina with Other Adsorbents

Silica gel-alumina, in order to estimate its value and application, was compared with several other common adsorbents, the common analytical tests being the means of comparison. The following adsorbents were used: silica gel-alumina, super filtrol, fuller's earth and Canadian bentonite (28).

### (a) Removal of Color:

Raw hot-pressed linseed oil was passed through the adsorbents and the color of successive 25 cc. portions was measured. In each case, 43 grams of adsorbent were used in a Büchner funnel, 8.5 cm. in diameter.

Table XV

Removal of Color by Different Adsorbents

Adsorbent	Galvanometer Reading(440 filter)		
	1st Portion	2nd Portion	3rd Portion
Silica Gel-Alumina	82	70	56
Super Filtrol	74	63	60
Fuller's Earth	52	54	48
Bentonite	60	55	50

The silica gel-alumina gave the lightest colored oil in the first 50 cc. This adsorbent has given results as high as 90-100. The factors controlling its preparation are important and slight changes in these cause a change in the adsorbent qualities.

(b) Yield, Retention and Time of Filtration:

The yield and retention of the oil before and after suction for each adsorbent was found. The time for filtration of 25 cc. of oil was obtained.

Table XVI  
Yield, Retention and Time of Filtration with Different Adsorbents

Adsorbent	Weight of Oil Used (g.)	Weight of Oil Obtained (g.)	Retention Before Suction (g.)	Retention After Suction (g.)	Time of Filtration (hrs.)
Silica Gel- Alumina	175	79	96	59	5
Super Filtrol	175	117	58	48	11
Fuller's Earth	175	73	102	92	32
Bentonite	175	96	57	53	30

The yield of oil after suction is approximately the same with all the adsorbents except with fuller's earth. The time of filtration varies greatly; in this respect the silica gel-alumina had a distinct advantage over the others.

(c) Odor of the Refined Oil:

The removal of odor from the oil refined by the different adsorbents was studied.

Table XVII  
Removal of Odor by the Adsorbents

Adsorbent	Odor
Silica Gel-alumina	Fishy odor (much less than the raw oil).
Super Filtrol	Sweet fishy odor.
Fuller's Earth	Strong fishy odor.
Bentonite	Fishy and clay odor.

The difference in the amount of odor left in the oils by the different adsorbents was slight. In each case, the refined oil had lost a large amount of the characteristic odor of linseed oil.

(d) Removal of Free Fatty Acids:

The removal of free fatty acids is an essential step in the refining of edible oils. The free fatty acid value (cf. Methods) was determined on successive 25 cc. portions of the refined oil.

Table XVIII  
Removal of Free Fatty Acids by the Adsorbents

Adsorbents	Free Fatty Acid Value (% Oleic Acid)		
	1st Portion	2nd Portion	3rd Portion
Silica Gel-alumina	.017	.010	.036
Super Filtrol	.165	.540	.730
Fuller's Earth	.053	.067	.250
Bentonite	.125	--	--
Raw Hot Pressed Oil	.750		

The silica gel-alumina preferentially adsorbs the free fatty acids to a greater extent than the other adsorbents. The free fatty acid value is as low as that given by an alkali-refined oil.

(e) Peroxide Content of the Refined Oils:

The following values are given to show the development of peroxides, if any, during refining. This is another important factor in the production of an edible oil, since the increase in peroxides indicates decreased stability of the oil.

Table XIX

Effect of Adsorbents on the Peroxide Content of the Oil

Adsorbent	Peroxide Value (me./kg. of oil)		
Silica Gel-alumina	10.3	10.6	11.4
Super Filtrol	8.6	9.3	8.7
Fuller's Earth	23.0	17.4	14.2
Bentonite	9.3	--	--

