A STUDY OF THE OXIDATION STABILITY OF LUBRICATING OILS

by

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A thesis presented to the Department of Chemistry of Union College in partial fulfillment of the requirements for the degree of Bachelor of Science in Chemistry.

By Frank A. Pepe

Approved by Charles B. Hurd

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ACKNOWLEDGMENT

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INTRODUCTION

This past year, research work was done on the oxidation of lubricating oils. It was done under a grant by the American Locomotive Company in Schenectady.

Since this is the first year that this research project has been carried out, our work was mainly directed towards finding ways of attacking the study of the oxidation of lubricating oils. We have found a few paths which warrant further investigations.

Lubricating oils are composed almost completely of paraffins, naphthenes, and aromatics (1). To this basic composition, however, are added many organic and metal-organic compounds to give the finished oil the desired properties (2) (3) (4). Among these additives are:

1. Antioxidants or Oxidation Inhibitors

Organic compounds containing S, P, or N such as amines, sulfides, hydroxy-sulfides, and phenols.

These prevent varnish and sludge formation and also corrosion of metal parts.

These additives either oxidize in preference to oil or they decrease the amount of O_2 taken up by the oil.

2. Anticorrosives, Passivators

Organic compounds containing active S, P, or N such as organic sulfides, phosphites, metal salts and sulfurized waxes.

They prevent corrosive attack of metal surfaces by forming a protective film on the metal. This film also prevents the metal from acting as a catalyst.

3. Detergents

Metallo-organic compounds such as phosphates, phenolates, and alcoholates, High molecular weight soaps containing metals like Mg, Ba, and Sn.

They prevent deposits of sludges and thus keep metal surfaces clean.

They may react with oxidation products of the oil preventing them from further reactions resulting in insoluble products.

4. Dispersants

Metallo-organic compounds such as naphthenates and sulfonates. Organic salts containing metals like Ca, Co, and Sr.

This keeps oxidation products such as sludge in a peptized form, that is in a finely dispersed colloidal suspension.

This keeps metal surfaces clean.

5. Extreme Pressure Agents

These are phosphorous compounds like tricresyl phosphate as well as sulfurized lard oil, and halogenated compounds. Lead soaps such as lead naphthenates are also used.

These prevent unnecessary wear of moving parts.

A film is formed on the metal surface by chemical reaction. This film prevents damage to the metal if the lubricating film is ruptured.

6. Rust Preventives

Amines, fatty oils and certain fatty acids. Halogenated derivatives of certain fatty acids and also sulfonates.

These additives are used to prevent rust in new or overhauled engines during storage or shipment.

They do this by preferential wetting of the metal surfaces by added adhesiveness.

7. Pour Point Depressants

High molecular weight condensation products such as phenols condensed with chlorinated wax. Also methacylate polymers.

These additives lower the pour point of lubricating oils by coating the wax crystals in the oil thus preventing their growth at lower temperatures.

8. Viscosity Index Improvers

Polymerized olefine or isoolefine, butyl polymers, cellulose esters and hydrogenated rubber are used.

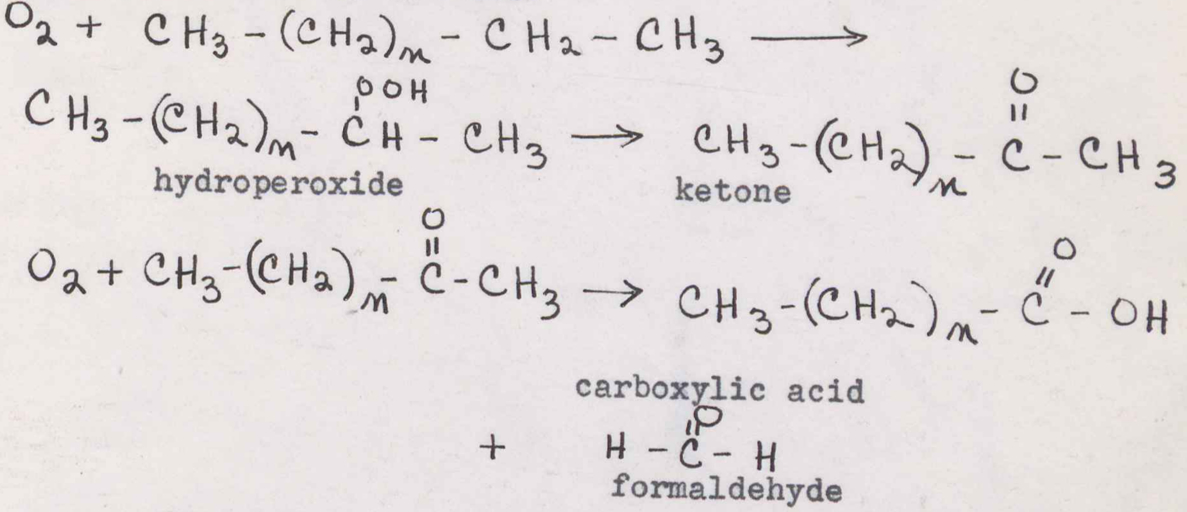
These additives lower the rate of change of viscosity with temperature. They do this because they themselves are less affected by temperature change. Also they are more affected by an increase in viscosity at high temperature than at lower temperatures.

These are only a few of the many additives used in lubricating oils for obtaining an oil with exactly the desired properties.

Of the compounds used in compounding the oils, only the polycyclic naphthenes and the aromatics, have lubricating properties. The tricyclics are more viscous than the bicyclics (5).

Some work has been done on studying the oxidation of pure hydrocarbons (6). From this work, reaction mechanisms have been postulated which help to explain the reactions taking place when an oil is heated and air or oxygen is passed through it. These studies with the pure hydrocarbons give an idea of the kinds of oxidation reactions taking place in actual lubricating oils and help in picking substances to prevent this oxidation or at least slow it down.

At high temperatures it was found that the terminal carbon atom in a long chain hydrocarbon was attacked. However at the lower temperature of about 150°C the beta carbon atom was attacked primarily and the gamma carbon atom secondarily and so on down the carbon chain. A mechanism for the oxidation of such paraffins has been postulated as follows:



$$O_2 + CH_3-(CH_2)_m-CH_2-CH_3 \longrightarrow$$

$$CH_3-(CH_2)_m-\overset{OOH}{\overset{|}{C}}H-CH_3 \longrightarrow CH_3-(CH_2)_m-\overset{O}{\overset{\|}{C}}-CH_3$$

hydroperoxide ketone

$$O_2 + CH_3-(CH_2)_m-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow CH_3-(CH_2)_m-\overset{O}{\overset{\|}{C}}-OH$$

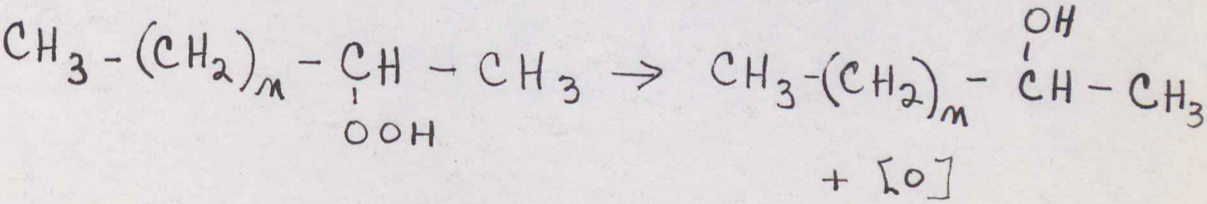
carboxylic acid

$$+ \quad H-\overset{O}{\overset{\|}{C}}-H$$

formaldehyde

The formaldehyde formed has actually been isolated from the oxidation products of paraffins. There is also some attack of the gamma carbon atom, but to a lesser extent.

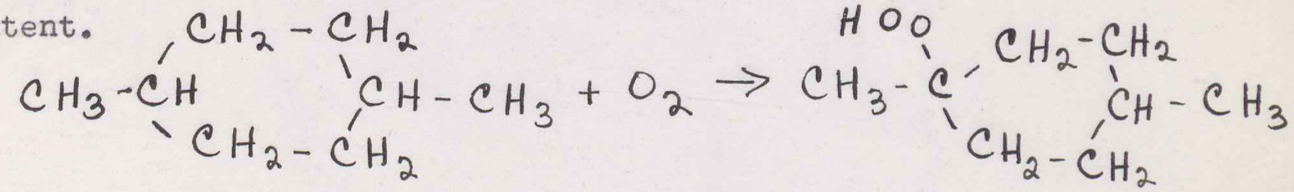
The acids resulting from the oxidation may be oxidized further by attack of other carbon atoms in the chain. Also the aldehydes may be oxidized to acids or to water and CO_2. The hydroperoxide formed in the first step of oxidation may act as an oxidizing agent and thus be reduced to an alcohol.

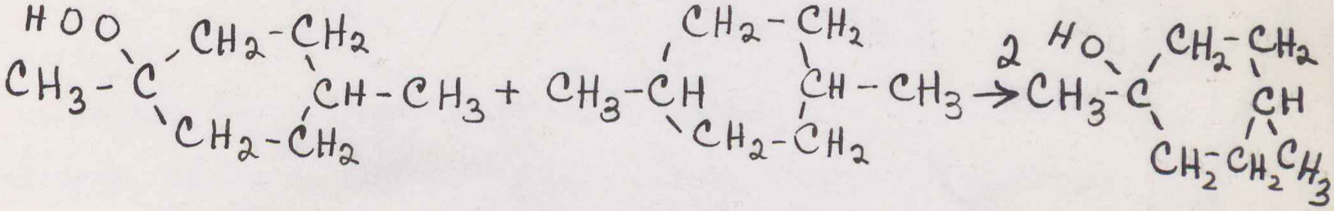


$$CH_3-(CH_2)_m-\underset{OOH}{\underset{|}{C}}H-CH_3 \rightarrow CH_3-(CH_2)_m-\overset{OH}{\overset{|}{C}}H-CH_3 + [O]$$

The alcohols formed may then form esters with the acids present in the partially oxidized oil.

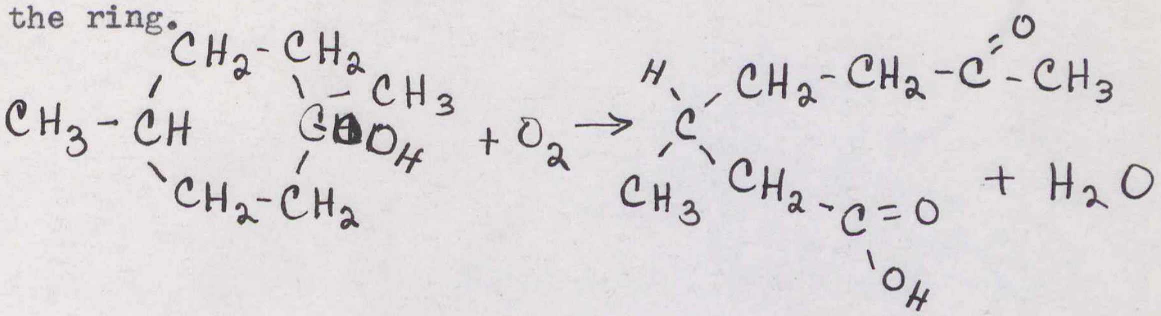
The mechanism postulated by Zuidema for the oxidation of naphthenes is similar to that for paraffins, however, in paraffins the formation of a hydroperoxide yields, for the most part, a ketone and then an acid. The reduction of the hydroperoxide to an alcohol occurred to a small extent. In the oxidation of naphthenes, the formation of the alcohols occurs to the greatest extent.



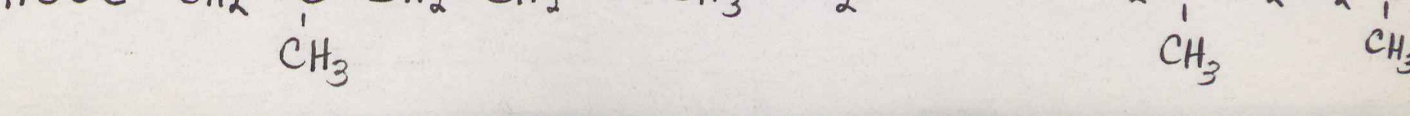


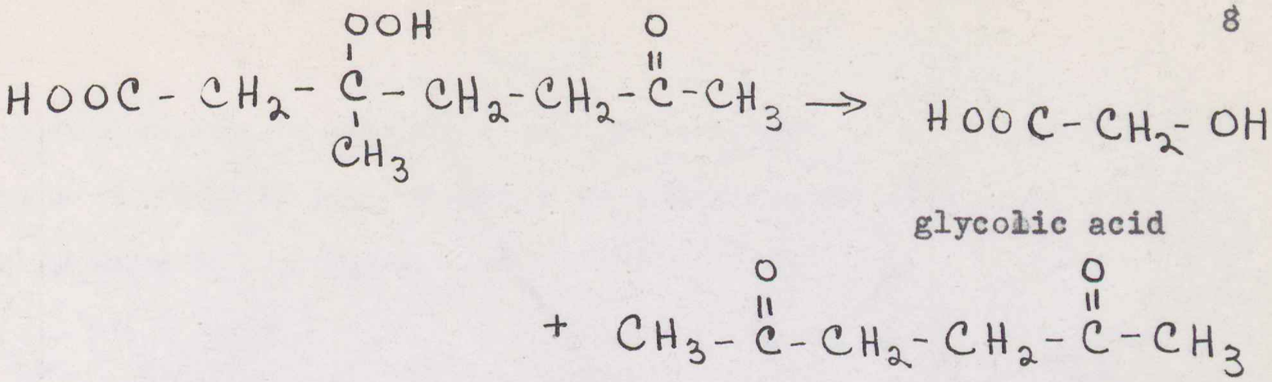
The 1,4 dimethylcyclohexandiol 1,4 may also be formed by the same mechanism.

The hydroperoxide on further oxidation may lead to rupture of the ring.



The tertiary carbon on this product may then undergo further oxidation.

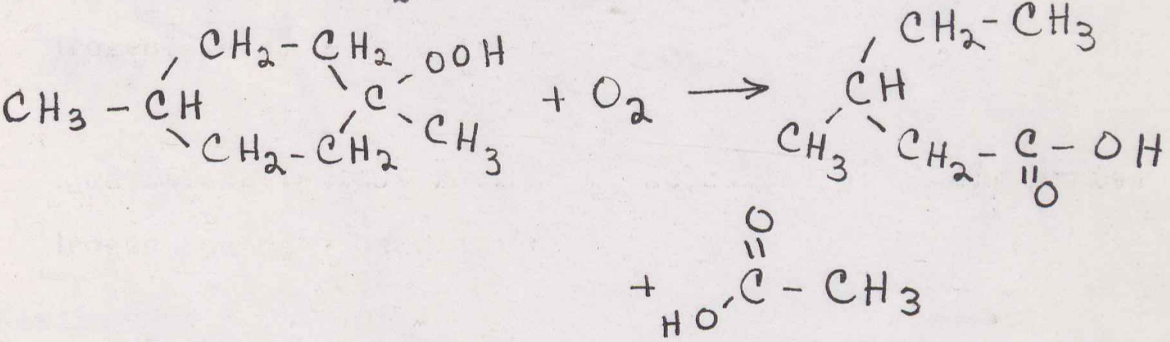




$$HOOC-CH_2-\overset{OOH}{\underset{CH_3}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow HOOC-CH_2-OH + CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

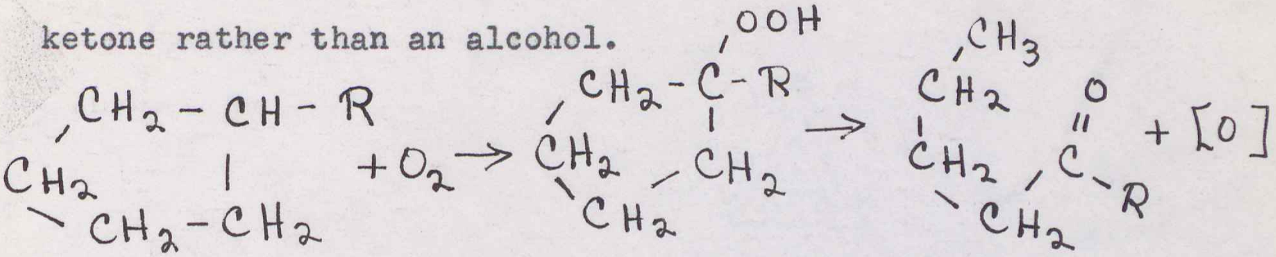
The glycolic acid then probably oxidized further to CO_2 and H_2O.

