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Semi-micro combustion and solvent extraction of natural and synthetic drying oils, Part I.

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UNIVERSITY OF LOUISVILLE

SEMI-MICRO COMBUSTION AND SOLVENT EXTRACTION
of
NATURAL AND SYNTHETIC DRYING OILS
PART I

A Thesis
Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the requirements
for the degree of

MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

MAN MOHAN MOUDGILL
September, 1948

SEMI-MICRO COMBUSTION AND SOLVENT EXTRACTION
of
NATURAL AND SYNTHETIC DRYING OILS
PART I

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September, 1948

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the kind assistance and helpful guidance
of Dr. G. C. Williams
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ABSTRACT

The rates of oxidation and solvent solubility, of natural and synthetic drying oil films were studied by semi-micro-analytical methods. These methods were employed in order to lessen the time-factor, and to economize on the use of the rather expensive synthetic drying oils.

The thesis consists of two kinds of experiments:

I. An ultimate analysis to determine the oxygen content of the film at desired intervals of time.

II. An extraction to determine the solvent solubility of the films as a function of time.

The materials analyzed were:

A. Cane Sugar ($C_{12}H_{22}O_{11}$) C.P. grade

B. Linseed Oil

C. Soybean Oil

D. Glyceryl Trilinoleate (synthetic preparation)

Sugar was used to check the efficiency of the combustion apparatus, linseed and soybean oils were used, so that some experience could be gained in manipulating oil films.

Experimentation with sugar indicated the inadequacy of the absorbents in the initial apparatus which was based on a publication of Natelson and Conner (1). After modifications and alterations, analyses of linseed oil gave fair results, when the combustion temperature was raised to 650°C. Glyceryl trilinoleate combustions were unsuccessful at first, but were apparently corrected by the use of a combustion period of two hours. It is indicated that different oils will necessitate the further variation of technique; however, a two hour combustion at 650°C., using Drierite and Ascarite as absorbents will be satisfactory.

Acetone, benzene, carbon tetrachloride, ethyl acetate, methanol, methyl-ethyl ketone, and petroleum ether, were tried as solvents for film extraction. Results varied in both range and absolute attainable values. Of these solvents, use of carbon tetrachloride in the extraction tests, gave most suitable results for the range and distribution of insolubility.

INTRODUCTION

The chemical industries have for sometime used numerous natural products of animal, vegetable, or mineral origin. Of them, the protective coatings industry has used their fair share, and a major portion of these materials has been imported into the United States. Over the period of use, the quality of these raw materials has fluctuated appreciably to the detriment of the standards for the ultimate product. To combat these difficulties, in some branches of the protective coatings industry, a considerable study has been made on the physical and chemical properties of the materials. These results, followed by selection research on active ingredients, have resulted in the formulation of various synthetic products. Many of these synthetic compounds have satisfactorily replaced the natural products; and some few are, by virtue of their purity, far superior to the natural products. Besides the improvements in quality, manufacture of synthetic materials has appreciably altered the economics of the respective industries.

This change is very marked in the resin industry, where, because of previous research work, it is now possible to obtain several resins to serve any particular purpose.

In the field of drying oils, however, relatively very little similar work has been done. Though a fair knowledge of the physical characteristics of these materials is available, there still is no definite understanding of the accompanying chemical changes, or the parts played by the various components.

This was the problem that instigated the sponsoring of a research program by the National Federation of Oil, Paint, and Varnish Clubs (hereafter referred to as the Federation). To study the chemical and physical changes involved in the setting of drying oils, their component active ingredients were synthesized. Analyses of these pure compounds were expected to indicate the exact nature of the changes. With this knowledge available, it should be possible to mix to prescription, drying oils of varying degrees of drying power. Further investigations of their economics might even make it feasible to activate some slow-drying oils like cocoanut, castor, or olive oil by addition of suitable quantities of adequate active ingredients such as the glycerides of linolenic or eleostearic acids.

Of the projects sponsored by the Federation, work on the rate of oxidation, and the solvent solubility of drying oil films, has been assigned the University of Louisville. This thesis forms the first part of work on these two projects. It covers, essentially, the development of a procedure for analyses and the early investigations on synthetic drying oils.

HISTORICAL

Although it is known that driers and drying oils were used in ancient days, it appears that Galen (2), in the second century, was the first person to record their use. With the advent of art and the birth of canvas painting, the necessity of drying oils as a vehicle for paint pigments was increasingly felt. These oils, as the artists discovered, gave the canvas a tough and durable protective film; and in so doing, lessened weathering action, which heretofore had destroyed the effects of color. However, it was not until the twelfth century that regular procedures for mixing pigments with drying oils were generally adopted.

Jacobus de Tholeto, in 1440, is reported as the first person to formulate a varnish, and in his record states (3):

> "...take the gum of Juniper (Sandarac) two parts and one part of Linseed Oil. Boil them together over a slow fire, and if the varnish appears too stiff, add more of the oil, and take care not to let it take fire because you would not be able to extinguish it, and even if you could, the varnish would be too dark and unsightly. Let it boil one-half hour and it will be done."

In the above account, there is no mention of a thinner. The first to disclose the use of turpentine as a thinner was Alberti of Magdeburg in 1750. Proper mixing and utilization of driers for the purpose of accelerating the rates of drying of these oils was started in the fifteenth century.

With the progress of science and industry came a more, and fuller knowledge of the chemistry of drying oils and driers.

They were separated and purified prior to use as carriers or vehicles for paints, varnishes, and lacquers.

It is noticed that at that stage, a seemingly peculiar attitude developed in the minds of manufacturers and scientists involved in research. To quote one authority in the field, -- "the concept of the God's-gift philosophy took deep root. These oils had certain very beneficial properties granted by God, and so were to be used as is, with only very essential and slight alterations."

In fairness to the philosophers, it should be remembered that at the time very little else could be done, as the knowledge on driers and drying oils was very incomplete and highly confused. However, it was not until about two or three decades ago, that attention was turned towards synthesizing these oils, and getting them to suit a purpose in view, rather than making the best use of what was available.

Examining consumption statistics (4,5) of about a decade ago, the United States used annually between 700 and 800 million pounds of drying oils. In spite of the heavy protective tariffs levied for the local production, over one-half of this quantity was imported.

At this stage, the Federation took up the problem of investigating the true chemical and physical nature of the reactions of these oils.

THEORETICAL

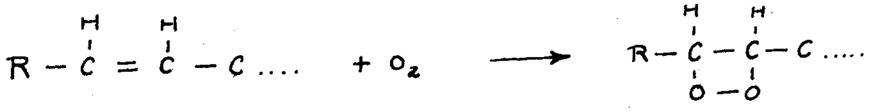
Drying oils are unsaturated fatty acid esters, mainly glycerides of the C_{14}, C_{16}, C_{18}, acids. Their drying is a conversion from a liquid oil film to an apparently solid, non-tacky coating. The chemical changes accompanying this process are something about which considerable diversity of opinion exists. However, most chemists are agreed on its being a two-stage reaction:

1. Oxidation at the unsaturated carbon bonds.

2. Polymerization of the products formed on oxidation.

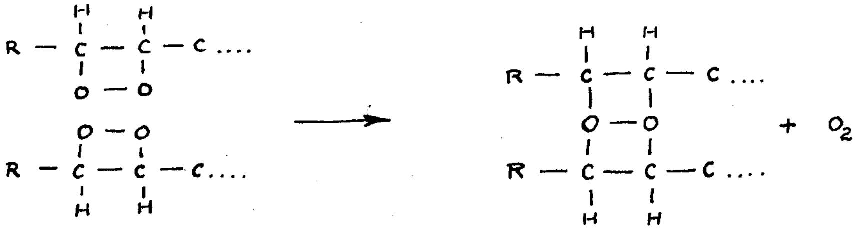
In undergoing these reactions, an essentially linear chain of carbon atoms becomes a cross-linked or three dimensional polymer. This can be effected by heat, light, oxidation, or the catalytic action of metals on these oils. Although the addition of oxygen saturates the acid radical, the material retains its oily nature. It is with the starting of polymerization that a change of state to solid gel commences.