Raw hot-pressed linseed oil 7.0

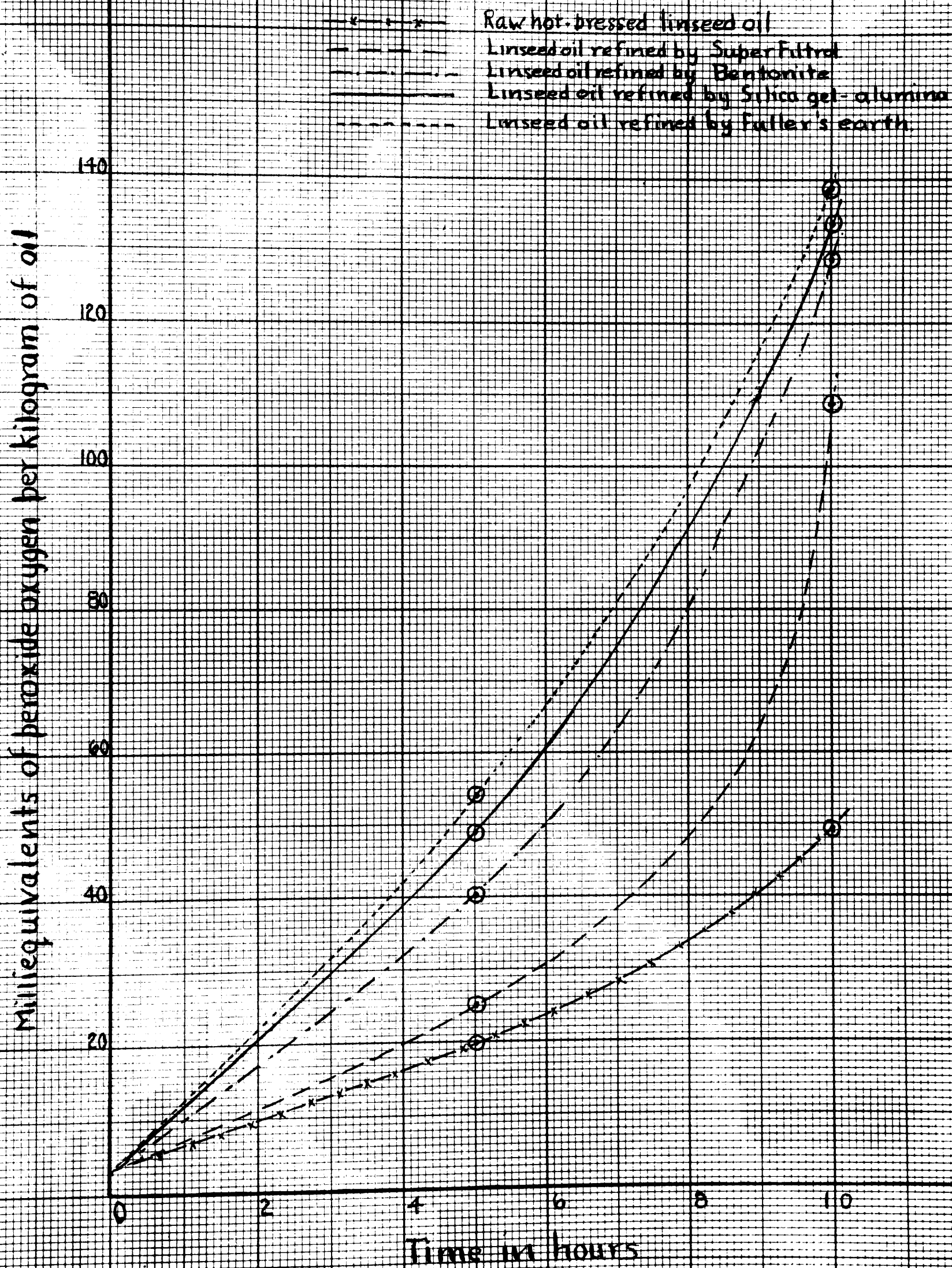
The increase in peroxides in the oil is not marked except in the case of the oil refined with fuller's earth.

(f) Stability of the Refined Oils:

The oxygen uptake of the refined oils was found in the oven test. The filtrol refined oil produces a slightly more stable oil; however, all the refined oils were much more unstable than the raw oil (Graph II).



Graph II





(g) Nitrogen Content of the Refined Oils:

The removal of nitrogen compounds by the various adsorbents was determined. The importance of this will be discussed in a later section on the nitrogen content of linseed oil.

Table XX

Nitrogen Content of the Various Refined Oils

Adsorbent	Amount of Nitrogen (mg./100g. of Oil)
Silica Gel-alumina	18.1
Super Filtrol	20.3
Fuller's Earth	10.2
Bentonite	20.1

Raw hot-pressed linseed oil 40.1.