The 1,4 dimethylcyclohexane hydroperoxide may react with a second molecule of O_2 giving two acids.

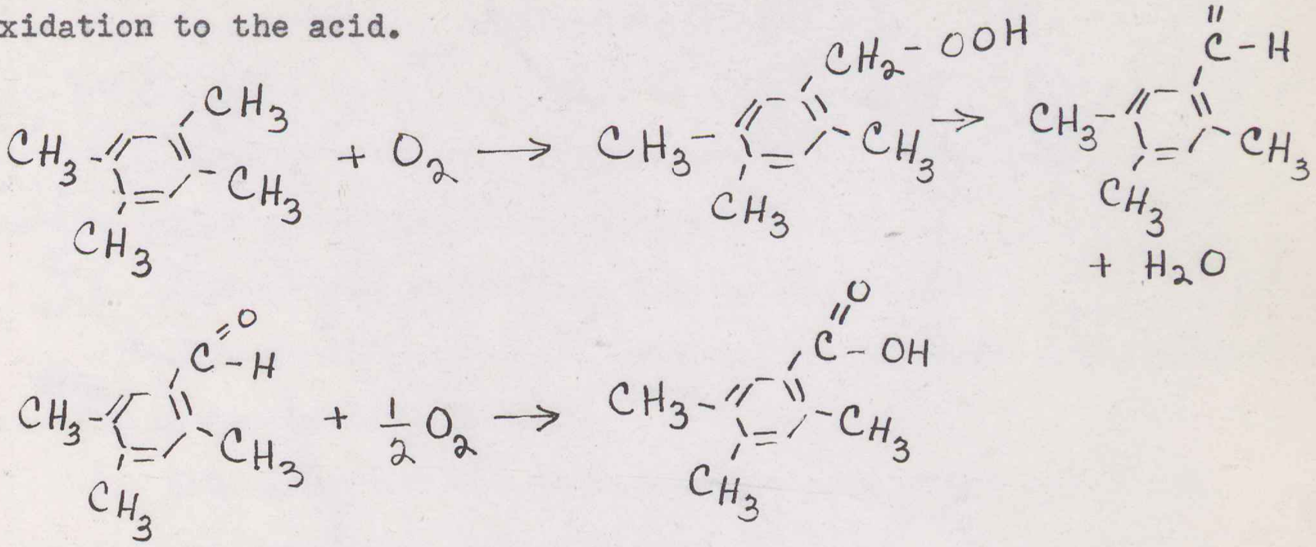


At the same time that these reactions are being carried on, hydrogen, methane, and ethane are formed along with carbon. These products occur to a smaller extent and are due to cracking of the oil.

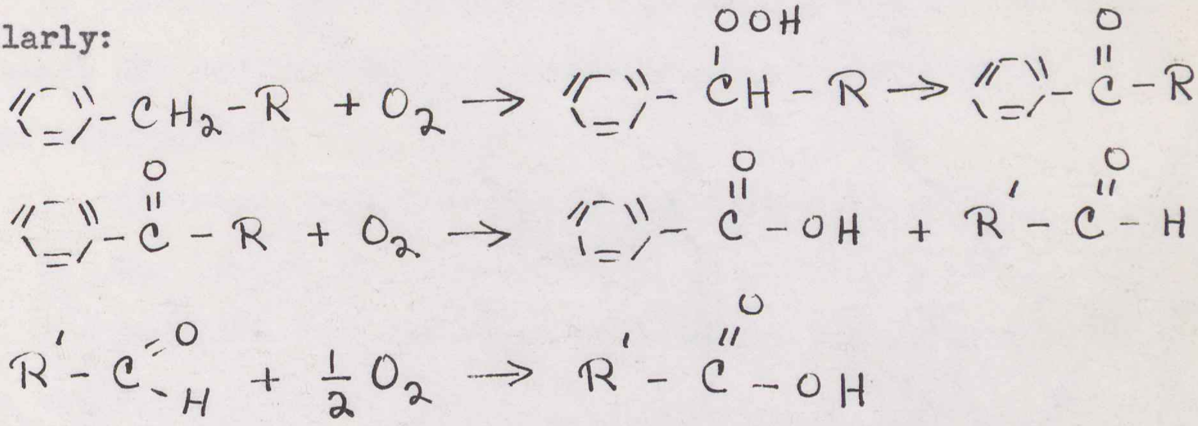
Another reaction which may occur in the oxidation of a naphthene, is the reduction of the hydroperoxide to produce a ketone rather than an alcohol.



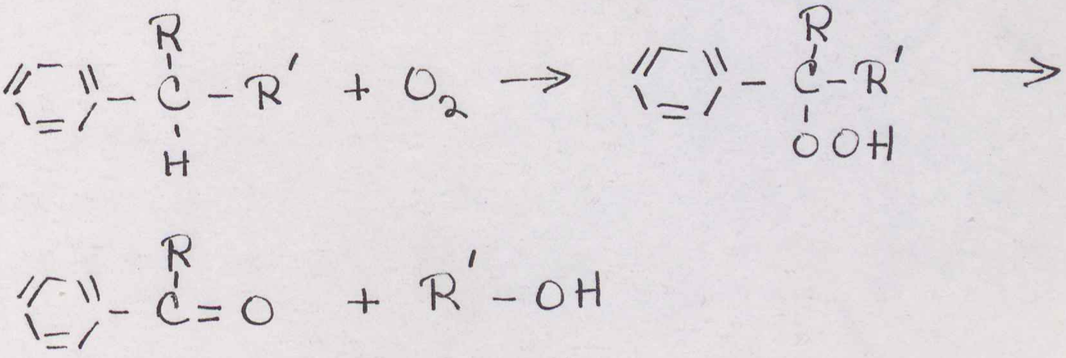
In the oxidation of benzene derivatives the carbon atom attached to the ring is almost invariably attacked, and the mechanism may be explained by the formation of a hydroperoxide with subsequent decomposition to the aldehyde or ketone and oxidation to the acid.



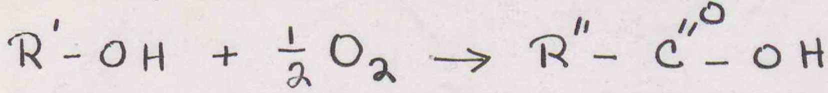
Similarly:



If we have a tertiary carbon, one of the substituents being a benzene ring, an alcohol will be formed as well as a ketone.



The alcohol may then be oxidized to an acid.



$$R'-OH + \frac{1}{2}O_2 \rightarrow R''-\overset{O}{\overset{\|}{C}}-OH$$

A list of generalities can be made about the stability of various types of hydrocarbons. These are:

1. Naphthalene derivatives are the most stable.

2. Hydrogenation of alkyl benzenes giving alkyl cyclohexanes results in increased stability.

3. Hydrogenation of a naphthalene ring reduces stability, especially if partially hydrogenated.

4. Tertiary butyl benzene is the most stable of the butyl benzenes and tertiary butyl naphthalene is the most stable of the butyl naphthalenes.

5. Chainless polynuclear aromatics are very stable.

6. The longer the side chain the less the stability.

7. The beta derivatives of naphthalene are more reactive than the alpha derivatives.

8. The intermediate linkage of two aromatics by carbon atoms lowers the stability.

9. The higher molecular weight compounds are less stable than the lower molecular weight ones.

Larsen, Thorpe, and Armfield (7) have made an extensive study of the rate of oxidation of pure hydrocarbons. They measured the amount of O_2 absorbed at 110°C for most of the hydrocarbons.

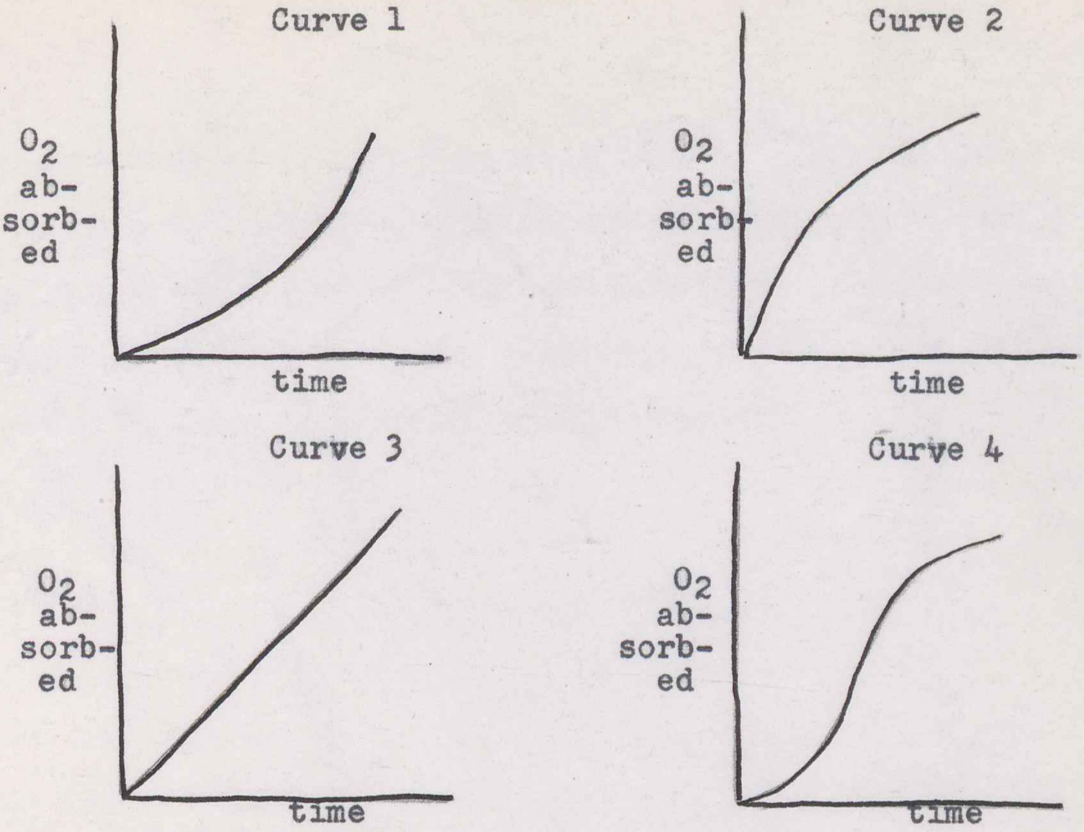


Figure I
Oxidation Curves

They reported their results in time (in hours) taken to absorb 2000 cc of O_2 per gram mole.

The rate of absorption of O_2 was found to change with time. If the oxygen absorbed is plotted against time, four major types of curves are obtained as shown in Figure I. In curve 1, as the oxidation proceeds, the oxidation products act as catalysts and increase the rate of oxidation of the oil. This is called autocatalysis. In curve 2 the oxidation products retard the oxidation. This is called autoretardation. Another explanation for the shape of this curve may be that the more oxidizable substances are used up and removed, the more stable substances remaining will absorb less and less oxygen and the curve will tend to flatten out. In curve 3 the rate of absorption of O_2 is constant. This exhibits neither autocatalysis nor autoretardation. Curve 4 shows a combination of autocatalysis and autoretardation. At the beginning of the oxidation the rate of absorption of O_2 increases, but as the reaction proceeds the rate begins to decrease until the reaction is very nearly completely retarded.

SECTION I. DIPPING LIGHT BULB TESTS

The dipping light bulb test is a test devised at the chemical laboratory of the American Locomotive Company by Mr. A. C. Mengel and Mr. J. A. McGowan. The purpose of the test is to simulate actual working conditions of the lubricating oils in the diesel locomotives. In this test 300 g samples of the lubricating oils are placed in 500 ml electrolytic beakers. To this is added a piece of "Admiralty Metal" having a surface area of 5 square centimeters, which acts as a catalyst. The beakers are then placed in an aluminum block which holds six of them at one time. The block is equipped with a heating unit whose temperature is controlled by a precision thermoregulator placed in a hole in the aluminum block. Air is then bubbled through the oil at the rate of approximately 200 cc per minute. The whole unit is kept at a temperature of about 300°F. A G.E. T-6-½-25 watt, 110 volt electric light bulb is hung vertically above the oil and allowed to dip into the oil at the rate of once per minute.

This test is keptin operation until the oil becomes black and the light bulb becomes coated by a brown or black deposit. This time is then recorded and taken as proportional to the stability of the oil under actual working conditions.

Some of the very poor used oils that were tested formed this deposite as soon as they were placed on the test. Other more stable oils lasted for as long as thirty days.

There are many sources of error in this procedure. Some of them are:

1. Regulation of the rate of flow of the air through the oil is difficult and therefore not too accurate.

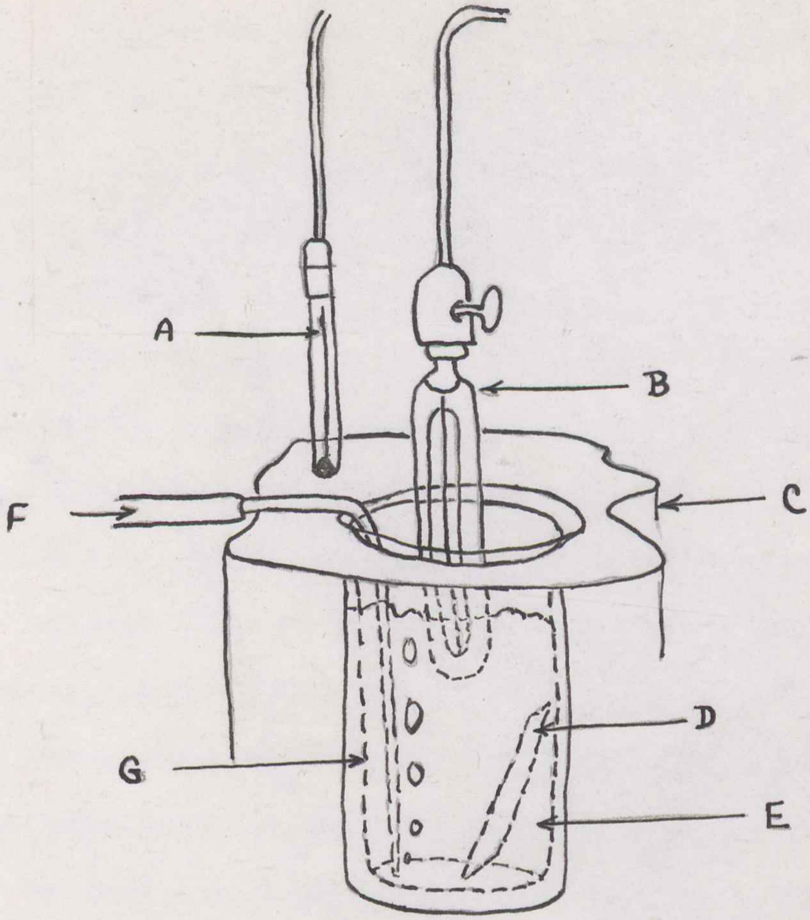


Figure I - 1

A	Thermoregulator set at 300°F
B	Electric light bulb - G.E. T-6-½-25 watt, 110 volt
C	Aluminum block containing six holes for beakers
D	Admiralty metal catalyst
E	Lubricating oil being tested (300 g)
F	Compressed air fed in at approximately 200 cc per minute
G	500 cc electrolytic beakers

Apparatus for the Dipping Light Bulb Test

2. The temperature of the oil bath begins to rise as soon as the oil becomes dark.

3. The admiralty metal used, having an irregular surface, catches particles or pieces of oxidized oil which cannot be cleaned off and may act as catalysts.