Upon oxidation, the double bonds in the acid chain break up, and add on two atoms of oxygen per double bond, giving a peroxide-like structure:

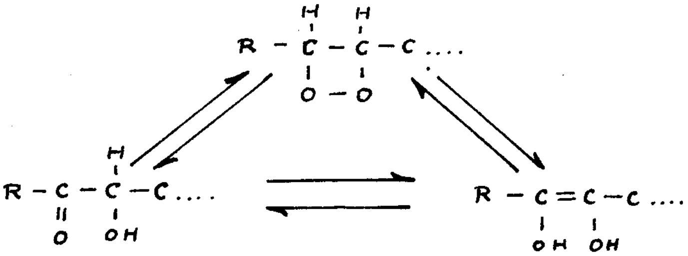


$$R-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-C\ldots\quad + O_2 \longrightarrow R-\underset{\underset{O}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{O}{|}}{\overset{\overset{H}{|}}{C}}-C\ldots$$

Evidence of this change is found in the peroxide-number increase, and the decrease in the iodine-number. The peroxide formation is rather unstable and exists only up to the point where the oil is tacky. Once the film is dry to touch, a second change occurs. Even now, there is considerable controversy about this second reaction. Marcusson (6) was of the opinion that the peroxides reacted between themselves, rejecting oxygen, and forming cross polymers in the following schematic manner:



Long (7), on the other hand, is of the opinion that these peroxide structures go through the following reactions, giving, in effect, a metastable state of equilibrium between the peroxide, a ketol, and an unsaturated diol.



Although there is evidence in support of each of the above mentioned hypotheses, the degree of validity has not yet been established. Latest experimental evidence inclines towards acceptance of Long's suggestions.

Recent work on drying oils by Terrill (8), indicates the formation of hydroperoxide groups in their oxidation. It is similar to that observed in the autoxidation of polyisoprenes. However, there is no clear notion of the exact chemical changes involved.

The purpose of an ultimate analysis was to determine the oxygen content at various time intervals, as this figure presents an index of the degree of oxidation. From the reaction suggested by Long, it is seen that once the oxidation is complete, no further change in molecular ratio occurs.

The rate of polymerization must be judged by the second series of tests, as conducted for solvent extraction of the film.

Whatever the nature of oxidation, it is known that in polymerization the oxidized oils formed cross-linked polymers of very high molecular weights. Since the inter-molecular linkages are secondary valences, it is possible to extract, with organic solvents, the lower polymers. Thus, from the insolubility figures, it is possible to determine the extent to which the oil has polymerized beyond a certain molecular weight, which, in turn, is a function of the solvent power of the solvent. No quantitative figures are available on the molecular weights that form the margin between soluble and insoluble polymers for each individual solvent. Extraction results, therefore, form a comparative, rather than absolute index of the extent of polymerization.

It is noticed that although the two reactions are successive, in actuality they are simultaneous; the surface molecules in the oil film undergo oxidation, and start polymerizing, although the molecules in the center are not completely saturated. If the velocity of the two reactions is approximately equal, the hardening of the film should occur at about the same time as complete saturation. It follows, therefore, that the setting rate of a drying oil, is a compound function of its rates of oxidation and polymerization.

Estimation of oxygen in an organic compound can be done by any number of short and rapid methods, such as the determination of the alcohol-solubility of the compounds. Long (10), however, is of the opinion that such analysis is unsatisfactory because of the difference in oils, their degree of gelation, age of gel etc. It was, therefore, preferable to go through the relatively long procedure of ultimate analysis.

Miniature Soxhlet flasks were chosen for extractions, as it was possible to get a thorough and efficient extraction with a relatively small quantity of solvent. From the extraction flask, pure solvent distilled over into the syphon-cup, in which it attacked the oil film, and drained out as soon as it filled to the syphoning-point.

EXPERIMENTAL

The experimental procedure and results for each of the projects are listed separately under:

I. Film Formation, which includes
    a). Mixing
    b). Casting
    c). Scraping
    d). Thickness measurement
II. Combustion
III. Extraction

The materials analyzed (in the order they were experimented with) were as follows:

A. Cane Sugar
B. Linseed Oil
C. Soybean Oil
D. Glyceryl Trilinoleate (synthetic preparation)

In actual operation, the necessity for care and caution cannot be overemphasised, in view of the fact that minute quantities of samples are handled. All glassware weighed must be carefully wiped with a clean dry cloth, and a similar counterpoise unit must be used (Figure 1). This procedure facilitates weighing, as no weights other than those on the keyboard are needed.

The time factor plays a significant part in obtaining reproducibility, especially in extraction, where the test is more nearly a carefully controlled quantitative experiment than an absolute analysis.

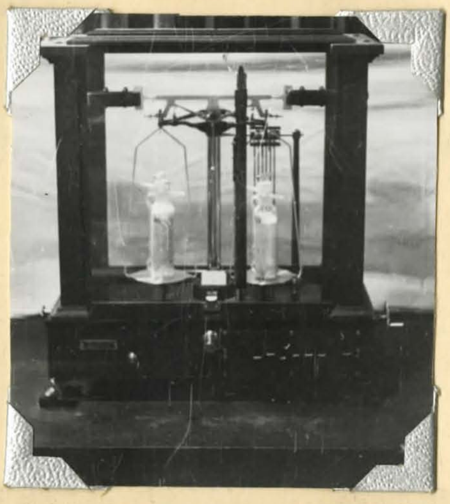


Fig. 1. Chainomatic Keyboard Balance

(Used for all weighings)

I. FILM FORMATION

a). Mixing

Of the two driers used for accelerating the drying-rates of the oils tested, lead naphthenate was found to give better results. Cobalt, 0.015% by weight, or lead, 0.5% by weight, in the mixture, were found to give the desired drying. Linseed and soybean oils, being available in fairly large quantities, were weighed and mixed in half-pint paint cans. To ensure thorough diffusion of the drier into the oil, the cans were rotated on mixing rolls for about 15 minutes.

Glyceryl trilinoleate was mixed in a small 25 ml. pyrex Florence flask, using a hypodermic needle and syringe, to avoid waste of the sample. It was found possible, by this method, to pour out minute drops of the fluid, and thus obtain great accuracy in weighing both the drier and oil. Since it is not possible to transfer exact quantities of liquids by weight, it was found better to pour the drier into the mixing flask, weigh it accurately, and then add the desired quantity of oil calculated to give the required percentage of drier. (See sample calculations in Table VIII.)

b). Casting

Both an Ethocel Cylindrical applicator and a Bird applicator were used in casting films. The glass plates upon which the casting was done, were first cleaned with soap and water, and then with a piece of cotton soaked in acetone. (A final wiping with clean dry cotton cleared the wet marks of the acetone). The applicator edges were cleaned in a like manner.

In using the Ethocel applicator, about 2 ml. of the mixed oil were poured inside the instrument, and the film was cast by drawing the applicator evenly across the glass surface, which was kept horizontal. Excess oil inside the applicator was sponged out by a wad of cotton, and the applicator removed from the glass plate. In the case of the Bird applicator, however, a considerably lesser quantity of the oil mixture was poured in front of the doctor blade. The applicator was then drawn evenly across the glass plate till the heap of oil was utilized in the formation of the film (Figure 2a).

Films formed using the Bird applicator were far superior and better defined at the edges than those cast with the Ethocel Cylindrical applicator.

c). Scraping

A clean razor-blade mounted on a holder was found to give very satisfactory results, provided that the blade was inclined at about its cutting-edge (Figure 2b). The blades used for scraping film were not used for any other purpose, to avoid any damage to its sharp honed edge. A dented blade was seen to leave streaks of the film on the plate in the direction of scraping.