The nitrogen content of the refined oil is about 50% of that of the raw oil, except in the case of the oil refined with fuller's earth.

(h) Removal of Odor by a Number of Adsorbents:

Although the color is removed efficiently by silica gel-alumina, a large amount of the odor still persisted. Since the removal of undesirable odor is essential, a large number of ordinary adsorbents were used to refine linseed oil, and the odors of the refined oils were compared.

Table XXI  
Removal of Odor by a Number of Adsorbents

Adsorbent	Odor of the Refined Oil	Galvanometer Reading (440 filter)
Diatomaceous Earth	Strong fishy odor	30
Bennet's & Clark's Activated Earth	Less fishy odor	55
Soapstone	Strong fishy	65
Aluminum Silicate	Fishy	20
Activated Charcoal	Vary fishy	90
Filtol-Carbon (mixture 5:1)	Fishy	82
Silica Gel-alumina	Less fishy	95
Filtrol	Strong fishy	90
Bentonite	Clay & fishy odor	83

The adsorbents removed the odors in different proportions. It was well noted that the color bodies were not tied up with the odoriferous substances altogether, since filtrol, activated carbon and bentonite removed a large proportion of the color but the oils had noticeably stronger odors than the oils refined by the other adsorbents.

It was noticed in this experiment that the fluorescence of cold-pressed oil when passed through the above adsorbents was strongest in the case of refining with silica gel-alumina. Filtrol refined oil had only a slight fluorescence, and a mixture of aluminum silicate, silica gel-alumina and filtrol removed the fluorescence completely. Activated carbon re-

moved most of the fluorescence.

## 7. Recovery of the Adsorbent

The use of silica-gel as a refining agent for vegetable oils would not be economically possible if the adsorbent could not be recovered efficiently.

The reclaiming of the adsorbent was carried out in two manners: (i) removing the adsorbed fat with a solvent such as benzine; (ii) burning the oil off the adsorbent and then heating in the muffle furnace.

The adsorbent reclaimed by solvent still had a greenish tinge. If this is heated in the muffle, the strongly adsorbed material can be removed. The activities of the various reclaimed adsorbents were compared.

Table XXII

### Activities of Reclaimed Silica Gel-Alumina Adsorbents

Treatment	Galvanometer Reading (440 filter)
Fresh Adsorbent	90.2
Solvent Recovered	72.5
Solvent Recovered and Heated in the Muffle	85.1
Oil Burned and Heated in the Muffle	84.0

The full activity was not restored, however, the reclaimed adsorbents were still effective in removing color.

## 8. Nitrogen Content of Linseed Oil

The nitrogen (cf. Methods) was determined on linseed oil before and after percolation through silica gel-alumina adsorbent. One sample was treated with sodium bisulphite, which removed a portion of the odor, and then it was refined with the adsorbent. The nitrogen of a rancid sample was also determined.

Table XXIII

Nitrogen Content of Variously Treated Linseed Oils

Treatment	Amount of Nitrogen (mg./100g. Oil)
I Hot-pressed Linseed Oil	32.1
Refined by Silica Gel-Alumina	14.3
Refined by Bisulphite and Silica Gel-Alumina	15.1
Rancid Refined Oil	3.8
II Cold-pressed Linseed Oil	36.9
Alkali Refined	37.1
Alkali and Adsorbent Refined	16.8
Alkali, Adsorbent Refined and Deodorized	7.4

50% of the nitrogen is removed in hot-pressed oil and 60% in cold-pressed oil after filtration. The removal of the nitrogen will be discussed completely in the following section.

## 9. Stability of Linseed Oil

The stability of linseed oil is important if the oil is to be used for edible purposes.

Samples of linseed oil were placed in the oven, their peroxide content being obtained at various intervals. The various samples were prepared in the following way.

A sample of linseed oil, refined by silica gel-alumina which was purified by nitric acid, was compared with a sample of linseed oil refined with unpurified silica gel-alumina. This was to determine if heavy metals on the silica gel-alumina were catalyzers of the oxidation of the oil.