4. The temperature of the beakers of oil does vary somewhat from beaker to beaker. This is probably due to the poor conductivity of the oil.

An investigation of the influence of a change in rate of flow of air through the oil on the dipping light bulb test as well as an investigation of the effect of temperature change would be useful in increasing the dependability of the results of the test. Such an investigation would determine whether these quantities should be more accurately controlled or not. For lack of time we were unable to do this during the past year.

Following are the results of the dipping light bulb tests obtained from July 1952 through April 1953.

Table I

DIPPING LIGHT BULB TEST RESULTS

Lab. #	Oil	Days
18101	New York Central, Gulf-Shell	15
18728	New York Central, Utica, New York, Grade 40, Rerefined, Class 5	14
31814	New York Central Oil, #1089	16
31822	New York Central Oil, #1107	2
31826	New York Central Oil, #3359, 8/18/52	6
31827	New York Central Oil, #3363	3

TABLE I (Cont.)

Lab. #	Oil	Days
31721	Texas Dieseltex, #1675, Great Northern R.R.,276A	1
31726	" " " " " 310B	4
31727	" " " " " 310C	5
18901	John L. Ray Co.,R-55A, Diesel Lube (Fortified 5% Paranox #68) Reclaimed	19,33
18902	John L. Ray Co.,R-55A, Diesel Lube (not fortified)	3
18899	John L. Ray Co., Boston and Albany R.R., Diesel Lube, Rerefined (fortified 5% Paranox #68)	11
18900	John L. Ray Co., Boston and Albany R.R., Diesel Lube, (not fortified)	3
18575	B & A reclaimed oil from John L. Ray Co.	14
18870	Mid Continent Diesel Oil G75, Base oil	10,8
18887	" " " " " Finished oil	5,7,8
18669	" " " " G76B	7
5533	Esso #1312, 250 hrs.	4
18574	Reclaimed Esso, #2325 & Esso RD76 with 2325 concentrate, New Haven R.R.	7
18821	Rerefined Esso Lube Oil with Esso additives, L.V.R.R., 11/7/52	8
18820	Rerefined Esso Lube Oil without additives, L.V.R.R., 11/7/52	1
18886	Lehigh Valley R.R., Rerefined Esso, #2325, Diesel Oil, Berks Refining Co.	7
18875	Lehigh Valley R.R., Rerefined Lube Oil without #2325 additive	2
18833	Western Maryland R.R., Rerefined Esso #2325	10
18832	Western Maryland R.R., Rerefined Esso #7138, Mineral Oil	5

TABLE I (Cont.)

Lab. #	Oil	Days
18058	Esso oil Blend, WS 2461	11
18104	New Haven Railroad, Esso 1247, Reclaimed	5
18133	New Haven Railroad, Esso 2325, Reclaimed	17
32479	Esso 2325, New Haven R.R.,#0412,over 5000 mi, 9/18/52	3
32459	Esso 76 & 2325, New Haven R.R.,#0466,over 5000 mi, 9/15/52	2
32372	Esso Lehigh Valley, #571	13
18894	McColl-Frontenac Oil Co. Ltd., 1-600 C.T.,Pale oil	5
18895	" " " " 85/90 at 210°F,Pale oil	2
18896	" " " " H.V.I. Series SAE 50 oil	28,25
18897	" " " " Dieseltex HD 40 (1675)	9
34468	" " " " " " (1606) Used oil, Sample No. 12	4
34469	McColl-Frontenac Oil Co. Ltd.,Dieseltex HD 40 (1606) Used oil, Sample No. 23	11
34470	McColl-Frontenac Oil Co. Ltd.,Dieseltex HD 40 (1606) Used oil, Sample No. 31	9
34471	McColl-Frontenac Oil Co. Ltd., Dieseltex HD 40(1606) Used oil, Sample No. 44	10
34474	McColl-Frontenac Oil Co. Ltd., Dieseltex HD 40(1675) Used Oil, Sample No. 74	7
34484	McColl-Frontenac Oil Co. Ltd., Dieseltex HD 40(1675) Used oil, Sample No. 1, Loco. No. 9410	4

TABLE I (Cont.)

Lab. #	Oil	Days
	Standard of Indiana, LF 0431	7
	" " LF 0432	5
	" " LF 0433	5
	" " LF 0434	15
	" " LF 0435	5
	" " LF 0436	14
	" " LF 0566	10,7
18891	New HD 40, #1675, Reading R.R.	8,15
18890	Reclaimed HD 40, Reading R.R.	14,15
18822	Reclaimed Standard of Indiana, HD 40, L.V.I. Special D.R.G.W.R.R.	4
18874	Texas, #1675, Dieseltex HD 40, Base oil	3
18885	" " " " Finished oil	14,8
18904	Standard of Indiana, HD 45, Reclaimed Belt R. Co.	19,11
18881	" " HD 40, HD 45, HD 45 special base oil	15,10
18880	" " HD 40, Special base oil	7
	Std. HD 40, Used by Alton and Southern R.R.	18
	Std. W.R. 1717, HD 40, Spec. C & NWRR	9
	Std. HD 40, Nol Pac. R.R.	17
18619	S.V. 3209-22	11
18618	S.V. 3209-21	11
31784	Socony Vacuum, D&H, #4034	4
31832	Socony Vacuum, D&H, #4012	13
31974	Socony Vacuum, D&H, #4077	5
31973	Socony Vacuum, D&H, #4076	8

TABLE I (Cont.)

Lab. #	Oil	Days
32477	Socony Vacuum New Haven, #0410, over 5000 mi, 9/12/52	5
	Socony Vacuum, SV 4BM, Boston & Maine, R.R.	6
17300	Std. of Cal., Orange Sq., New oil, Rock, Is. R.R.	18
17301	Std. of Cal., Orange Sq., Used oil, Rock Is. R.R.	6
	Rock Island Reclaimed, 3/24/52	5
18928	Reclaimed oil sample, Rock Is. R.R.	8
18977	Rerefined oil, Silves R.I. R.R.	11
18978	Rerefined oil from outside refiner R.I. R.R.	12
18979	R.I. Special 300 oil, Sample 3	10
18980	R.I. Special 300 oil, Sample 4	11
18871	Shell Talona 40, Base Stock	3,4
16047	Shell T 833, 200 hrs.	2
18831	Shell Talona, R 40, D&H R.R.	20
18889	Shell Talona, R 40, Finished oil, code 4028	8,16,16
18468	Shell T 2682, SAE 30	7
32467	Shell Talona, New Haven R.R. 0551 over 5000 mi, 9/15/52	1
18872	Shell Rotella, base oil	13
18888	" " finished oil	15,30
18487	" " C of U, Sample 1	very good
18488	" " " Sample 3	very good
18489	" " " Sample 5	very good
18379	Shell 3-1156, 1500 hrs. Eng. 4253	4
17204	Shell 3-1156, new oil	26
	Shell Rimula, 500 hrs. Eng. 10052	0

TABLE I (Cont.)

Lab. #	Oil	Days
17199	Shell Rimula, new oil	31
	Blend of 75% Shell Talona R40 & 25% Shell Rotella 50	19
M-1168	Monsanto	5
M-1169	"	4
M-1170	"	4
M-1171	"	9
M-1172	"	15
M-1173	"	11
M-1174	"	13
M-1175	"	14
M-1176	"	15
M-1177	"	15
M-1178	"	14
M-1179	"	13
18186	Sinclair Gascon, GLCC	4,10,7
27864	Sinclair GL-CC S.P.	1
17634	Sinclair Gascon, GL-CC	8
18808	Sinclair Gascon, GL-HR	4
18187	Sinclair Gascon GL-HD	5,5,6
18960	Reclaimed Sinclair Gascon GL-HD, rerefined oil	6
18601	R.P.M. Delo 6147-2	5
18486	R.P.M. Delo 6146-32	5
18926	Base Stock used in R.P.M. Delo R.R. oil SAE 40	10
18927	R.P.M. Delo R.R. Oil, SAE 40	9
19049	Used Oil 6148-3, 13020, #1	7
19048	Used oil 6148-2, 13019, #4	2

TABLE I (Cont.)

Lab. #	Oil	Days
18326	Sunvis 540 HD	10,7,5
18097	Erie R.R. (no additive)	4
18098	Erie R.R. (with additive)	5
18099	Erie R.R. (blended)	6
18873	Gulf Diesel Motive "B", Base oil	7
18884	Gulf Diesel Motive "B", finished oil	5,6
	Gulf (star) Dieselmotive "B", Diesel Enginer Lube oil, Pakistan Govt. Railways	7
12766	Atlantic 334, 1109 hrs., 10002	0
	Atlantic 334, 300 hrs. 9470	0
	Atlantic 537	12,13,18
18810	Great Northern R.R., Reclaimed oil	7
18898	British American Railway Diesel Crankcase oil	25,18
18106	L&H R.R. Unit 2, 71,098 mi	2
17346	Texas 2156, 500 hrs. Eng. 10052	3
18103	U.P.R.R., R.P.M. drainings, reclaimed by Talley Bros.	3
17135	Home H.D. oil, SAE 40	7
13207	Imperial Q x S-109C, 1554 hrs.	3
18134	Kellog Alcode "C"	19
51651	9521 Std. Cal., 1589 Hrs.	5
18729	Rereclaimed oil, Term. R.R. of St. Louis	6
11058	Union Cal. M-2461	26
18829	Reclaimed Oil, S.P. & S.R.R.	4
18807	Seaboard Air Line R.R., Reclaimed Lube Oil	6
18485	Sta-Vis XP-195	19
18882	Tycol Adeltran 40	12

TABLE I (Cont.)

Lab. #	Oil	Days
18914	WS 2461, base stock (NB-2203-10)	8
18915	Diol RD-76, Base stock (CK 1180)	6
	Dieseltex TL-2280	3,5
18056	Franklin Creek	16
18788	SAE #40 oil, ES solube HD	12
	Nareco Q 20-13	3
	SV 4 BM	8
	Sunvis 640	12
	Galeno QXS-109E	16
	The Texas Co., Urso X Supplement 1, SAE 40	11
	The Texas Co., TL-2280, Beacon, 3/23/53	4

SECTION II. CHROMATOGRAPHIC ANALYSIS OF LUBRICATING OILS

Chromatography or "chromatographic procedure" was first invented by Tswett, a botanist, in 1906. The chromatographic process consists of separating a mixture into its constituents by taking advantage of the selective adsorbing power of the adsorbent.

The standard procedure as given by McBain (8) is first to pack the column (9) with a suitable adsorbent (10) (11). Then pass the mixture into the top of the column and wash or elute with a suitable solvent (12). This will separate the mixture into bands of its constituents, and this separation is referred to as "developing the chromatogram" (13). When the chromatogram has been developed, further eluant or solvent may be run through, thus washing out the bands one by one. The adsorbent may also be extruded from the column and cut into sections separating the bands (14).

Colored materials are located on the column by their color. The colorless materials may be located by observation under ultraviolet light, by formation of colored derivatives before or after adsorption, by refractive index, and by other methods (15).

A diagrammatic representation of what happens when a chromatogram is developed is shown in Figure II - 1 taken from Strain (16).

The reason for starting work on the chromatographic separation of the lubricating oils was to be able to place them into groups or classes of similar composition. Subsequent application of physical constants and stability relations would

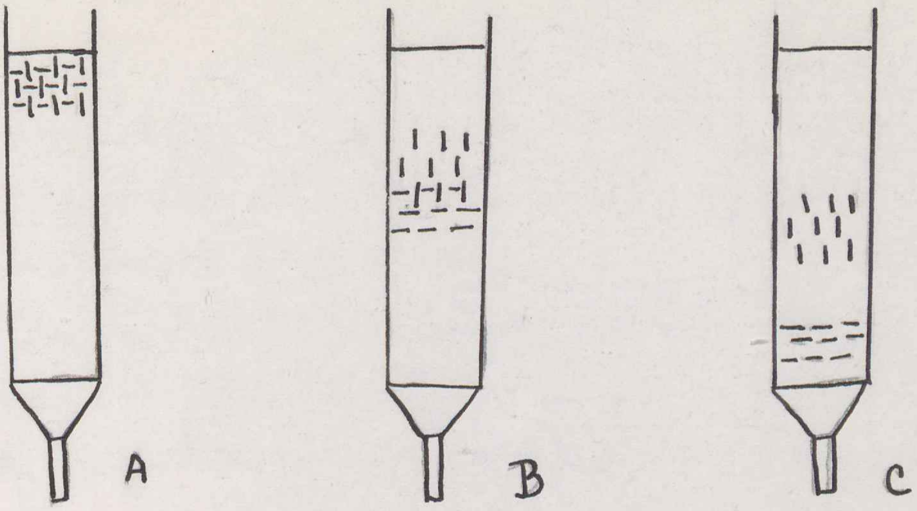


Figure II - 1
Development of the Chromatogram

A	Solution of two compounds (l) and (-) passed into upper portion of the column.
B	Column washed with fresh solvent that carries (l) and (-) along at different rates.
C	Complete separation of (l) and (-) with slight widening of bands.

then probably hold better. As the work turned out, the necessary procedure for the separation would take too much time to make it practicable for such a use. However the procedure does seem to show promise for a rather complete analysis of the oil, or even of crude petroleum fractions.

Various solvents were used for development of the chromatograms on an alumina column. First the non-polar solvents were tried, then some increasingly more polar ones were tried. Finally a gradation of various solvent mixtures was found to give the best separation. The bands of adsorbed material were eluted through the column and fractions were collected.

The procedure used was first to make a run of solvents only, taking the refractive index of the fraction collected. Then a run was made using the same succession of solvents, only with oil on the column and the index of refraction of the same fractions was taken again. The difference in the refractive index of the pure solvent and the solution of oil for each fraction was then plotted against the number of the fraction, which is proportional to the volume of eluant.

The assumption made in this procedure is that the refractive index of the oil and the solvent is additive. This probably is not strictly true, however, since the additivity of the refractive index will only affect the height of the maxima or minima, and we are only interested in the position of the bands, our results are not affected. If a quantitative analysis of the constituent was desired the low boiling solvent could be evaporated and the resultant higher boiling substance could be analyzed.

The refractive index of each fraction was taken at 25.0°C, the first column used was approximately 25 cm long by 2 cm in diameter. After making a run of solvents only, 3 ml of oil were added to the column and the same succession of solvents was then used to elute the oil, refractive indexes being taken for both runs.