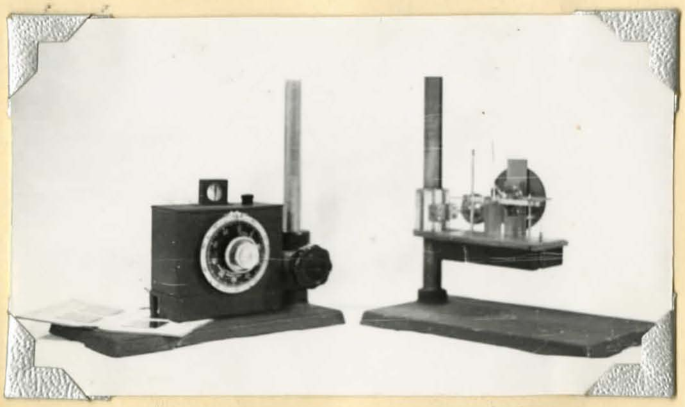
d). Thickness Measurement

At first, using a Randall and Stickney Gauge, film thickness measurements were made by scraping some film off the glass plate, and taking differences in thickness of coated and uncoated glass plate at several points. This method, however, gave very poor accuracy in measurement. Results, using a Magnetic Plating Thickness Micrometer (Magne-Gauge), were somewhat better. The Magne-Gauge (Fig. 2c) consisted of a small permanent bar magnet 2 mm. in diameter, suspended from a horizontal lever-arm. The arm was actuated through a spiral spring by turning a dial. The tip of the magnet was brought into contact with the oil film cast on a steel sheet, and the dial turned till the magnet was detached. The instrument had to be calibrated at first with the help of calibrating standards; from the data obtained, a semi-log plot (Figure 3) of the gauge reading vs. the film thickness was made for use as reference.

The Ethocel applicator gave a finished film thickness ranging from 1.75 to 2.25 mils, for a setting of 5 mils in casting the film. Films formed by the Bird applicator were not checked on the Magne-Gauge, since the applicator was new, and the materials, being synthetic, were known to be free of any volatile components.

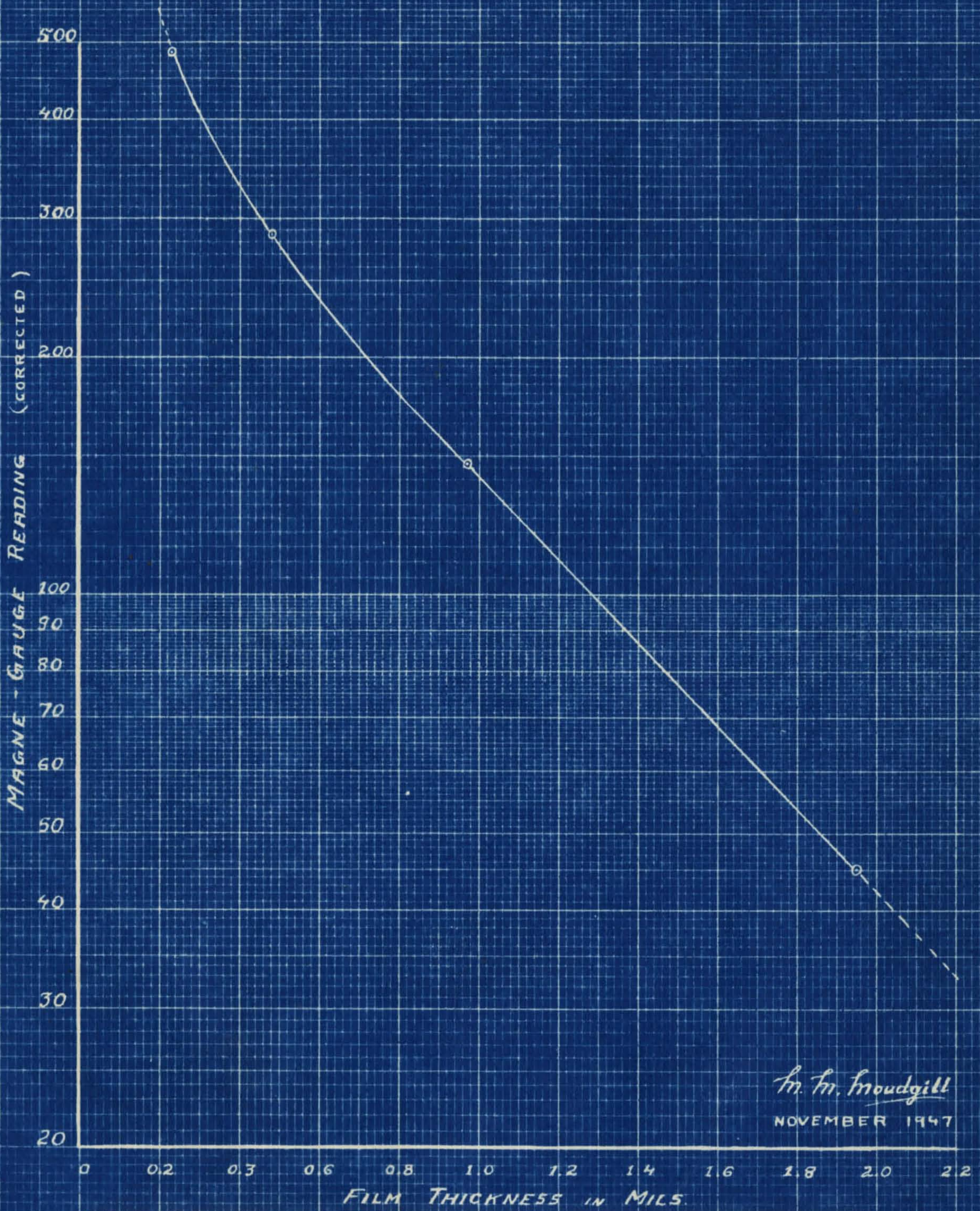
a. Casting of Film (Bird Applicator)

b. Scraping aged film



c. Magnetic Plating Gauge Micrometer

Fig. 2



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NOVEMBER 1947

Fig. 3. Calibration Curve for Magne-Gauge.

II. COMBUSTION

The combustion train used for the ultimate analysis of drying oil films, consisted, essentially of three parts:

a). The feed gas purifying apparatus

b). The combustion tube section

c). The absorption tube section

It was based on the apparatus of Natelson and Conner (1), who, in the course of experimental work had the necessity to do "rapid and reliable .... analysis of compounds containing carbon and hydrogen". Modifications and alterations on their apparatus were made in order to utilize the equipment available, and make the necessary adaptations on their apparatus. (Figs. 4, 5 and 6).

Multiple unit furnaces, made by the Heavy Duty Electric Co., were used for heating the packed section of the combustion tube. The primary furnace was maintained at a temperature of 650°C. by using a rheostat in the circuit, while the secondary furnace was operated at 200°C. This sharp difference in temperature was achieved by allowing a gap of about one inch between the furnaces, and connecting a variac transformer in series with the secondary furnace. Both furnace temperatures were set by checking them with a copper-constantan thermocouple attached to a potentiometer.

A. SUGAR ($C_{12}H_{22}O_{11}$) C.P. GRADE

Sugar, which was tried first, to check for the accuracy of the apparatus, gave useful data, some significant portions of which are listed in Table I.