Phospholipids, obtained by ether extraction of the adsorbed oil after the removal of the acetone-soluble portion, were placed in a refined linseed oil and the stability of the resulting solution was determined.

Also a concentrate from the foots of linseed oil, believed to have antioxidant properties, was placed in a sample of refined linseed oil. The methyl alcohol solution was extracted with petrol ether. The residue of the methyl alcohol solution was extracted with the ethyl ether; this gave the above concentrate.

Graph No. III shows that the natural antioxidant is removed by the adsorbent in the same proportion as the color.

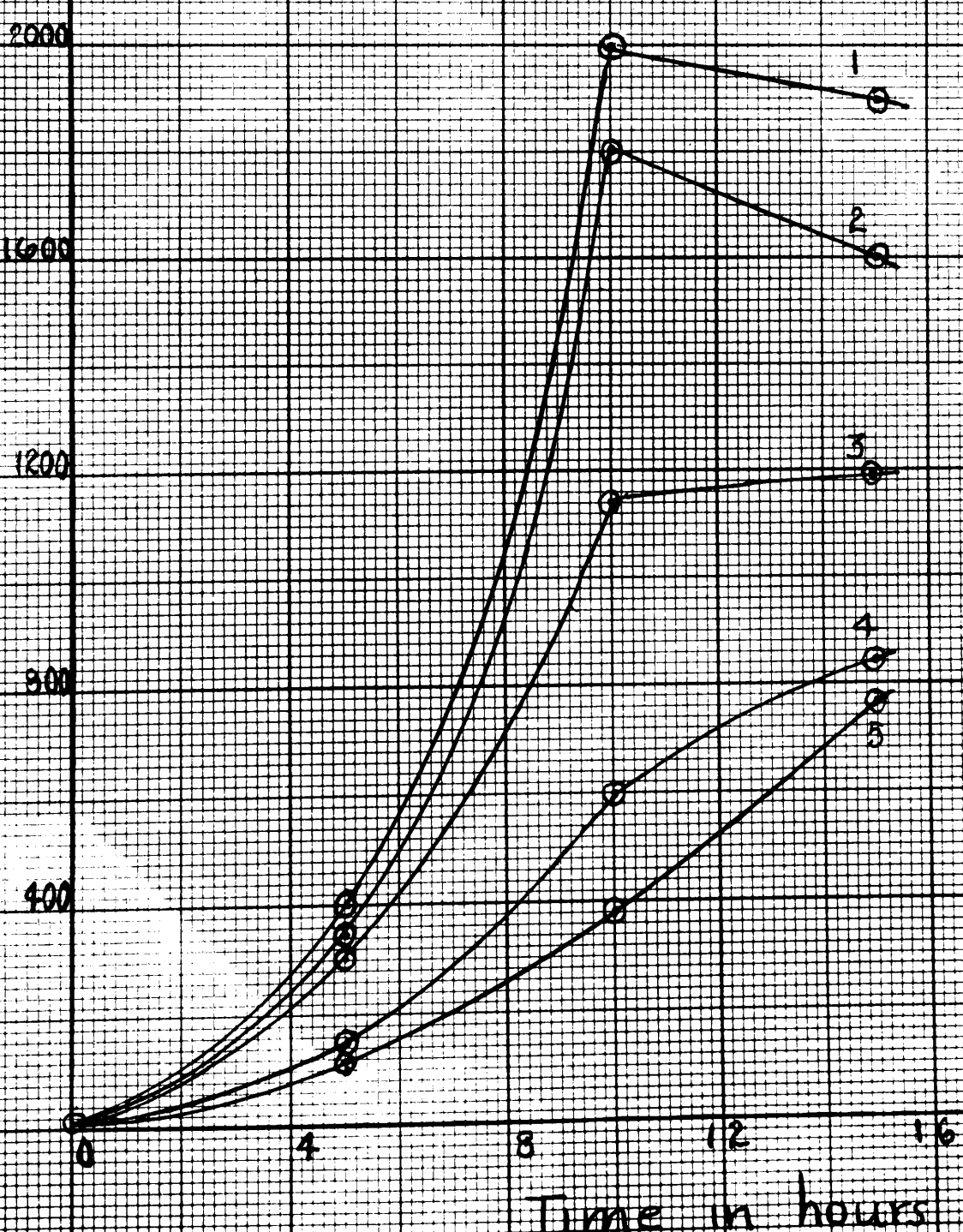
Graph No. IV shows that all the refined oils remained unstable, regardless of the extracts which they contained.