Figure II - 2 shows a plot of the index of refraction of the solvent against the number of the 10 ml fraction. Here successive 10 ml fractions were taken. Figure II - 3 shows a plot of the difference in index of refraction of the pure advent fraction and the fraction containing dissolved oil. The oil used was Sunvis 540 HD*. The places where the curve has a negative value represent constituents of the oil which have an index of refraction less than that of the solvent.

In order to get better separation, a longer column was constructed and more oil was used. This column was 69 cm long and 2 cm in diameter. A solution of 10 ml of oil in 10 ml of petroleum ether was used to pass the oil into the top of the column. The succession of solvents is as follows. For the run of pure solvents, the 10 ml portion of oil was replaced by 10 ml of petroleum ether.

1. 10 ml oil plus 10 ml petroleum ether
2. 30 ml petroleum ether
3. 30 ml (2 ml benzene plus 28 ml petroleum ether)

---

* Ash, sulfated	1.10 - 1.45%	
pH	9	
Total base #	3.5	
V.I.	55-65 C	
Ref. Index	$n_D^{25.0^\circ C}$	= 1.4982
Density	$d^{25^\circ C}$	= 0.914

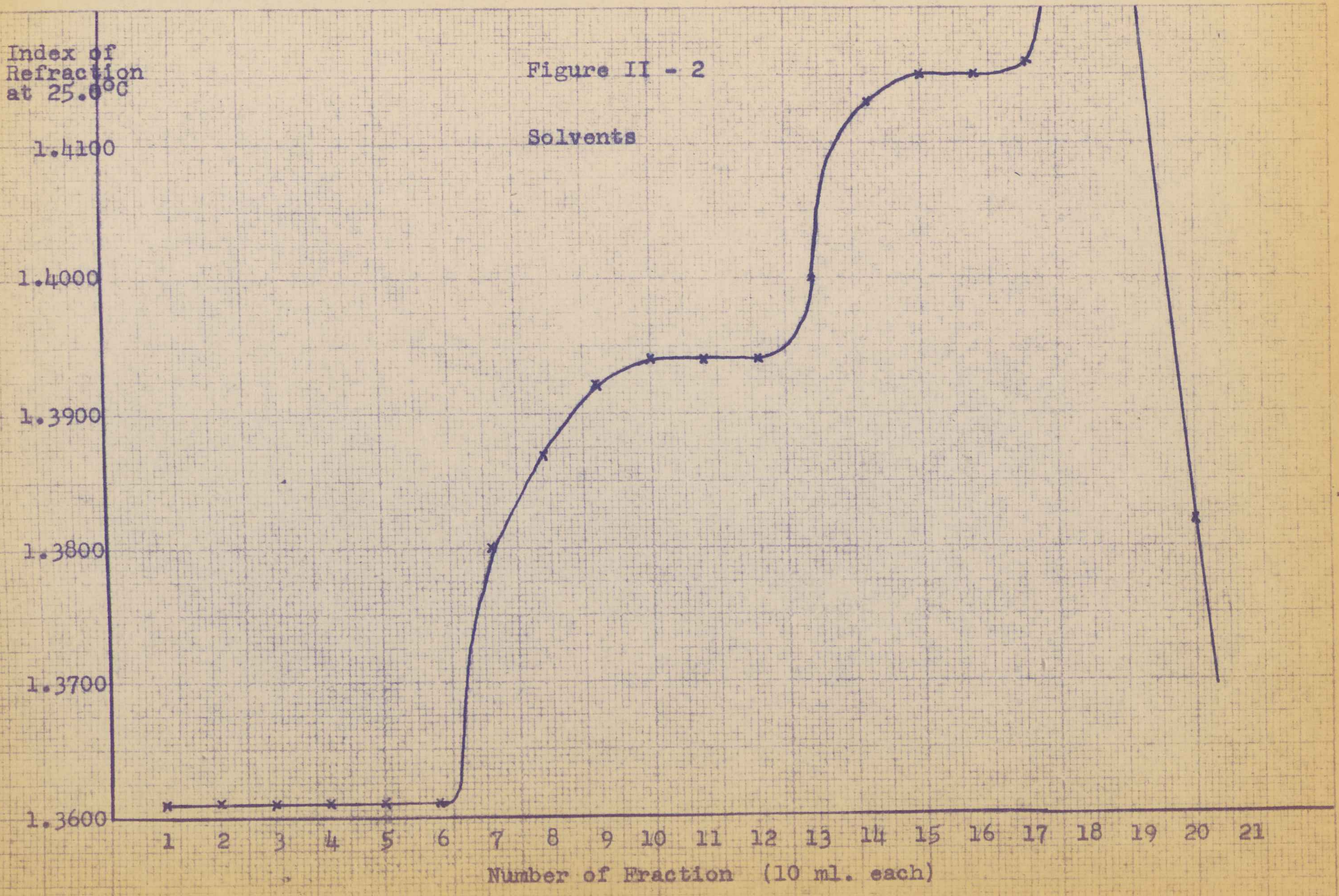


Figure II - 2

Solvents

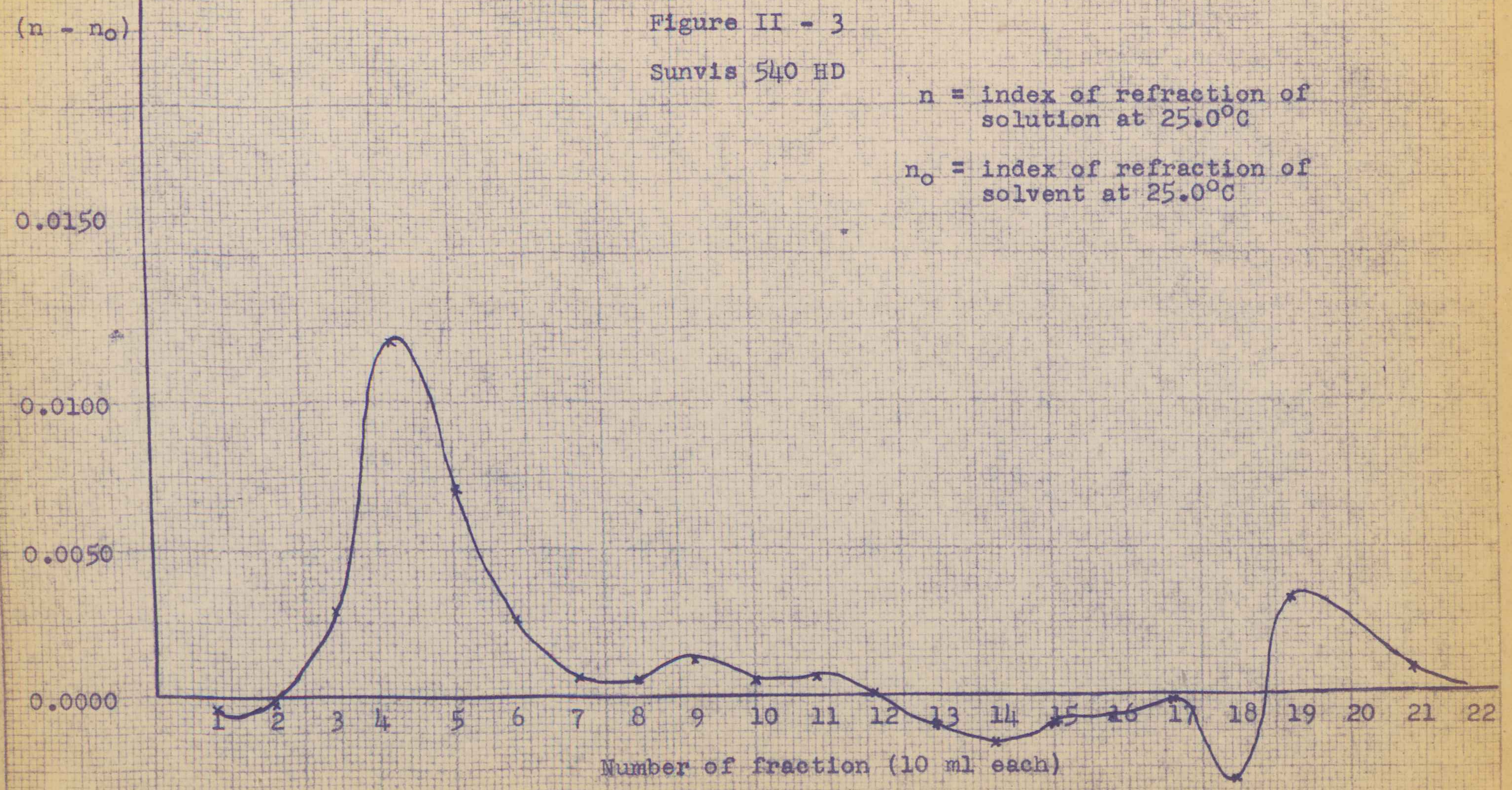


Figure II - 3

Sunvis 540 HD

4. 30 ml (4 ml benzene plus 26 ml petroleum ether)
5. 50 ml (10 ml " " 40 ml " ")
6. 100 ml (25 ml " " 75 ml " ")
7. 50 ml (14 ml " " 36 ml " ")
8. 50 ml (15.5 ml " " 34.5 ml " ")
9. 100 ml (40 ml " " 60 ml " ")
10. 50 ml benzene
11. 75 ml (25 ml acetone plus 50 ml petroleum ether)
12. 50 ml (33.4 ml " " 16.6 ml " ")
13. 75 ml acetone

Figure II - 4 shows a plot of index of refraction against number of the fraction for the succession of solvents alone. Alternate 10 ml portions of the eluant were taken as fractions. Figure II - 5 shows a plot of the difference in index of refraction of the pure solvent and the solution of oil for each fraction. The oil used here was also Sunvis 540 HD.

A comparison of Figure II - 3 and Figure II - 5 shows very clearly that they are the same oil. Also the separation obtained by the longer chromatographic column was much better. A small peak appeared in fraction #3 of Figure II - 5 which did not show up in Figure II - 3. Also the two minima between fractions 19 and 24 of Figure II - 5 showed up as one, rather flat minima in Figure II - 3. The minima at fraction 27 and the maxima at fraction 30 of Figure II - 5 were so steep that the scale had to be shortened in order to see their shape. In Figure II - 3 these did not show such steepness.

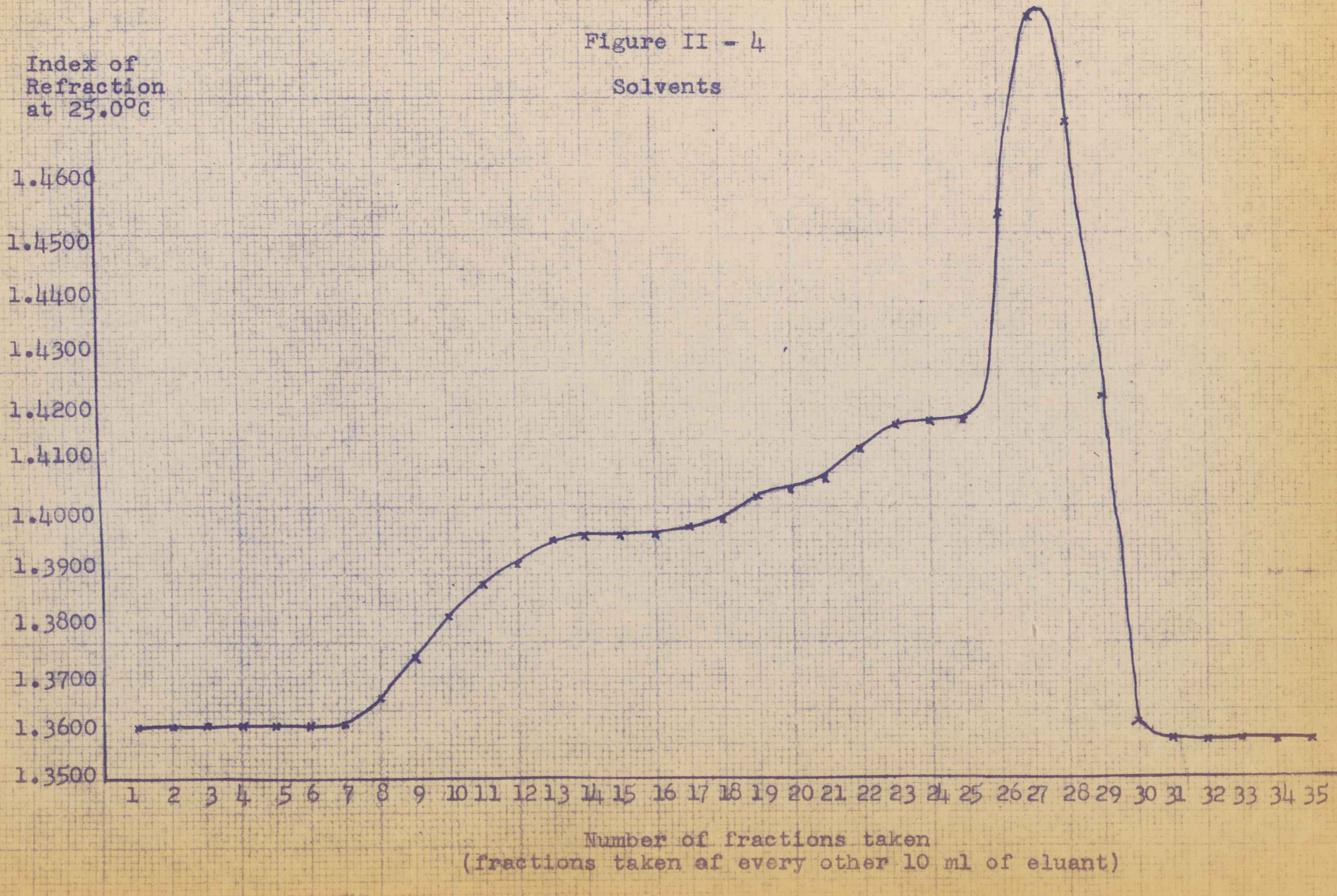
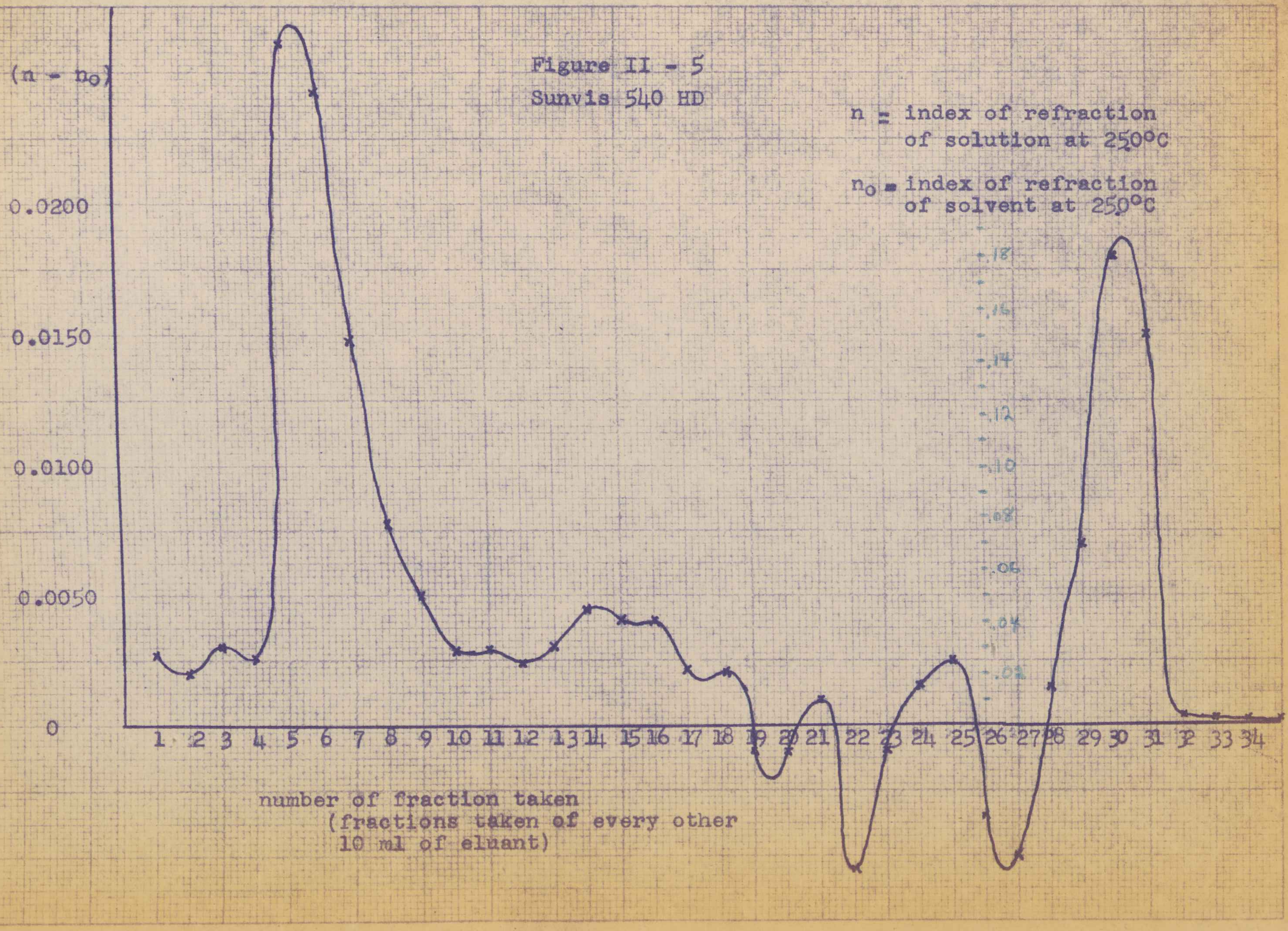