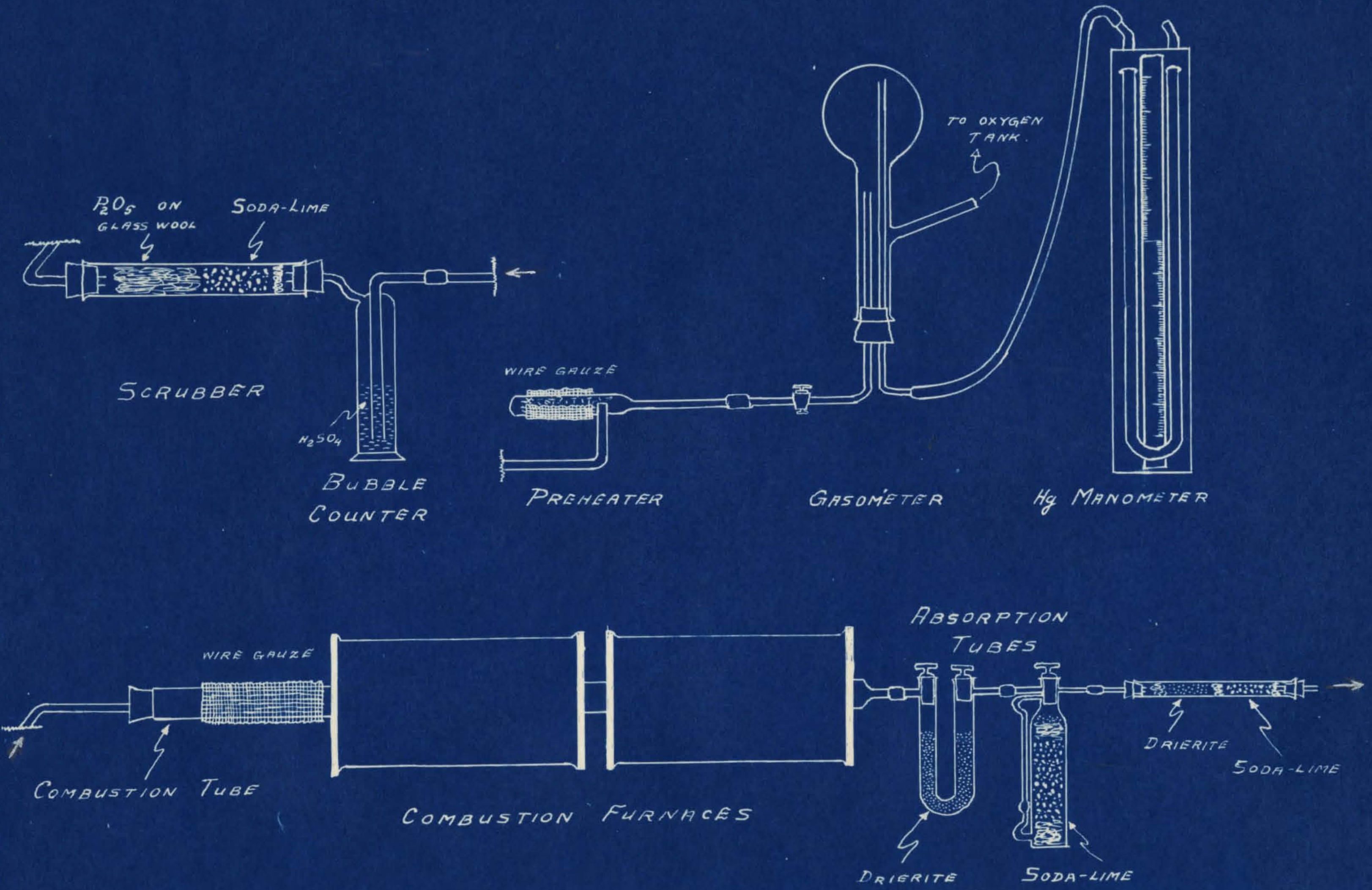


Fig. 4. Combustion Train - Diagrammatic

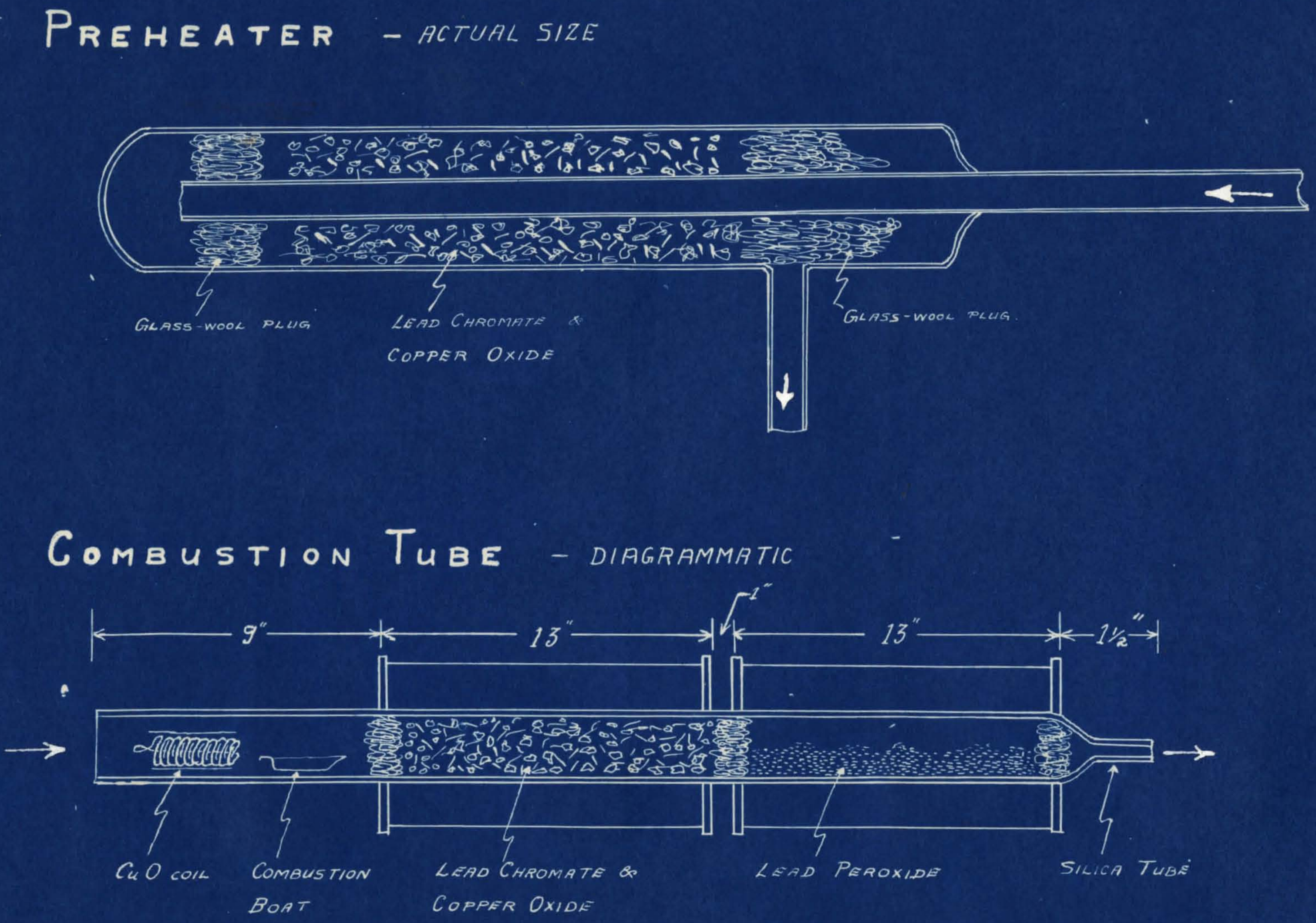
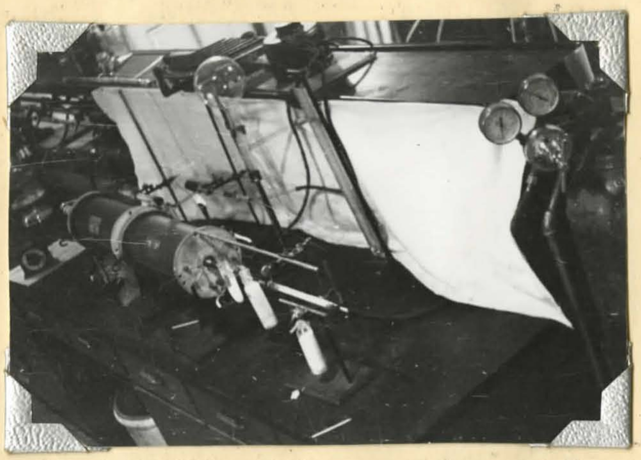


Fig. 5. Preheater and Combustion Tube - Details



a. Combustion Train — Absorption End

b. Combustion Train — Combustion End

Fig. 6

TABLE I. COMBUSTION ANALYSIS OF SUGAR ($C_{12}H_{22}O_{11}$)

Run Number	1	2	3	4	5	6	7	8	9	10	11
Wt. sample	.1014	----	----	----	----	----	----	.0941	.0952	.0951	.1113
H_2O absorb.	.1008	.0136	.0110	.0037	.0050	.0043	.0005	.0696	.0603	.0606	.0637
CO_2 absorb.	.0957	-.0040	-.0061	-.0042	-.0051	.0070	.0004	.1307	.1424	.1415	.1719
Theor. H_2O	.0587	----	----	----	----	----	----	.0545	.0551	.0551	.0644
Theor. CO_2	.1565	----	----	----	----	----	----	.1452	.1467	.1467	.1717
Total absorb.	.1965							.2003	.2027	.2021	.2356
Total theor.	.2152							.1997	.2018	.20.8	.2351

Details of runs:

1. $CaCl_2$ and soda-lime in absorp. tubes
2. Blank for 1.
3. Nothing between gasometer and comb. tube.
4. Gasometer - bubble-counter - comb. tube.
5. Gasometer - preheater - comb. tube.
6. Gasometer - scrubber - comb. tube
7. Blank with complete assembly, and P_2O_5 instead of $CaCl_2$ in the scrubber.