# Graph III

50

- 1 First portion of refined oil
- 2 Second .. .. .
- 3 Third : .. .. .
- 4 Fourth .. .. .
- 5 Raw linseed oil.

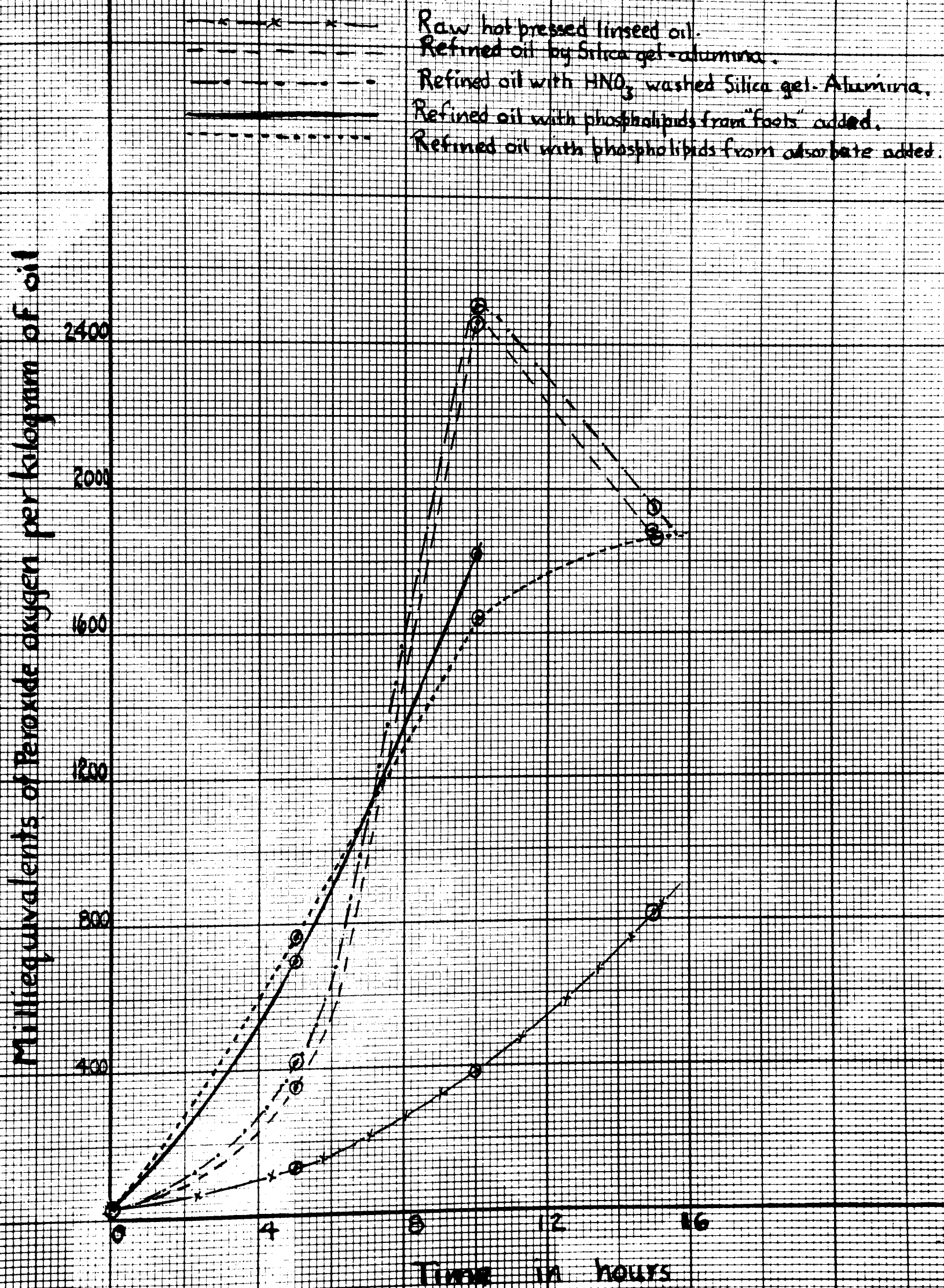
Millicquivalents of Peroxide oxygen per kilogram of oil





# Graph IV

51



## IV. DISCUSSION OF RESULTS

### 1. Silica Gel-Alumina Adsorbent

Silica gel with alumina precipitated on the particles of the former gives an adsorbent which is very active in removing color from linseed oil. The procedure for its preparation can be described completely after studying certain controlling factors.