Figure II - 4

Solvents



We think a much better pciture of the bands of separation could be obtained if samples were taken of alternate five milliliter fractions of the eluant. We think some of the peaks in graph II - 5 would be split even further showing better separation. Some of the fractions could also be worked on separately by chromatographic separation until individual compounds could be isolated. This could be done for both used and unused oils and it may give more information about the chemical reactions of the oxidation and polymerization of the oils. The only way that this more extensive chromatographic separation could be carried out practically is by using an automatic sampling device such as that developed by L. A. Boggs, L. S. Cuendet, Michel Dubois and Fred Smith of the University of Minnesota (17).

A method for decreasing the time required for a chromatographic separation was tried. This consisted of allowing the eluant to pass between two aluminum electrodes imbedded at the bottom in the alumina column. These were then connected by means of a cable, to a dielectric constant meter model 3A and relative capacitance readings were takenaas the eluant came through the column. The object was then to plot capacitance against volume of eluant thus getting a plot of the bands on the chromatogram. The more polar solvent brought down the more polar constituents of the oil while the more non-polar solvents brought down the more non-polar constituents. The capacitance changed only when the polarity of the eluant changed. Therefore, the change in polarity of the oil constituents was masked by the almost equal change in polarity of the solvent. Consequently no bands showed up.

However, the dielectric constant has been used by Arnold (18) for:

1. The determination of moisture in coal, coke, oil, shale, and sand.

2. The determination of the effect of oxidation on lubricating oils (which is also the purpose of the research done this year).

3. Following the distillation of binary mixtures of liquids.

We tried to use dielectric constant to predict the oxidation stability of lubricating oils, but no correlation could be found.

SECTION III. CORRELATION OF INDEX OF REFRACTION AND DENSITY WITH STABILITY

In this phase of the work, a method was sought to determine the stability of lubricating oils by measurements of their physical constants. The two constants used were the index of refraction and the density. Various combination of these were plotted against the stability of the oil determined by the dipping light bulb test described in Section I.

An abbe refractometer containing amici prisms giving the index of refraction for the sodium D line was used for measurement of the index of refraction. The instrument that was available was not too accurate in the vicinity of an index of refraction of 1.5, therefore the readings taken in this vicinity should only be regarded as accurate to about three decimal places. All indexes of refraction were taken at 25.0°C. The densities were measured with a hydrometer. These were also taken at a temperature of about 25°C, although the temperature here could not be as accurately controlled. It has been shown that for a given structural type of hydrocarbon the index of refraction varies linearly with the density. From this, a useful quantity called the refractivity intercept has been defined. It is b in the following equation.

$$\text{refractive index} = 0.5 \text{ density} + b$$

$$b = (n - 0.5\ d)$$

In Table III - 1 the refractivity intercept is given for different types of structural hydrocarbons.

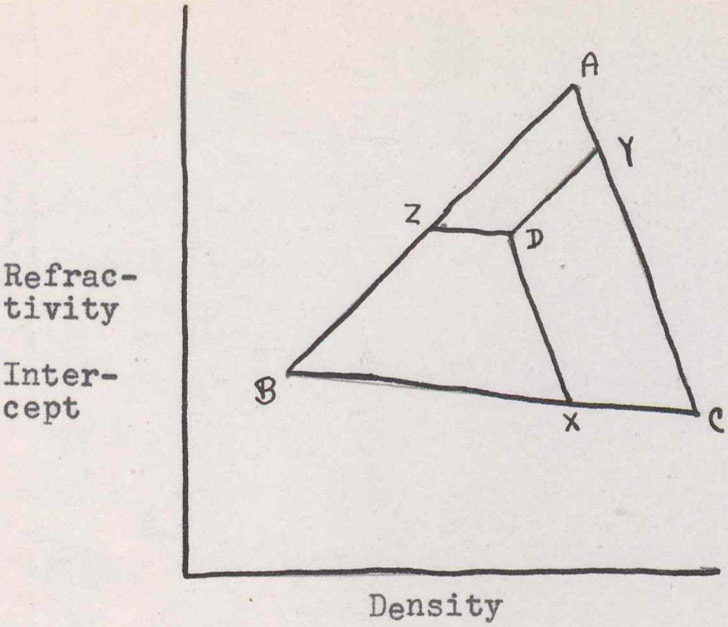
TABLE III - 1

Hydrocarbon Type	Refractivity Intercept
Paraffins	1.0461
Naphthenes	1.0400
Aromatics	1.0627
Cyclic monoolefins	1.0461
Non-cyclic monoolefins	1.0521
Cyclic conjugated diolefins	1.0643
Non-cyclic conjugated diolefins	1.0877
Cyclic non-conjugated diolefins	insufficient data
Non-cyclic non-conjugated diolefins	1.0592

By using refractivity intercept and density (20) a mixture of any three hydrocarbon types may be analyzed graphically as shown in Figure III - 1.

The line of reasoning taken in undertaking this phase of the research was that since these physical constants were indicative of the type of hydrocarbon present, and the stability is dependent on structure, an examination of these constants might give us a very general idea of stability of the oil. We realized that the oils were a mixture of many types of hydrocarbons and also the complications set in by additives, however we thought we might get at least an idea of a stability range.

In Table III - 2 are found all the physical constants measured for the oils, as well as some useful artificial quantities calculated from the measured constants.



$$\frac{DX}{AC} \cdot 100\% = \% \text{ Aromatics}$$

$$\frac{DY}{AB} \cdot 100\% = \% \text{ Paraffins}$$

$$\frac{DZ}{BC} \cdot 100\% = \% \text{ Naphthenes}$$

Figure III - 1

In the graph shown above:

A represents the density of a pure individual aromatic.

B represents the density of a pure individual paraffin.

C represents the density of a pure individual napthene.

TABLE III - 2

Oil #	Days	$n_D^{25.0^\circ C}$	$d^{25^\circ C}$	n/d	Refractivity intercept (at 25.0°C)	1/nd
Monsanto						
M-1168	5	1.5010	0.910	1.650	1.0460	01731
M-1169	4	1.5010	0.910	1.650	1.0460	0.731
M-1170	4	1.5010	0.915	1.640	1.0435	0.727
M-1171	9	1.5010	0.923	1.628	1.0395	0.721
M-1172	15	1.4959	0.906	1.650	1.0429	0.737
M-1173	11	1.4958	0.905	1.652	1.0433	0.739
M-1174	13	1.4960	0.910	1.643	1.0410	0.734
M-1175	14	1.4973	0.918	1.630	1.0383	0.727
M-1176	15	1.4849	0.886	1.678	1.0419	0.759
M-1177	15	1.4850	0.886	1.678	1.0420	0.759
M-1178	14	1.4855	0.891	1.669	1.0400	0.755
M-1179	13	1.4870	0.900	1.651	1.0370	0,748
Standard of Indiana						
LF0431	7	1.5055	0.916	1.642	1.0475	0.724
LF0432	5	1.5055	0.917	1.641	1.0470	0.724
LF0433	5	1.5060	0.917	1.641	1.0475	0.724
LF0434	15	1.5052	0.916	1.643	1.0472	0.724
LF0435	5	1.5060	0.916	1.639	1.0465	0.722
LF0436	14	1.5055	0.919	1.639	1.0460	0.722
LF0466	10,7	1.5018	0.914	1.645	1.0448	0.720
Base Oils						
18870	9	1.4960	0.900	1.661	1.0460	0.742
18881	10,15	1.4907	0.889	1.679	1.0462	0.754
18914	8	1.4940	0.902	1.658	1.0430	0.741
18915	6	1.5000	0.908	1.650	1.0460	0.734
18926	10	1.4980	0.907	1.650	1.0445	0.736
18871	3,4	1.4920	0.900	1.659	1.0420	0.744
18880	7	1.5013	0.912	1.648	1.0453	0.730
18873	7	1.4940	0.904	1.653	1.0420	0.720
18872	13	1.4911	--	--	--	--
18874	3	1.5005	0.912	1.647	1.0445	0.730
Texas Dieseltex 1675						
31721	1	1.4990	0.910	1.647	1.0440	0.732
31726	4	1.5000	0.912	1.645	1.0440	0.730
31727	5	1.5000	0.912	1.645	1.0440	0.730
McColl-Frontenac						
18894	5	1.5001	0.906	1.658	1.0471	0.735
18895	2	1.5180	0.940	1.615	1.0480	0.700
18896	28	1.4880	0.887	1.679	1.0445	0.757
18897	9	1.5011	0.912	1.648	1.0451	0.730

TABLE III - 2 (Cont.)

Oil #	Days	$n_D^{25.0°C}$	$d^{25°C}$	n/d	Refractivity intercept (at 25.0°C)	1/nd
18902	3	1.4908	0.888	1.680	1.0468	0.755
18899	11	1.4950	0.902	1.659	1.0440	0.741
18900	3	1.4945	0.900	1.660	1.0445	0.743
18887	8	1.4965	0.904	1.655	1.0445	0.740
18669	7	1.4970	0.904	1.655	1.0450	0.740
18889	16	1.4940	0.905	1.651	1.0415	0.739
18831	20	1.4935	0.906	1.650	1.0405	0.738
18326	10,7,5	1.4982	0.914	1.640	1.0412	0.730
18186	4,10,7	1.5049	0.923	1.631	1.0434	0.720
18187	5,5,6	1.5040	0.922	1.631	1.0430	0.720
18134	19	1.4870	0.891	1.669	1.0415	0.755
18885	14,8	1.5000	0.912	1.644	1.0440	0.731
18891	8,15	1.5000	0.912	1.644	1.0440	0.731
18890	14,15	1.4999	0.912	1.644	1.0439	0.731
White paraffin oil	38	1.4810	0.885	1.675	1.0385	0.762
Shell Pure oils						
Talpa 30	--	1.4892	0.896	1.660	1.0412	0.750
WTE 250 neutral	--	1.4852	0.877	1.692	1.0467	0.767
Ondina 133	--	1.4769	0.873	1.691	1.0404	0.775

Oil #	Days	$n_D^{25.0°C}$	Oil #	Days	$n_D^{25.0°C}$
18106	2	1.5045	34468	4	1.5042
17135	7	1.4869	34469	11	1.5040
18134	19	1.4870	34470	9	1.5040
18098	5	1.4993	34471	10	1.5040
18103	3	1.5023	34474	7	1.5030
18099	6	1.5020	34484	4	1.5031
27864	1	1.5058	18104	5	1.4960
18097	4	1.5004	18133	17	1.4948
18056	16	1.4851	18927	9	1.4980
18058	11	1.4940	Nareco Q20-13	3	1.5032
18101	15	1.4942	SV 4BM	8	1.5070
17634	8	1.5050	Sunvis 640	12	1.4850
18326	10,7,5	1.4982	Galeno QXS-109E	16	1.5000
18186	4,10,7	1.5049	Atlantic 537	12,13,18	1.4911
18187	5,5,6	1.5040	B&MRR Socony		
18468	7	1.4892	SV 4BM	6	1.5071
18379	4	1.4940	Blend 75% Shell		
17204	26	1.4930	Talona R40		
17199	31	1.4932	& 25% Shell		
17300	18	1.4982	Rotella 50	19	1.4913
17301	6	1.5009	Rock Island		
17346	3	1.5042	Reclaimed	5	1.5000

As a start in the correlation of physical constants and stability, a plot of index of refraction against stability was attempted for all the oils regardless of base stock or additive. The results are shown in Figure III - 2. Although the agreement is not very good, a general trend of decreasing stability for increasing index of refraction, is noticeable. The agreement might have been closer if the errors in the index of refraction and the stability test had been smaller. For oils of the same stock the index of refraction was approximately constant.

A plot was also made of 1/nd against density for all the oils regardless of base stock. This is shown in Figure III - 3.