8-10. Runs with apparatus as in 7

11. Drierite instead of $CaCl_2$ in absorp. tube.

By referring to the table, it is seen that run 1 gave very poor results, with far too much absorption in the Schwartz tube. This tube contained anhydrous calcium chloride instead of Drierite as indicated in Fig. 4. The next run, a blank for the previous one confirmed the fact that water was coming through the absorption train. The following runs listed, were tried with

i) 3. nothing
ii) 4. only the Bubble-Counter
iii) 5. the Preheater alone
iv) 6. just the Scrubber

between the gasometer and the combustion tube. All these runs confirmed the inefficiency of scrubbing. Substituting phosphorus pentoxide for anhydrous calcium chloride in the scrubber, (Run 7) did away with water in the incoming feed of oxygen.

The next three runs showed a deficiency in CO_2 and an excess in the H_2O absorbed, and yet the total theoretical absorption equaled the total experimental value. It followed that some of the CO_2 was absorbed by the anhydrous calcium chloride in the Schwartz tube. Substitution of Drierite (anhydrous $MgSO_4$) for anhydrous calcium chloride gave good results, as seen in Run 11 and subsequent runs.

B. LINSEED OIL

A check analysis on linseed oil was run next, and found at first to give uniformly high oxygen percentages. Repeating the combustion in a silica tube at a temperature of

650°C. instead of 550°C., gave more reasonable and better distributed figures for the results (Table II and Figure 7).

C. SOYBEAN OIL

Some data on the combustion of soybean oil were obtained (Table III), but analysis on this material was soon discontinued because of the difficulties encountered in its extraction.

D. GLYCERYL TRILINOLEATE - synthetic material

On testing, a one hour period of combustion was found to be insufficient for glyceryl trilinoleate. Increasing the time by a half-hour did improve results to a certain extent, but it was not until the time was raised to two hours, that the results indicated a complete combustion. Data for all three combustions are plotted on Figure 8. Disregarding the free-moisture on the film, the theoretical maximum oxygen content should be 26.9% However, since no moisture corrections were made (for reasons explained later), a maximum percentage of 29-30% stands within limits of tolerance.

Substitution of Ascarite for soda-lime in the Nesbitt tube was tried, and found to give better absorption of the carbon dioxide.

TABLE II. COMBUSTION ANALYSIS OF LINSEED OIL

Film Age Days	1	2	3	4	7	9	12	14
% C	61.88	58.93	59.48	59.29	55.70	56.70	59.84	61.59
% H	11.19	10.35	9.83	9.93	11.75	9.19	12.49	9.44
% O	26.93	30.72	30.69	30.78	32.55	34.11	28.67	28.97
% C	59.48	59.78						
% H	12.91	10.01						
% O	27.61	30.21						
% C	63.83							
% H	11.78							
% O	24.39							

This series of combustions was conducted using a silica combustion tube at 650°C. and 0.1% (wt. % Pb) lead naphthenate drier.

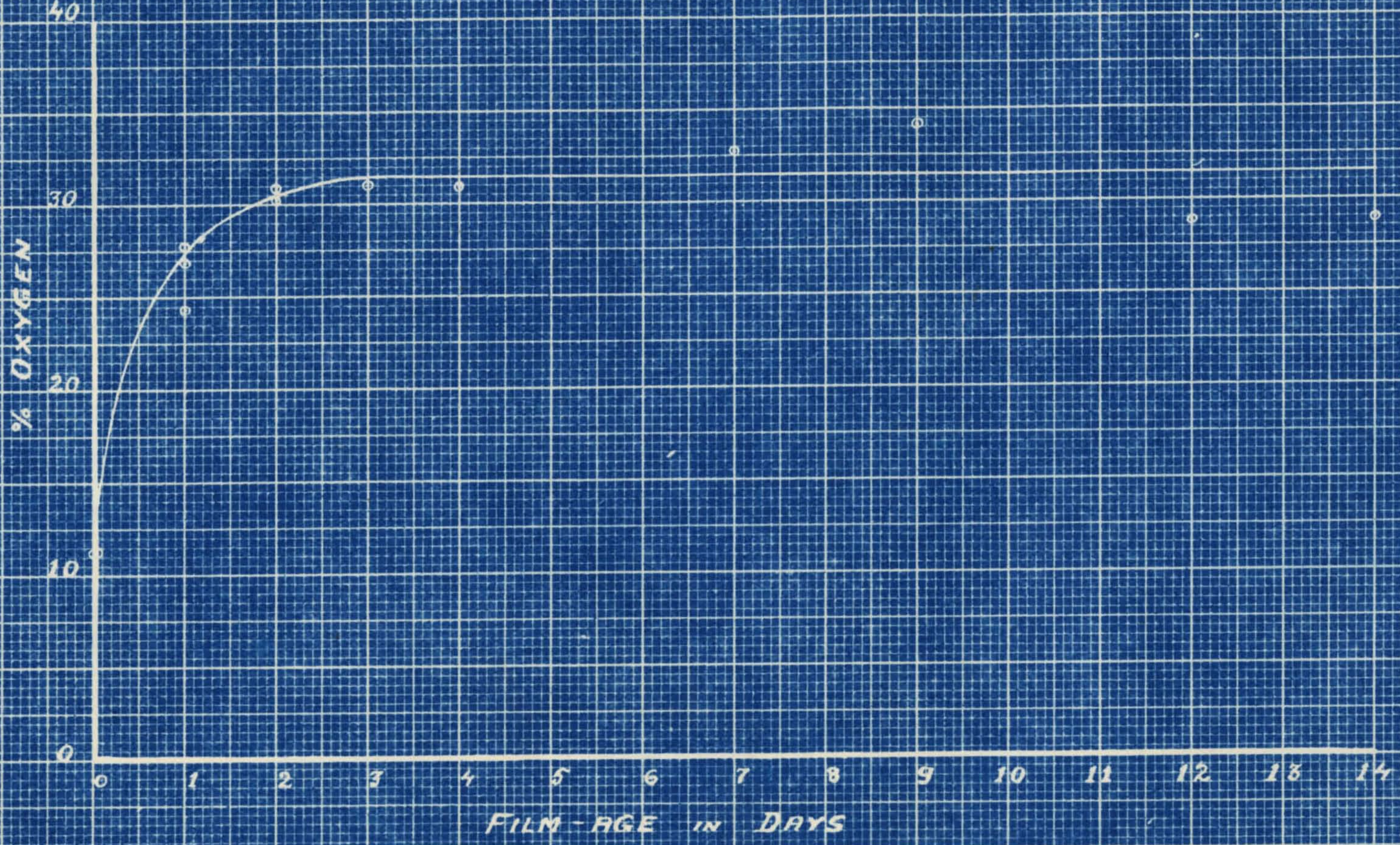


Fig. 7. Rate of Oxidation of Linseed Oil

TABLE III. COMBUSTION ANALYSIS OF SOYBEAN OIL

Film Age in Days	1	2	3	4	5
% C	57.7	53.5	58.4	54.5	54.0
% H	7.32	7.4	6.3	9.4	8.5
% O	34.98	39.1	35.3	36.1	37.5

This series of combustions was conducted using a silica combustion tube at 650°C. and 0.1% (wt. % Co) cobalt naphthenate drier.

TABLE IV. COMBUSTION ANALYSIS OF GLYCERYL TRILINOLEATE

Film Age in Days		1	2	4	7	14
	% C	56.4	41.4		38.53	
1 hour combustion	% H	7.96	10.8		6.84	
	% O	36.64	47.8		54.63	
	% C	59.7	57.9	59.3		
1½ hr. combustion	% H	10.8	8.9	13.0		
	% O	29.5	33.2	27.7		
	% C	61.5	57.7	59.0	61.0	61.8
2 hour combustion	% H	11.6	10.7	10.1	10.0	9.3
	% O	26.7	31.6	30.9	29.0	28.9

This series of combustions was conducted using a silica combustion tube at 650°C. and 0.5% (wt. % Pb) lead naphthenate drier.