Thirty-five grams of aluminum nitrate, dissolved in 250 cc. ethanol, are mixed with sixty-five grams of 100 mesh silica gel. The ethanol is evaporated and the mixture is placed at 750°C. in the muffle furnace for three hours.

### 2. Use in Refining Linseed Oil

The efficiency of this adsorbent in agitation at room temperatures was investigated. It was found, as would be expected, that an increase in refining resulted with increased contact, time and concentration of adsorbent.

The use of the column was quite applicable and gave better refining than the agitation process. The conditions controlling the choice of column are many; the optimum length of column varies with the width, the greater the width the shorter is the optimum height. If the column is lower or higher than the optimum height, a yellow oil is obtained.








Fig. 4.



Fig. 5.

 Dark Zone  
 Transparent yellow layer  
 Colorless oil

This may be explained by the method in which silica gel adsorbs. A dark zone is formed at the top containing the color pigments and mucilaginous substances of the fresh oil, and a gradual yellow transparent layer is formed immediately below. It is suggested that the first colorless oil as it moves through the adsorbent is negatively adsorbed by the silica gel. This is reasonable since the solvent (oil) is slightly polar, and the silica gel is highly polar. This then uses up the adsorption capacity of the immediate layers of adsorbent (Fig. 4). The fresh oil following is only partially refined by the already used adsorbent and the remainder of the color bodies will not be held by the following layers of adsorbent due to their loss of activity. This action, of course, would repeat itself to the base of the adsorbent, and the resulting oil obtained would not be colorless, but would be yellow. If the column were shorter (Fig. 5), colorless oil would be obtained. However, the extra adsorbent in a long column could be used in a wider column and still better yields of water-white oil would be obtained.

### 3. Adsorbent Refining of Variouslly Treated Linseed Oils

Pretreatment of linseed oil resulted in coagulation of a large quantity of gums, and a certain removal of coloring matter. The refining of the pretreated oil by silica gel-alumina produced an oil which was slightly darker than the oil without preliminary treatment. Hassler (32) states that the amount of particles adsorbed depends upon the number present. For the same amount of adsorbent, less color molecules would be adsorbed in the case of a partially refined oil than in the case of the raw oil. This would explain why it is more difficult to remove the last traces of color. An oil which is partially refined by the adsorbent when passed through more of the fresh adsorbent does not become lighter in color. This along with the fact that a combination of pretreatment and adsorbent refining is not as advantageous as adsorbent refining alone, leads to the assumption that there are two types of particles of color: (1) large bodies which are easily adsorbed and (2) small ones which are much more resistant to adsorption. It follows, then, that the larger bodies occlude or attract the smaller bodies during refining of the raw oil, and produce a well refined oil. However, if most of the large bodies are coagulated by pretreatment, then it will be more difficult to adsorb the smaller, more resistant-to-adsorption particles, and produce as well a refined oil.

#### 4. Preparation of Silica Gel

The preparation of the silica gel is described in the experimental; a silica gel with slightly different properties is prepared by obtaining the proper conditions of pH, aging of precipitate, time of drying and temperature of drying. The silica gel-alumina, prepared with this gel, refines the linseed oil much more efficiently, the yield of colorless oil being doubled. This is due to the fact that the activity of the adsorbent is applied throughout the column rather than at the top. A change in the inner surface, due to varying the several factors, probably is responsible for the different method of adsorbing. With a short wide column, this advantage is minimized.