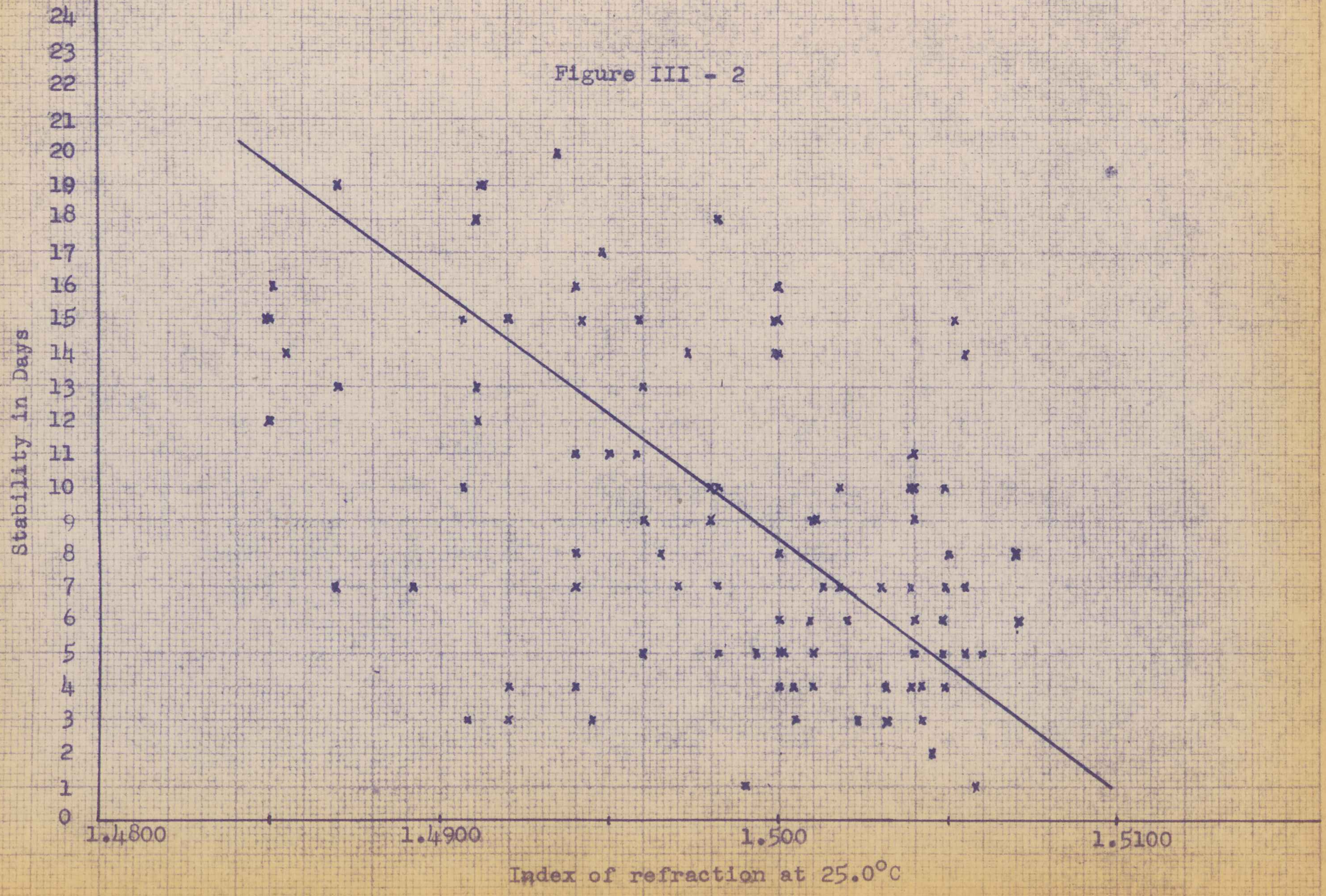
Here the oils may be separated intotthree classes: the "more stable", the "medium", and the "less stable". The dotted line (a) separates the "medium" and the "less stable" classes and the dotted line (b) separates the "medium" and the "more stable" classes. Out of 22 values obtained for the "less stable" oils, only 4 are above 10 days. Out of 8 values obtained for the "more stable" oils only one is below 10 days. In the "medium" class there are 8 values below 10 days and 5 values above ten days. Therefore the "medium" class represents an overlapping of the "more stable" and the "less stable" classes. The trend seems to be an increase in stability with an increase in 1/nd. We think that a closer examination of this relation may prove worthwhile. The roughness of our measurements of stability and the inaccuracy of the readings of the index of refraction around 1.5 may be the cause of the failures in the relationship, that is the 4 values above 10 days in the "less stable" class and the one value below 10 days in the "more stable" class.

A plot of the same quantities for oils of the same base stocks gives a very straight line for each base stock. This is shown in Figure III - 4.

We now will concentrate our efforts in finding stability relations, using only oils of the same base stocks. Various other artificial quantities were used besides 1/nd. Of these, n/d and refractivity intercept were the only ones that showed any promise.

In Figure III - 5, a plot was made of refractivity intercept and 1/nd. The oils of the same base stock fell along very straight lines. The stability seemed to increase in going from line D to line A or with increase in 1/nd as in graph III - 3. The series og four oils represented by line E and cutting across lines A, B, C, and D are McColl-Frontenac oils varying from a low viscosity to a high viscosity. Here the increase in stability with increase in 1/nd is very evident. Figures III - 6 and III - 7 show again, as in many of the other plots, the oils of the same base stock falling on a very straight line. These straight lines then being arranged from the poorest oils, line D, to the most stable oils, line A.

Figure III - 2


Stability in Days
24
23
22
21
20
19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
1.4800
1.4900
1.500
1.5100
Index of refraction at 25.0°C

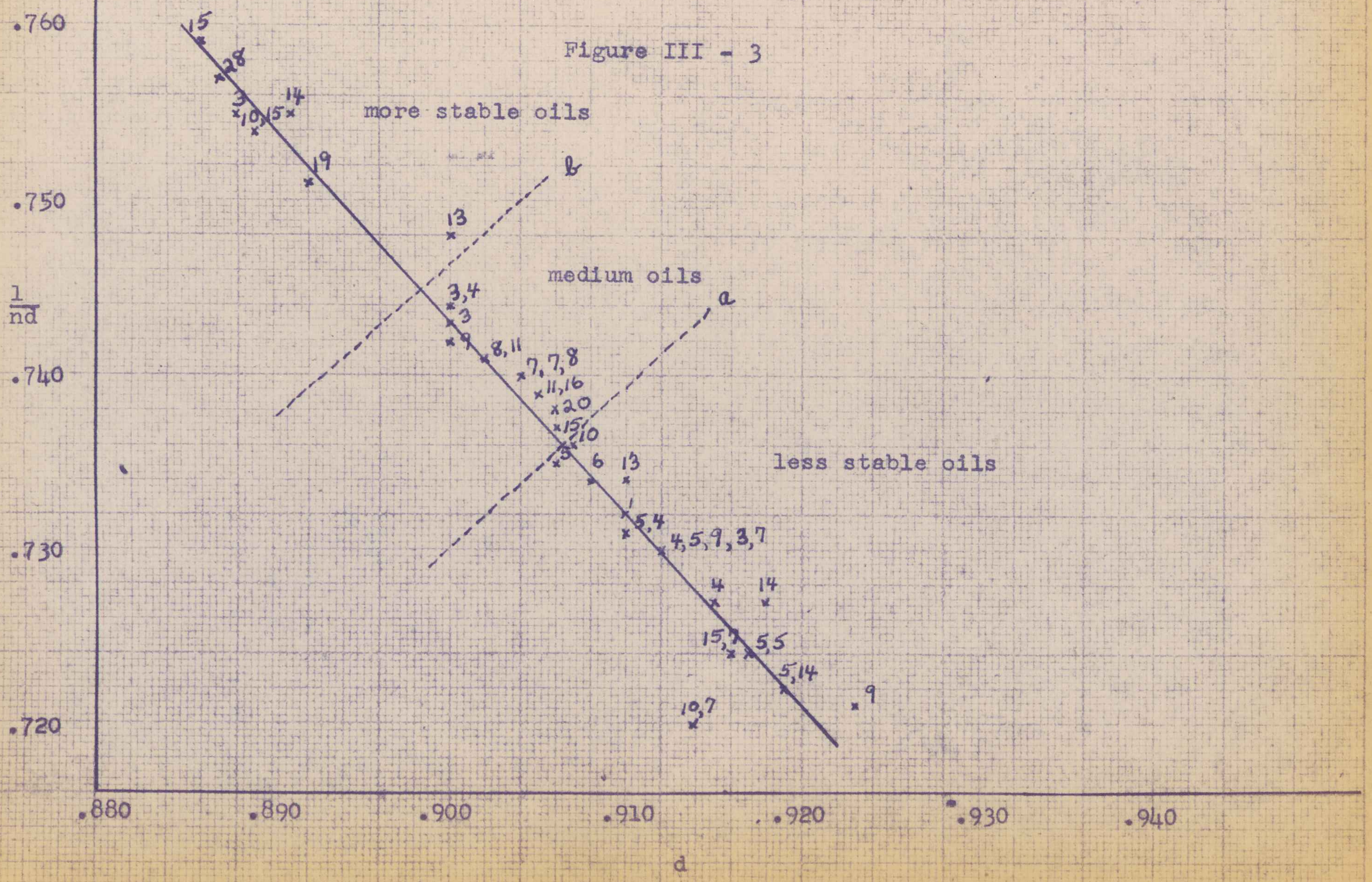


Figure III - 3

more stable oils
medium oils
less stable oils
b
a
1/nd
d
.760
.750
.740
.730
.720
.880
.890
.900
.910
.920
.930
.940
15
28
3
10
15
14
19
13
3,4
3
9
8,11
7,7,8
11,16
20
15
10
5
6
13
1
5,4
4,5,9,3,7
4
14
15,7
5,5
5,14
9
10,7

Figure III - 4

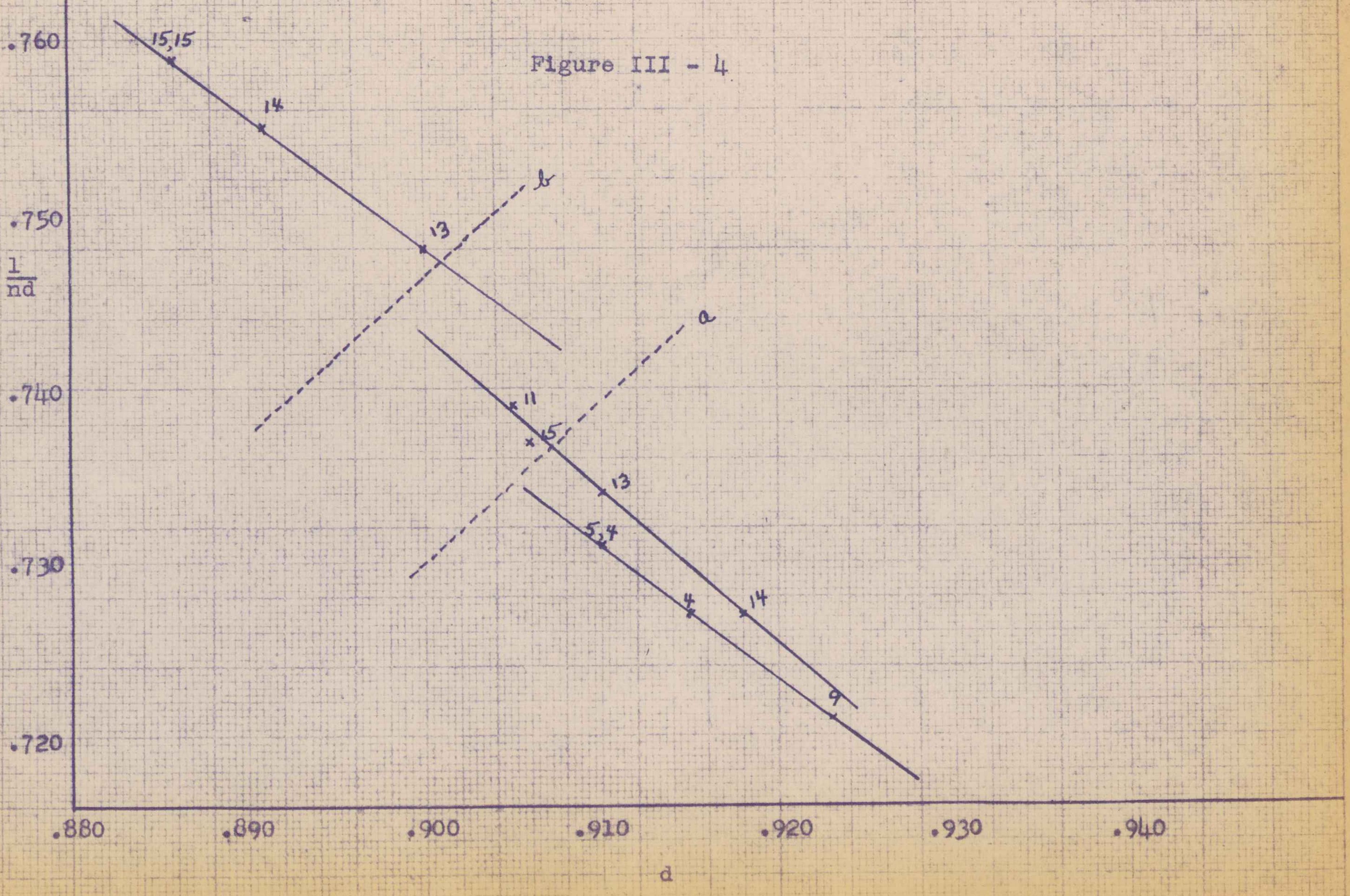

.760
.750
.740
.730
.720
$\frac{1}{nd}$
.880
.890
.900
.910
.920
.930
.940
d
15,15
14
13
b
a
11
15
13
5,4
4
14
9

Figure III - 5

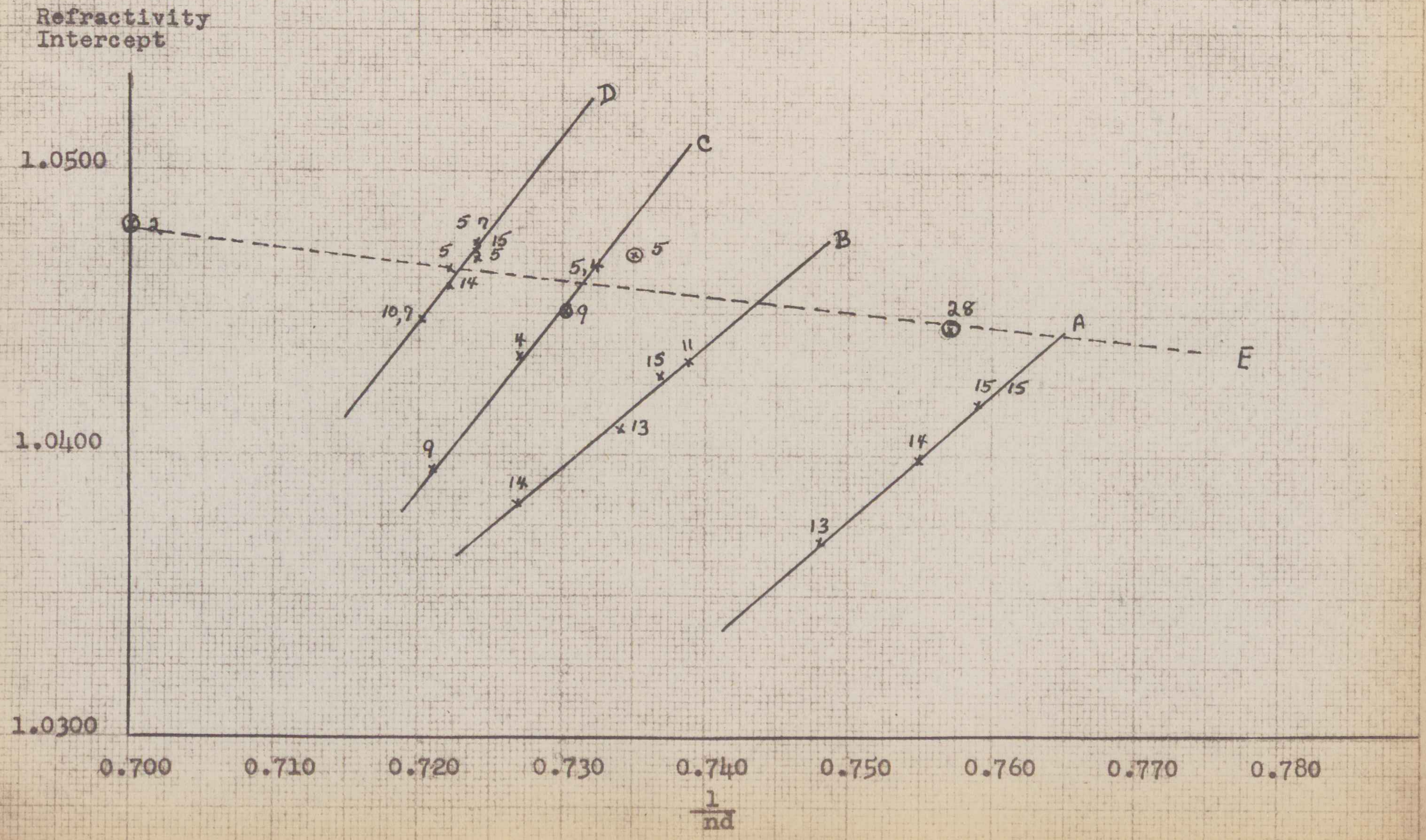

Refractivity Intercept
1.0500
1.0400
1.0300
0.700
0.710
0.720
0.730
0.740
0.750
0.760
0.770
0.780
$\frac{1}{nd}$
A
B
C
D
E
2
5
7
15
5
5
14
10,7
5,
5
9
4
9
15
11
13
14
28
15
15
14
13