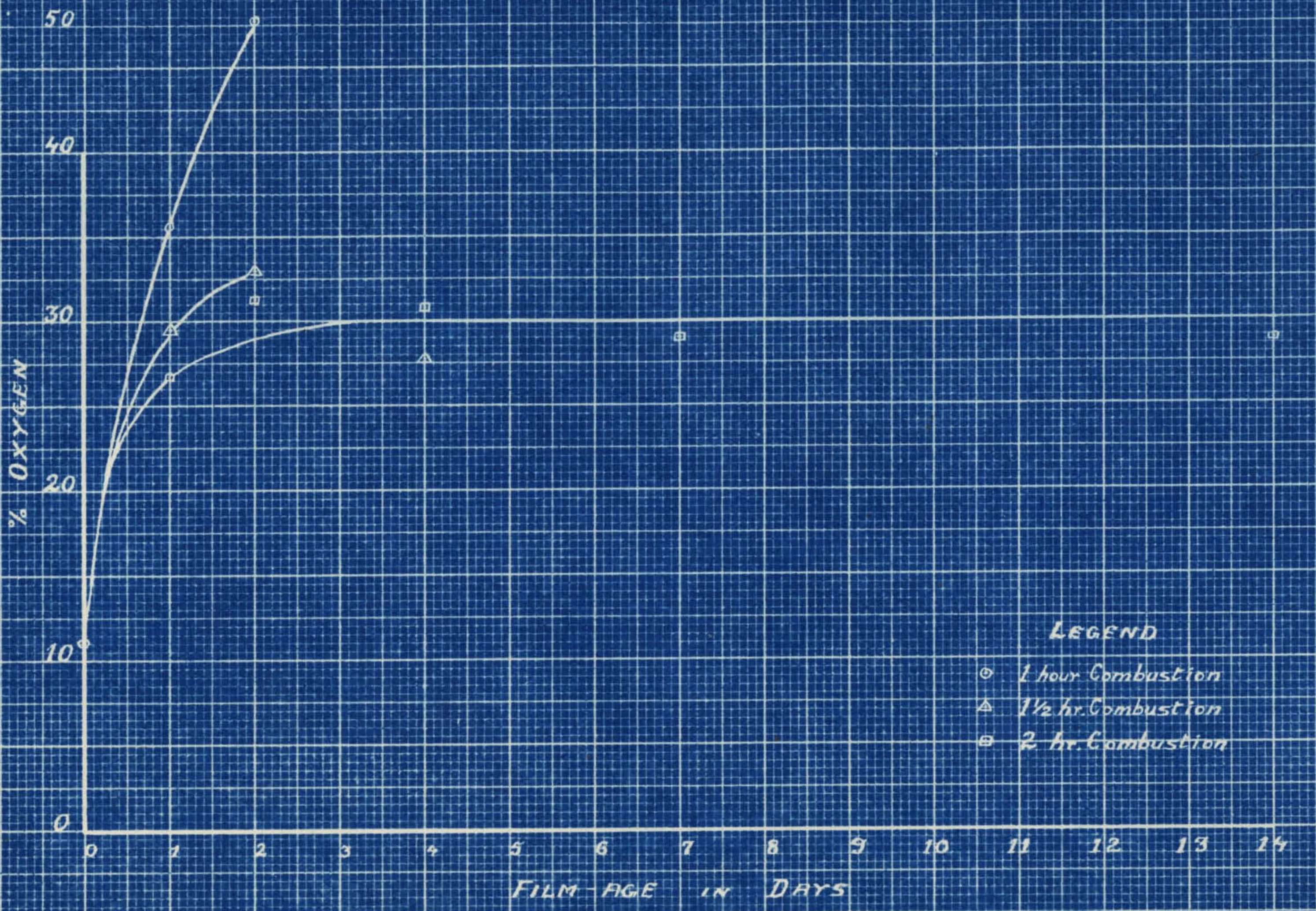


Fig. 8. Rate of Oxidation of Glyceryl Trilinoleate

Procedure

Samples ranging from 90 to 110 mgms. in weight were experimented with. A detailed procedure was worked out and adopted for this investigation, operating directions being as follows:

a). Turn on the combustion furnaces.

b). Three hours later light the burner below the Preheater, and regulate its temperature to 550°C.

c). Collect oxygen in the gasometer at a pressure of 40 cms. of mercury (gauge).

d). Flush the combustion train for 45 minutes at a rate of about 80-90 bubbles of oxygen per minute.

e). Detach the absorption tubes, wipe with a clean dry cloth, and weigh, using similar counterpoising tubes.

f). Attach the absorption tubes to the train.

g). Weigh the desiccated combustion boat; place about 100 mgms. of film sample (scraped off a glass plate) in the boat, and reweigh.

h). Insert the boat into the combustion tube, leaving it just outside the primary furnace. Place the copper oxide coil next to the boat.

i). Start heating the combustion tube, very gently directly outside the copper oxide coil, and leave the burner there for 10 minutes.

j). Refill the Gasometer as before - (see c)

k). Over a period of 20 minutes, move the burner below the combustion boat, and turn up the flame to about 650°C.

l). Leave the burner under the boat for 30 minutes.

m). Move the burner back under the copper oxide coil in about 10 minutes, and leave it there for 20 minutes.

n). Move the burner back under the boat again, and reheat for 30 minutes.

o). Turn off the burner under the boat; refill the Gasometer, and flush the system for a period of 30 minutes.

p). If necessary, heat the absorption end of the combustion tube to drive forward any moisture collected there. (Caution - use a very small flame)

III. EXTRACTION

The apparatus was a battery of Soxhlet extraction units (Fig. 9 and Fig. 10a). Each unit consisted of a 400 ml. extraction flask, a syphon-cup, a Whatman extraction thimble, and a condensing coil. The syphon-cup containing the extraction thimble was suspended by fine wire from the condenser cap, which rested on the neck of the flask. The battery was in the form of a rectangular wooden box lined with asbestos paper, and fitted with a removable lid in which holes were cut to receive the extraction flasks. The flasks containing the solvent were placed in cylindrical metal containers lined on the inside with a sheet of asbestos paper, and received their heat from 60 watt incandescent lamps. Cooling water for the condensers was supplied through an iron pipe manifold, and the cooling systems of the extraction units were connected in parallel.

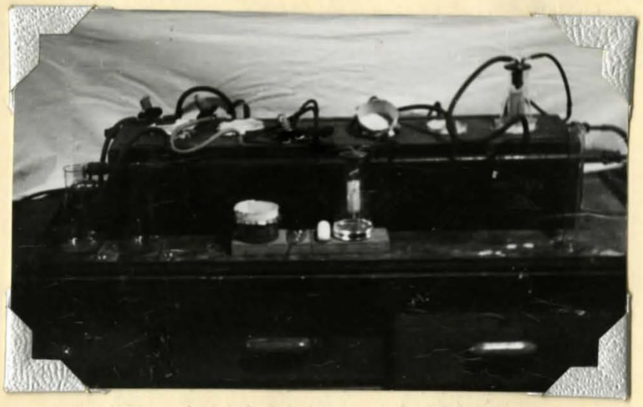
A. LINSEED OIL

On trying acetone, as suggested by the Federation, it was found to give an increase in insolubility from 0 to 47 per cent by weight over a period of 13 days. The extraction battery was seen, in earlier work by Sacra (11), to operate within a range of 4 per cent accuracy over duplicate tests. It was desirable to have an appreciably wide range of solubility in the earlier stages of analyses, when the oil films were undergoing most chemical changes. Since acetone was found to be too powerful, diverse other solvents of varying solvent power, were

EXTRACTION BATTERY

EXTRACTION UNIT

Fig. 9. Extraction Battery - Diagrammatic



a. Extraction Battery

b. Solvent Recovery Unit

Fig. 10

selected on the basis of their boiling points, and used for extraction. The results, as listed in Tables V and VI, show that carbon tetrachloride was the most desirable of the solvents tried.

Further analyses were continued, using carbon tetrachloride, and the results obtained are indicated in Table VI. (Also see Figure 11)

B. SOYBEAN OIL

Extraction of soybean oil films with carbon tetrachloride gave very irregular results. Methyl-ethyl ketone and benzene were tried with no better success; therefore, further work on this oil was discontinued.