The preparation of the active silica gel can be described specifically. Ten normal hydrochloric acid is added slowly to sodium silicate or commercial water glass (140°Tw) to a pH of 3.5 indicated by methyl orange. The precipitate is filtered and then suspended in N/5 hydrochloric acid for five days. The precipitate is washed and dried for 24 hours at room temperature and nine hours at 100°C. If the silica gel is to be used as an adsorbent alone, further drying is probably necessary.

#### 5. Comparison with Clays

The silica gel-alumina was compared with four common clays which are used in refining.

The particle size of silica gel-alumina allowed for the

best filtration, but the loss of oil was greater than in the case of either filtrol or bentonite. The silica gel-alumina gave superior color in the first fifty cc., while fuller's earth gave the poorest color and yield. A clay odor persisted in the bentonite refined oil. Silica gel-alumina seems to be preferential in removing free fatty acids. Since alumina is a basic anhydride, it is not unlikely that the free fatty acids should be adsorbed by it. In addition to this, the highly polar silica gel probably attracts the polar group of the acid and holds it by secondary valence forces. The other clays are not as polar as silica gel and in this respect would not have as strong activity.

A slightly greater oxygen uptake was noticed with the oil refined by fuller's earth. The others gave similar results.

It is interesting to note that the fluorescence in cold-pressed oil is removed to a certain extent by filtrol and activated carbon, and that a mechanical mixture of aluminum silicate, silica gel and filtrol removed the fluorescence completely. It is also shown that the odor is not associated with the color bodies. Activated carbon, filtrol and bentonite removed only a small amount of characteristic odor of linseed oil, and yet produced, with the exception of silica gel-alumina, the lightest colored products.

## 6. Recovery of Adsorbent

The recovery of the adsorbent and oil is of value since silica gel-alumina holds considerable oil and also is itself relatively expensive. The reclaimed adsorbent has only slightly less activity.

## 7. Nitrogen Content of Linseed Oil

Many workers have studied the presence of nitrogen compounds in oils and the possibility that these might be responsible for off odors.

Adsorbent, alkali and bisulphite refined oils were found to possess a reverted odor when hydrogenated and cooked. In these three refining procedures, the greatest amount of nitrogen removed is by the adsorbent; however, in all cases, over 50% of nitrogen compounds were not removed.

A rancid oil was found to be lower in nitrogen than the other treated oils. During the oxidation of the oil, volatile nitrogen compounds must have been removed. A rancid oil is an oil which might be considered to have advanced beyond the reverted odor stage, since it is shown that a connection between the oxidation of the oil and development of "off odors" exists.

These above two observations affirm the possibility that odoriferous nitrogen compounds might cause "reversion of odor".

## 8. Stability

The stability of linseed oil is decreased by adsorbent

refining, apparently due to the removal of natural anti-oxidants.

In the several experiments, it was found that the decreased stability of the adsorbent-refined linseed oil was not due to the presence of heavy metals on the adsorbent.

The phospholipids extracted from the "foots" of the alkali-refined oil and from the adsorbed oil, when placed in the refined linseed oil, acted as pro-oxidants. Heavy metals on the adsorbent may have changed the phospholipids such that they catalyzed the oxidation of the oil.

A relation between the stability and the color of the refined oil was observed. As the color was removed, the stability of the oil decreased.

## V. SUMMARY

1. The preparation of an active adsorbent consisting of alumina on silica gel is described. Methods for its recovery are also given.
2. The use of long columns in filtration methods leads to lower yields of colorless oil and less efficient refining. The optimum conditions must be worked out for each surface area. A wide column is most satisfactory.
3. Refining raw linseed oil with silica gel-alumina is superior to a combination of acid or alkali treatment and adsorbent refining.
4. Silica gel-alumina is compared with several common clays and is found to be superior in time of filtration and in the removal of color and free fatty acids.
5. The conditions for the preparation of a silica gel which adsorbs completely down the column are presented.
6. The possibility of odoriferous nitrogen compounds causing reversion of flavor is affirmed.
7. The stability of linseed oil is lessened by adsorbent refining, the removal of the natural antioxidants being proportional

to the removal of the color.

8. An explanation of the failure to obtain better adsorbent refining of the pretreated oil is given. Also the theoretical aspects of the use of columns of varying height and of the removal of free fatty acids with silica gel-alumina are discussed.



## VI. BIBLIOGRAPHY

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