Figure III - 6

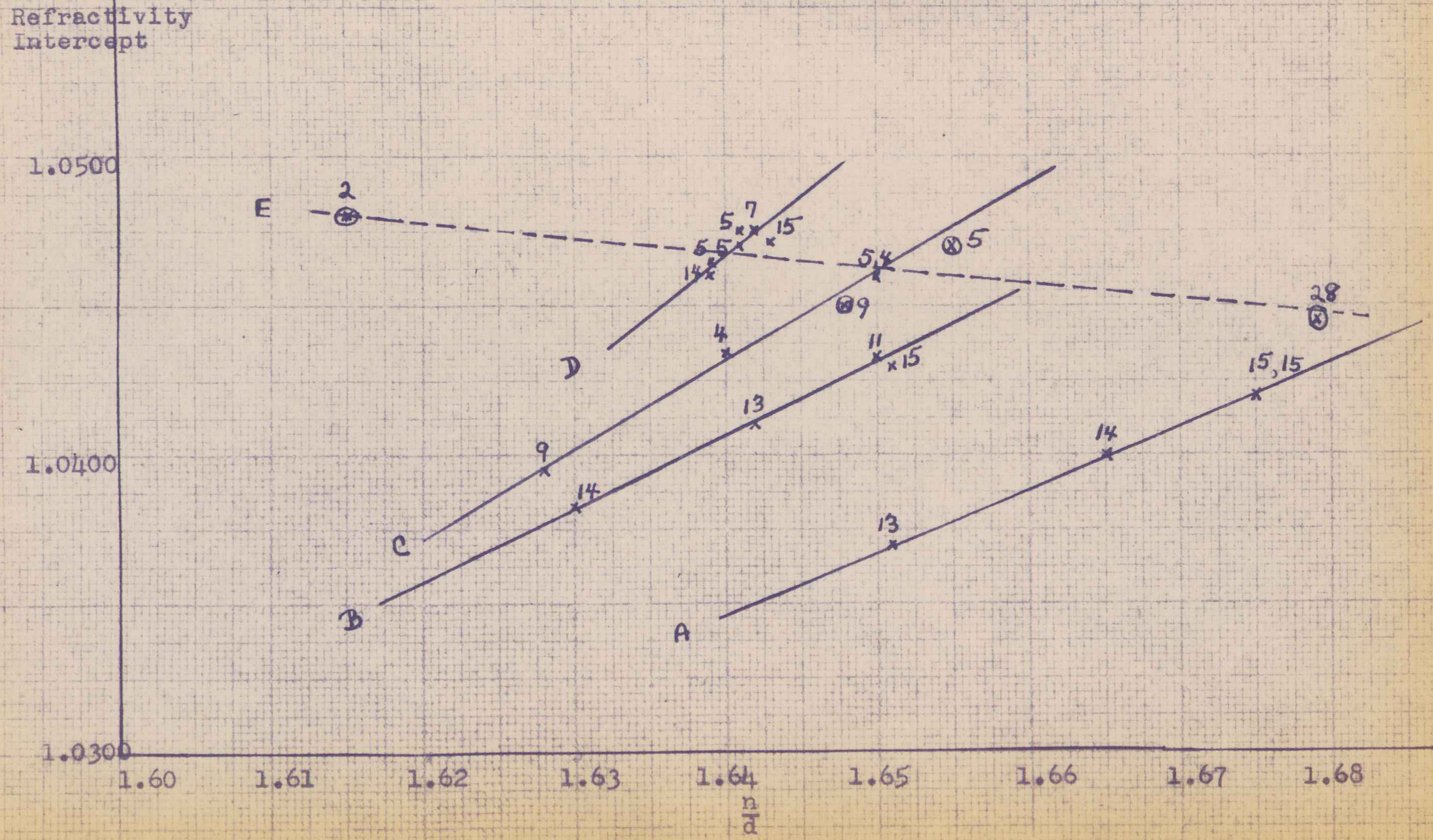
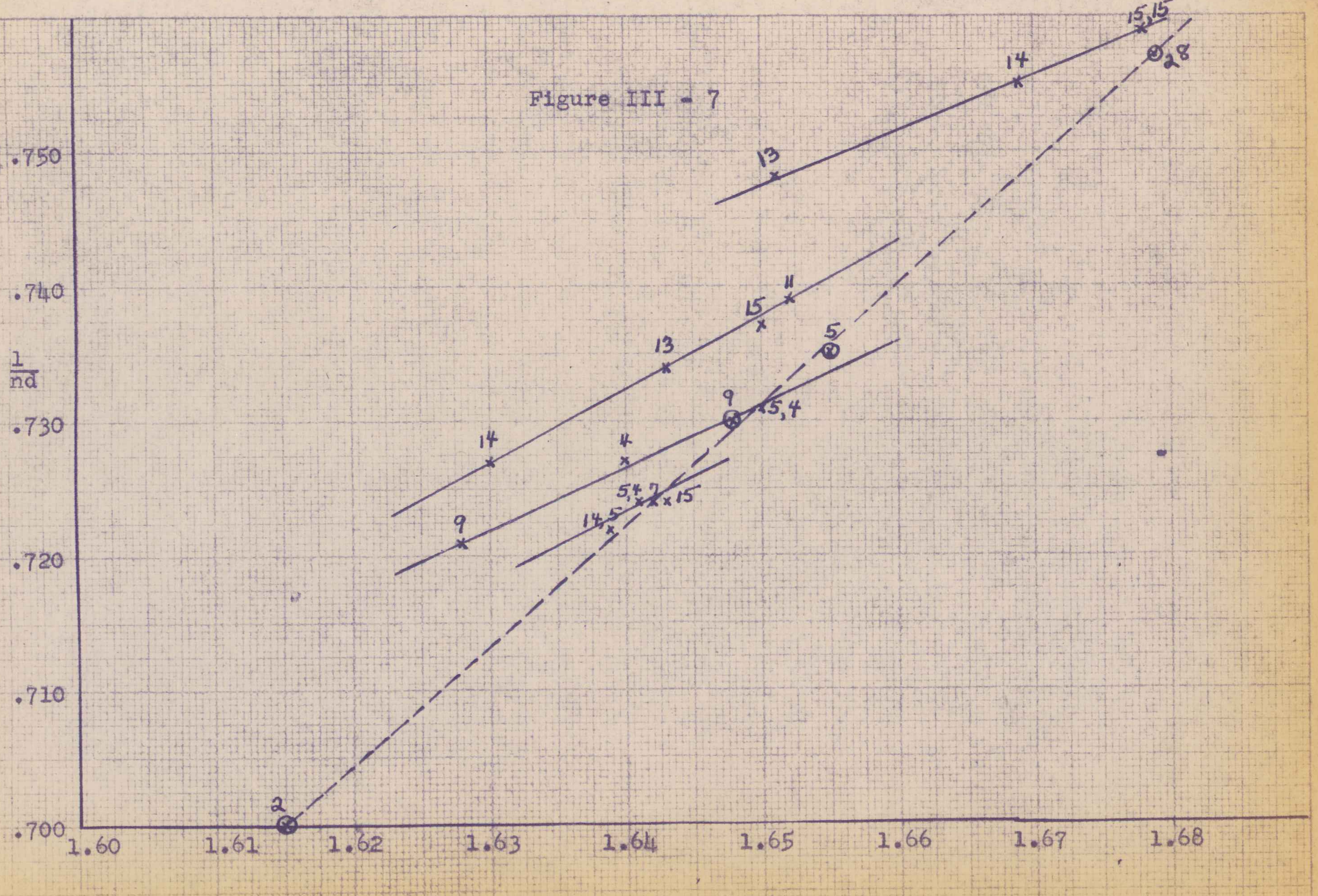

Refractivity Intercept
1.0500
1.0400
1.0300
1.60
1.61
1.62
1.63
1.64
1.65
1.66
1.67
1.68
$\frac{n}{d}$
A
B
C
D
E
2
5
7
15
5.5
14
5.4
5
9
28
4
11
15
13
15,15
14
9
14
13

Figure III - 7


.750
.740
$\frac{1}{nd}$
.730
.720
.710
.700
1.60
1.61
1.62
1.63
1.64
1.65
1.66
1.67
1.68
$\frac{n}{d}$
15,15
14
2,8
13
11
15
5
13
9
5,4
14
4
9
5,4,7
15
14,5
2

SECTION IV

A. There is very little reference in the literature to any work done with the ultraviolet absorption spectra of oils. E. Vellinger and H. Klinkenberg (21) have reported, however, that transformer oils of various origins show similar ultraviolet absorption curves and that aging of the oils only decreases the sharpness of the bands. We found this also to be true for lubricating oils. Figure IV - 1 shows the effect of aging of the oils on the ultraviolet absorption spectra and Figures IV - 2, IV - 3, and IV - 4 illustrate the similarity of the absorption spectra for all of the oils tried. In Figure IV - 1 a difference can also be seen between aging in an engine and aging in the light bulb test. The solutions on which these spectra were obtained were prepared by diluting 1 ml of the oil to 100 ml using petroleum ether, then taking 1 ml of this solution and diluting it to 100 ml. This final solution was then used.

Other than for a verification of Vellinger and Klinkenberg's work, the investigation of the ultraviolet absorption spectra of the lubricating oils did not prove useful.

These absorption spectras were taken with a model DU Beckman Spectrophotometer.

B. Other Investigations on Oils

In searching for ways of studying the oxidation stability of lubricating oils werhave discovered some rather interesting phenomenon or relations which although, at present do not seem to have any particular significance, may be worthy of further study.

As some of the oils were being tested for stability by the dipping light bulb test, samples were taken every day and the index of refraction was measured. Figure IV - 5 shows a plot of index of refraction and the number of days. It can be seen that for most of the oils the index of refraction increases as the oxidation proceeds. This is probably due to the volatization of the lower boiling constituents and products of oxidation, and also to the polymerization occurring, leaving a residue of increasing molecular weight and therefore of increasing index of refraction.

Figure IV - 6 shows a plot of relative capacitance of the oil read by a dielectric constant meter Model 3A and percent sulfated ash. Something critical seems to be happening at a value of approximately 0.065 for the sulfated ash in all three cases, but we are unable to explain that. The oils are all Monsanto oils containing varying amounts of the same additive and the ones joined by lines are of the same base stock.

Figure IV - 7 shows how surface tension varies with temperature for the lubricating oils. The variation is linear up to a point, when the surface tension drops sharply with increase in temperature. This sudden drop seems to come at a lower temperature for the least stable of the three oils tried and at increasing temperature for increasing stability of the other two oils. This phenomenon may also be worthy of further investigation.

In Figure IV - 8 we have the change in index of refraction with temperature for various lubricating oils. They all show very similar curves.

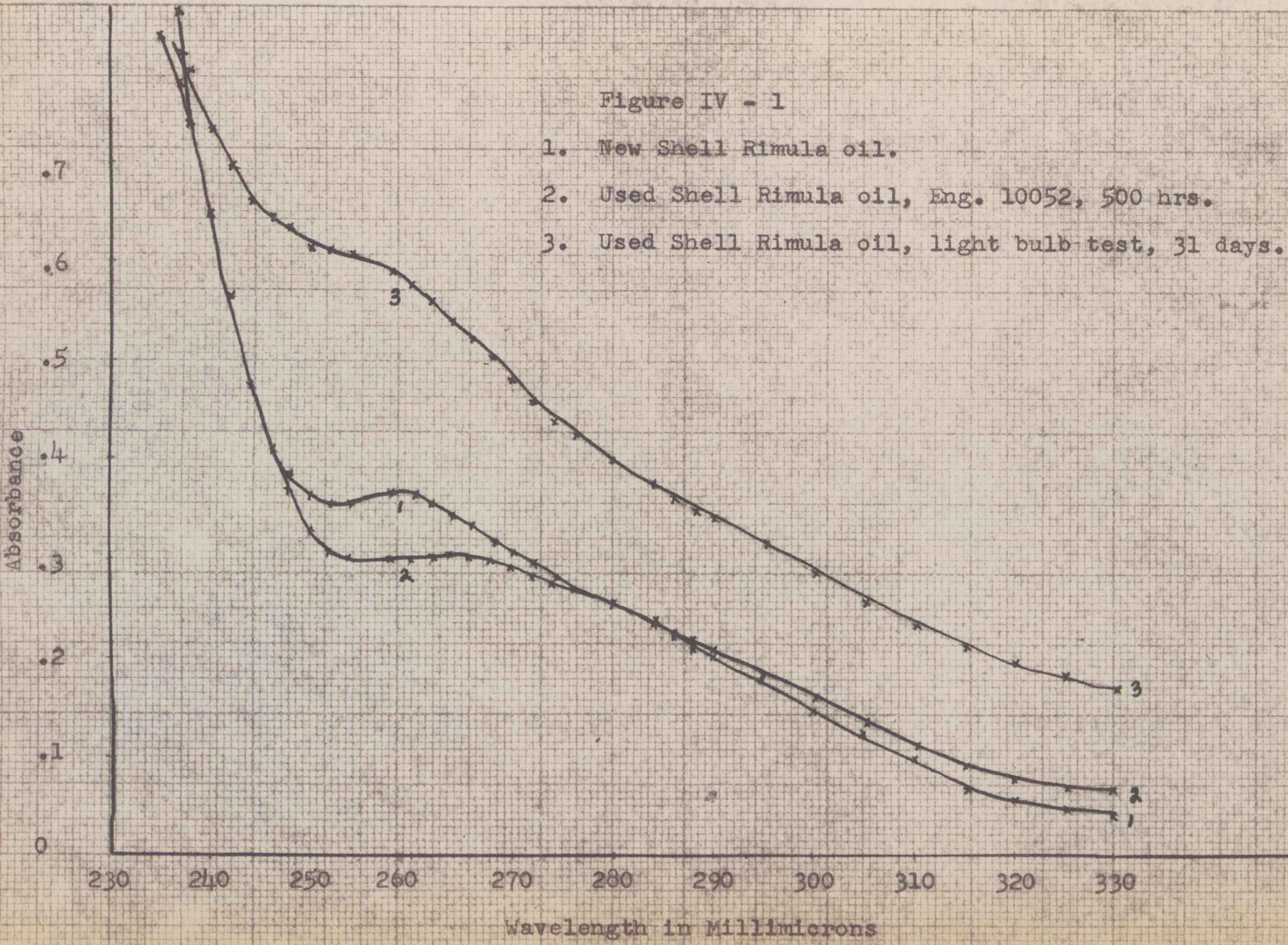
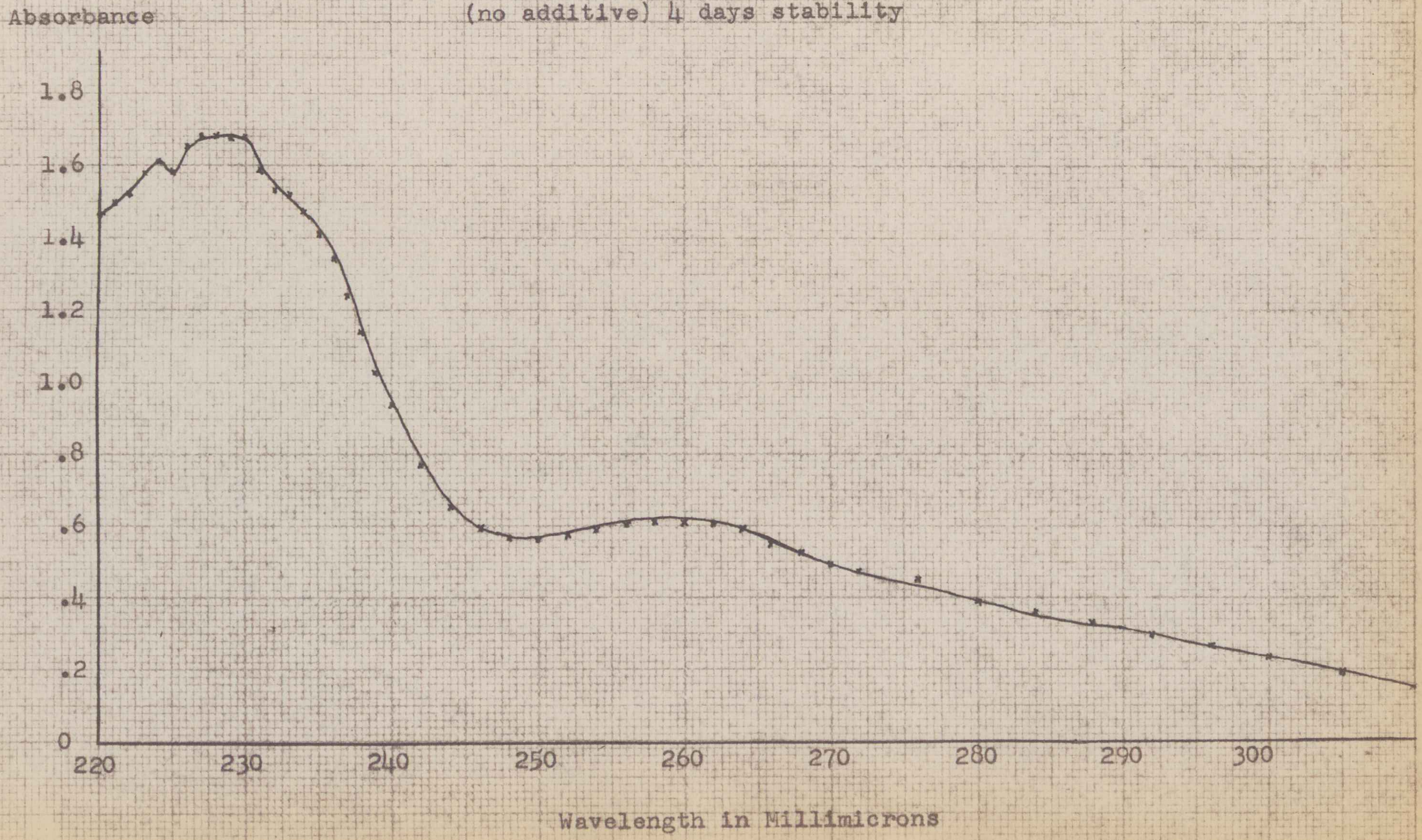