C. GLYCERYL TRILINOLEATE

There were no difficulties encountered in the extraction of this material. On the contrary, the duplicate runs appeared to check very closely, as seen in Figure 12. The solvent used was carbon tetrachloride.

TABLE V. EXTRACTION OF LINSEED OIL WITH VARIOUS SOLVENTS

Solvent	B.Pt.	Film-age	Insolubility	Approx. Solvent Loss.
	°C.	Days	Wt. %	Vol. %
1. Acetone	56	2	5	
		13	7	
2. Benzene	80.1	1	4	10-15
		27	27	
3. Carbon Tetrachloride	76.8	See Table VI and Figure 11.		
4. Ethyl Acetate	77.1	2	5	15
		7	2	
5. Methyl Alcohol	64.7	1	1	55-75
		27	4	
6. Methyl-Ethyl Ketone	79.6	1	56	5-15
		27	10	
7. Petroleum Ether	35-60	2	75	
		18	87	

NOTE: Raw oil is soluble in all the solvents listed above.

TABLE VI. EXTRACTION OF LINSEED OIL FILM WITH CARBON TETRACHLORIDE

Run No.	Film-age	Insoluble Percentage		
	Days	Original	Duplicate	Additional
1	1	27	16	
2	2	21	18	
3	3	--	26	
4	4	30	28	
5	5	35	32	
6	6	41	29	38
7	7	44	30	40
8	11	47	43	
9	12	35	44	
10	20	48	45	
11	26	47	37	
12	31	50	44	

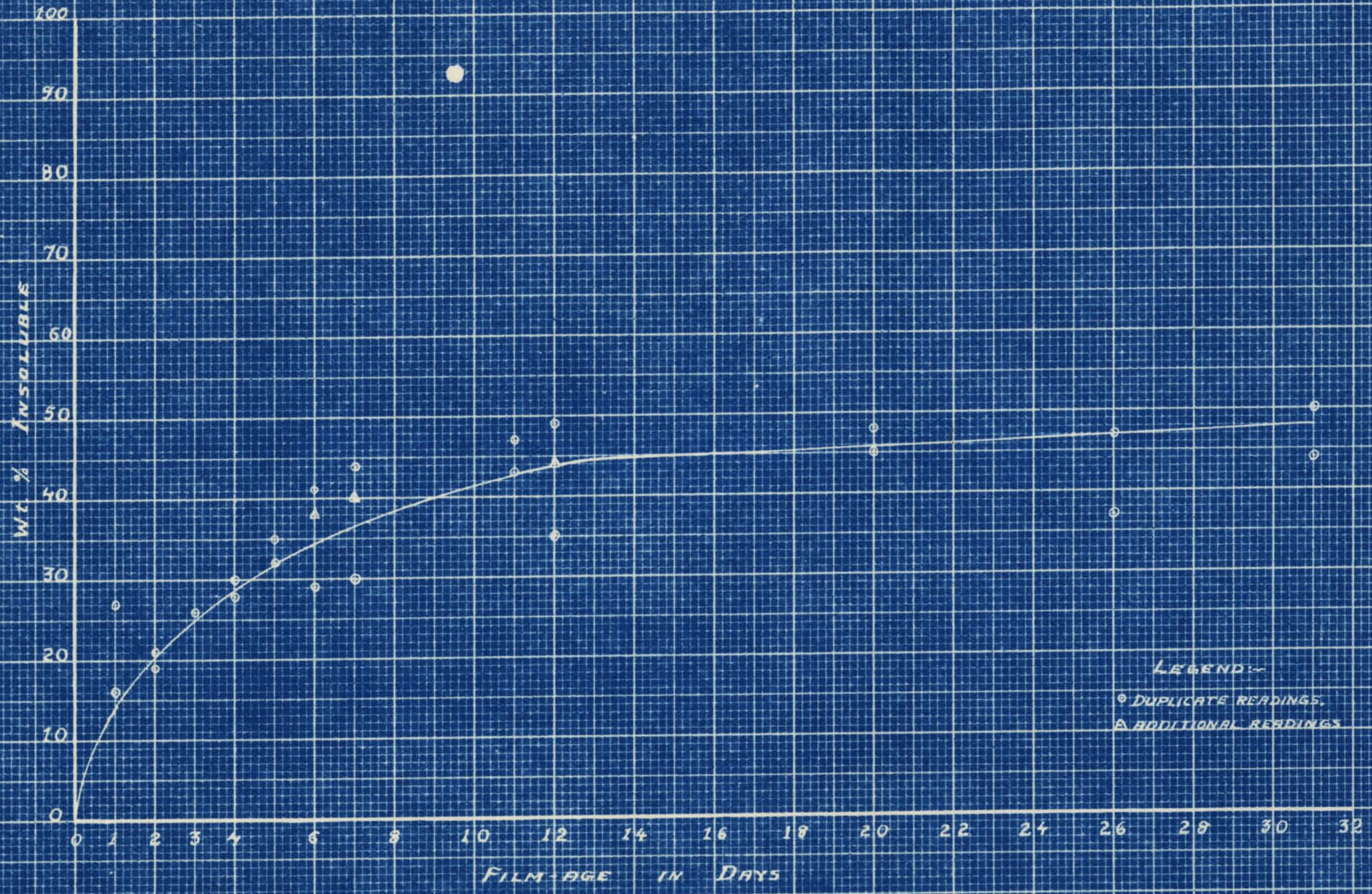


Fig. 11. Extraction of Linseed Oil

TABLE VII. EXTRACTION OF GLYCERYL TRILINOLEATE WITH CARBON TETRACHLORIDE

Run No.	Film-age	Insoluble Percentage	
	Days	Original	Duplicate
1	1	41	44
2	2	49	48
3	4	51	50
4	7	59	56
5	14	54	58
6	28	61	63

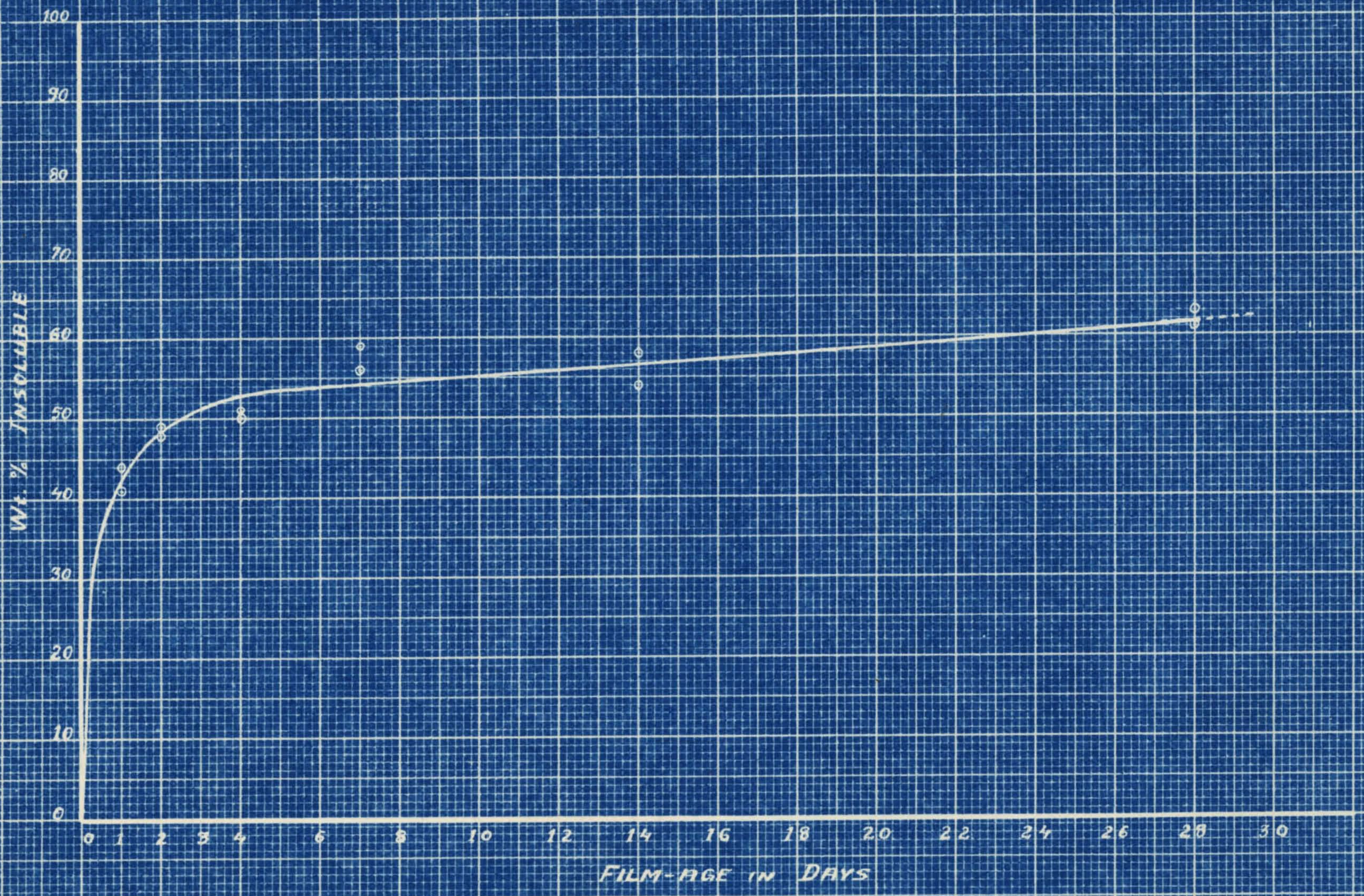


Fig. 12. Extraction of Glyceryl Trilinoleate

Procedure

As mentioned previously, experimental work on this project was of a controlled, rather than an absolute quantitative nature. It was, therefore, necessary to duplicate analyses on similar samples. A detailed procedure was worked out and adopted for the investigation. Operating directions are as follows:

a). Fold a Whatman, Number 30, filter paper six times to get a fluted cone, and insert it into the extraction thimble.

b). Start the cooling water for the condensers at a rate of about 2 liters per minute.

c). Insert the thimble into the syphon-cup.

d). Pour 80 ml. of the solvent into the outer extraction flask.

e). Turn on the lamps to start extraction.

f). Allow the battery to run about 18 hours, and then turn off the lamps.

g). Remove the thimble, and keep it in a drying oven, regulated at 94°C., for two hours.

h). Transfer the thimble to an air-tight weighing bottle, wipe and weigh, using a counterpoise for the weighing bottle.

i). Place about 200 mg. of the film in the cone formed by the filter-paper, and reweigh the weighing-bottle.

j). Repeat the extraction following directions as tabulated in b). to h). above.

It was found advisable to run parallel duplicates on extraction since this test did not give sufficient accuracy. A suitable method of tabulating the extraction data is given in the Sample Data Sheet (Figure 14 - Appendix). The used solvent was recovered by simple reflux distillation (Figure 10b).

CONCLUSIONS

It is evident from the results obtained that a semimicro quantitative combustion analysis will be sufficiently accurate for a determination of the oxygen addition in the oxidation of drying oils. Further studies on well-aged film will judge Marcusson's (6) theory of liberation of oxygen in the polymerization period. Qualitative and quantitative analyses on the groupings discovered and suspected in the drying of these oils, will supplement this work in arriving at finite decisions on the chemical nature of the changes occurring. Errors in results for combustion were attributed to the idiosynacracies of the individual material, for which, at the time, there were no explanations.

Corrections for moisture adsorbed on the films have not been made in these investigations, as the exact quantity was not determined at the time. The effect was not considered in the initial work. However, it was later discovered, and will be accounted for in future procedures. A two hour desiccation over phosphorous pentoxide has been found to satisfactorily remove the adsorbed moisture.

The solubility limit of a polymerized film, as was indicated previously, is some molecular weight, which varies with the extractive power of a solvent. Data for the effective power of various solvents (Table V) show that the best results were obtained in using carbon tetrachloride. Moreover, as seen in Figures 11 and 12, use of this solvent intensified the solubility in the earlier stages of polymerization where changes occur at the most rapid rate.

Figure 7 shows that the oxidation of linseed oil is almost complete in two days, after which, the oxygen content becomes constant. Glyceryl trilinoleate, which forms by weight about one half of linseed oil, does not reach the same stage until the film is about four days old. The faster oxidation of linseed oil may be explained by the presence of the glyceride of linolenic acid, which is a more unsaturated ester, and forms a major portion of the remaining one-half by weight, or some other fast curing ester or catalyst.

From the extraction experiments (Figures 11 and 12), it is noted that synthetic ester polymerized faster than linseed oil. The cause of this could be the purity of the synthetic material. With no other kinds of molecules present, the peroxide of the glyceryl trilinoleate might meet no interference in polymerization, and thus proceed at a faster rate.

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APPENDIX

TABLE VIII. SAMPLE CALCULATIONS FOR MIXING DRIER AND OIL

Drier used - Lead Naphthenate

Wt. % Pb in drier supplied = 24%

Wt. % Pb in mixture (specified) = 0.5%

Approximate weight of mixture = 2 gms.

Approximate weight of drier = $\frac{0.5}{100} \times \frac{100}{24} \times 2$ gms.

= 0.04 gms.

Let

Wt. of Florence flask empty = 17.2473 gms.

Wt. of Florence flask and drier = 17.2884 gms.

Wt. of Drier used = 0.0411 gms.

Corresponding weight of mixture = $0.0411 \times \frac{24}{100} \times \frac{100}{0.5}$ gms.

= 1.973 gms.

Wt. of oil to be added = 1.973 - 0.0411 gms.

= 1.9319 gms.

Wt. of Florence flask, drier and oil = 19.2203 gms.

Figure 13. SAMPLE DATA SHEET

Combustion of ....

Film Age in Days	1	2	3	7	14
(1) Wt. sample and combustion tube					
(2) Wt. combustion tube					
(3) Wt. of sample (1) - (2)					
(4) Initial wt. Drierite tube					
(5) Final wt. Drierite tube					
(6) Wt. of H_2O formed (5) - (4)					
(7) Initial wt. Ascarite tube					
(8) Final wt. Ascarite tube					
(9) Wt. of CO_2 formed (8) - (7)					
(10) %C $\frac{(9)}{(3)} \times \frac{12}{44} \times 100$					
(11) %H $\frac{(6)}{(3)} \times \frac{2}{18} \times 100$					
(12) %O $100 - (10) - (11)$					

Figure 14. SAMPLE DATA SHEET

Extraction of ....

Film Age in Days	1	2	3	7	14
(1) Wt. filter-paper and thimble					
(2) Wt. sample, " " initial					
(3) Wt. sample, " " final					
(4) Wt. of unextracted film (2) - (1)					
(5) Wt. insoluble portion (3) - (1)					
(6) Wt. % Insolubility $\frac{(5)}{(4)} \times 100$					

Solvent ....

B. Pt. ....

Approx. Solvent Loss (Vol. %) ....

VITA

The author was born in Trivandrum (S. India) on December 18, 1925. His father, Dr. K. L. Moudgill, and mother, Mrs. Sushiela Moudgill, are both from the Punjab (N. India), where they were born and reared.

Until the age of ten the author was tutored at home, and then sent to Doon School, the first of the Indian Public Schools in Dehra Dun (United Provinces). In December, 1941, he appeared for and passed the Cambridge School Leaving Certificate Examination. Continuing at the Doon School, in fifteen months he covered the Intermediate Course of the United Provinces Board of High School and Intermediate Education.

He then moved back to South India, and entered the University College of the Travancore University, where he received his B.Sc. in Chemistry, with Physics minor in 1945.

Coming to the United States, he entered Northwestern University, Evanston, Illinois, in April, 1946. At the end of the Summer of the following year, he was graduated from there, obtaining his B.S. in Chemical Engineering.

In order that he might work toward the degree of Master of Chemical Engineering, Mr. Moudgill entered the University of Louisville in September, 1947, as a Graduate Assistant in the Department of Chemical Engineering, and started work on two projects sponsored by the National Federation of Oil, Paint, and Varnish Manufactorers. In September, 1948, he completed his work and received the degree of Master of Chemical Engineering in June, 1949.