Figure IV - 1

1. New Shell Rimula oil.
2. Used Shell Rimula oil, Eng. 10052, 500 hrs.
3. Used Shell Rimula oil, light bulb test, 31 days.

Figure IV - 2
Erie R.R. Reclaimed Oil
(no additive) 4 days stability



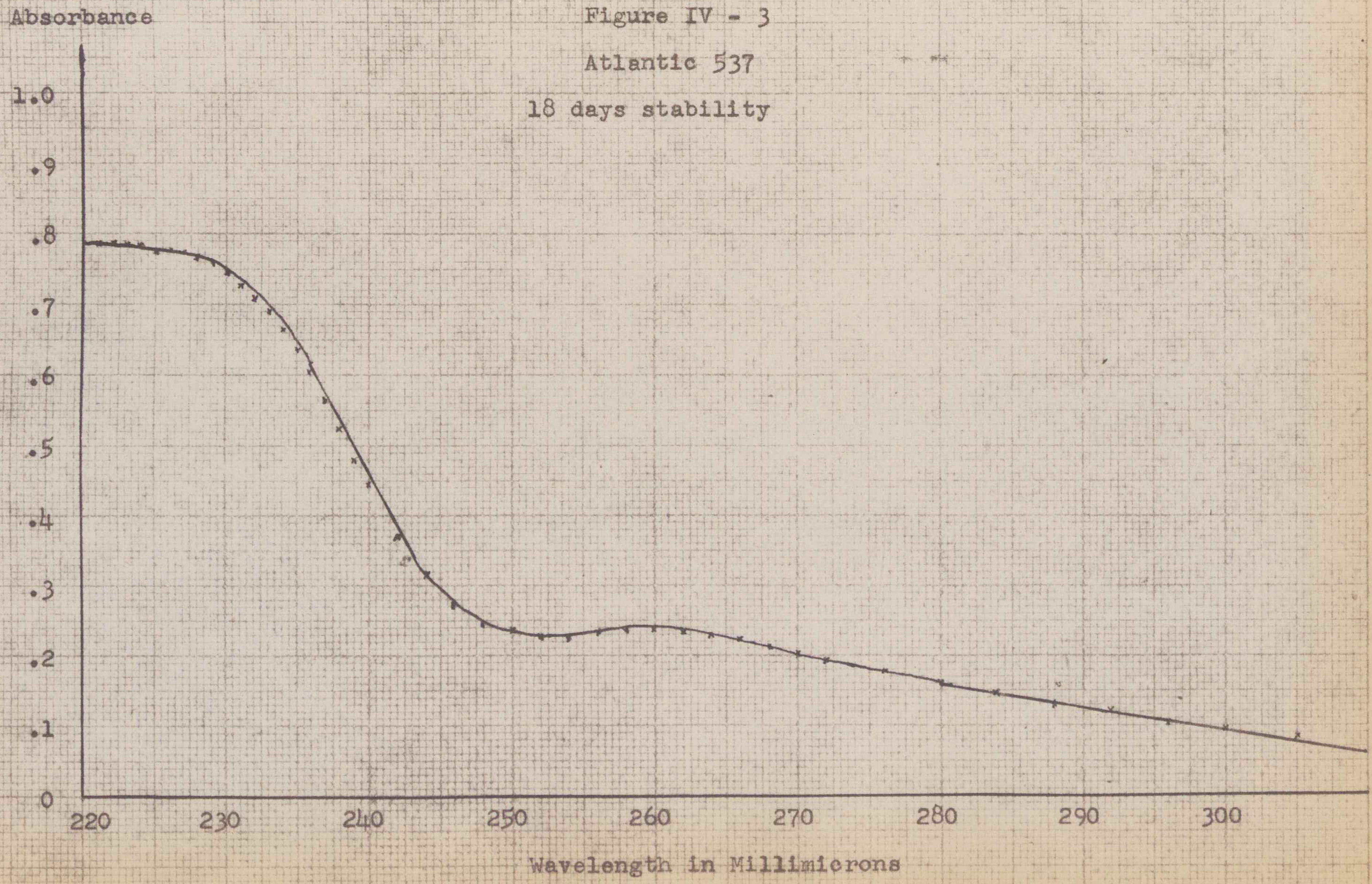


Figure IV - 3

Atlantic 537

18 days stability

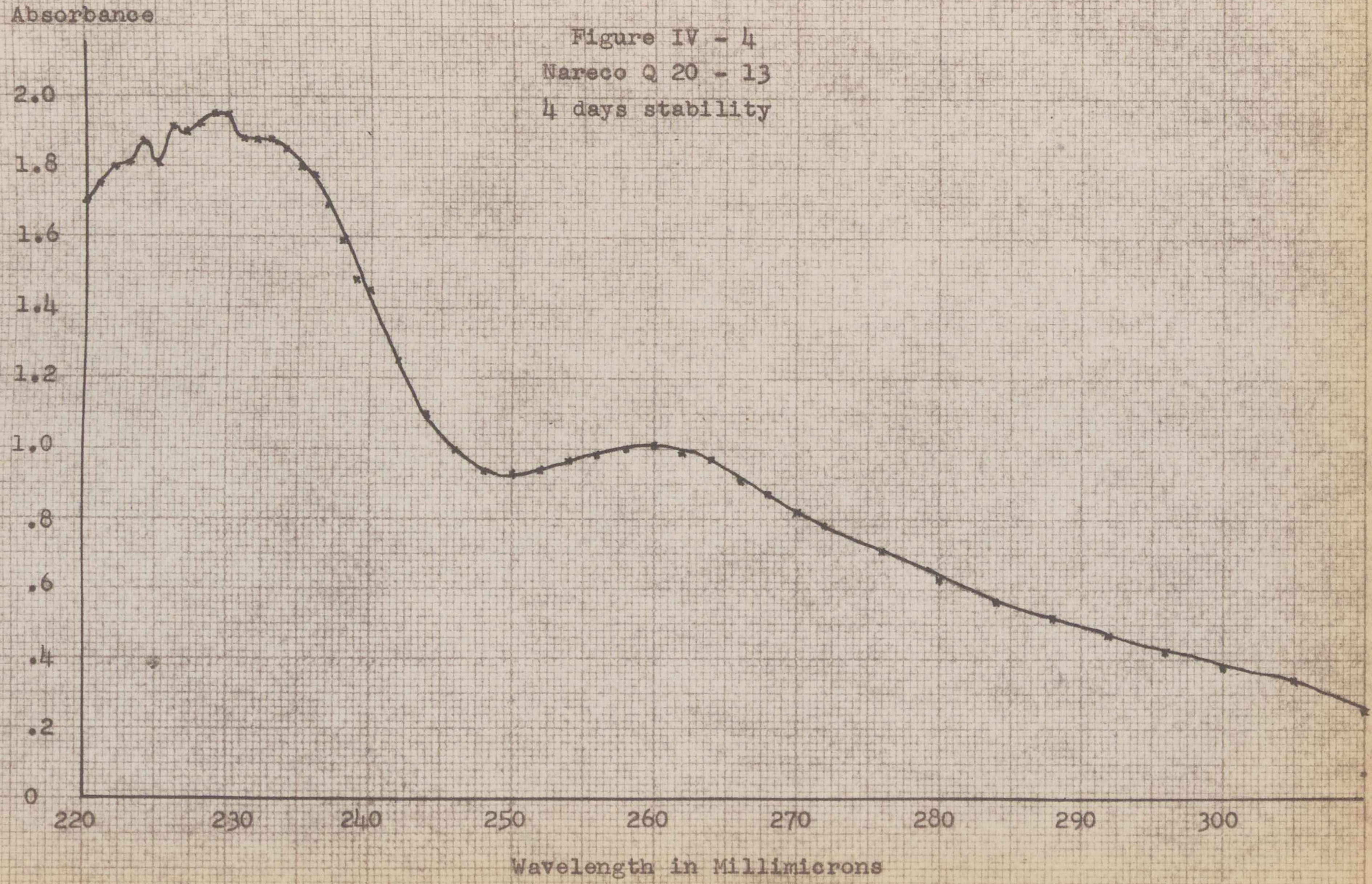


Figure IV - 4
Nareco Q 20 - 13
4 days stability

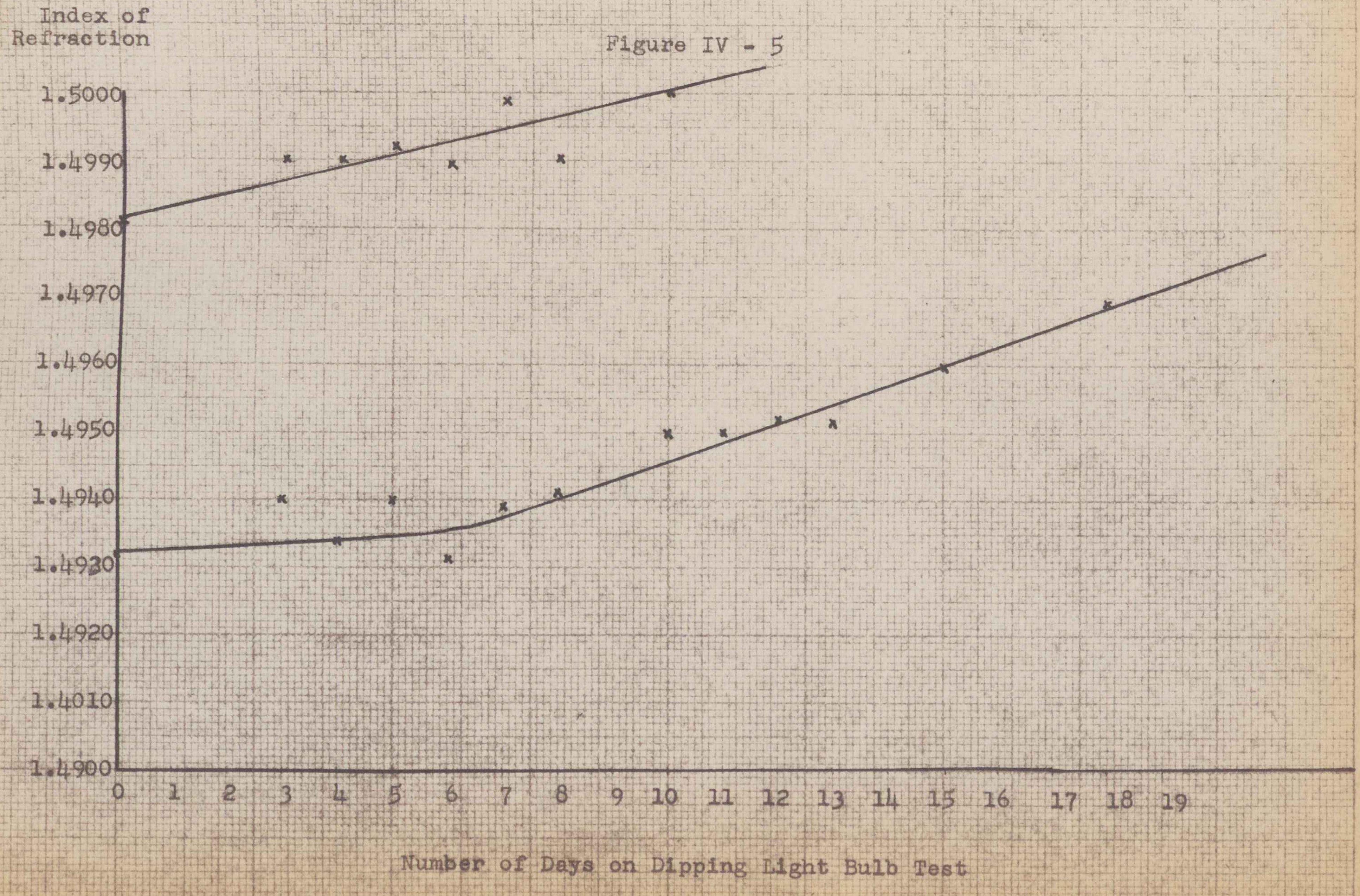


Figure IV - 5

Index of Refraction
1.5000
1.4990
1.4980
1.4970
1.4960
1.4950
1.4940
1.4930
1.4920
1.4010
1.4900
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
Number of Days on Dipping Light Bulb Test

Figure IV - 6

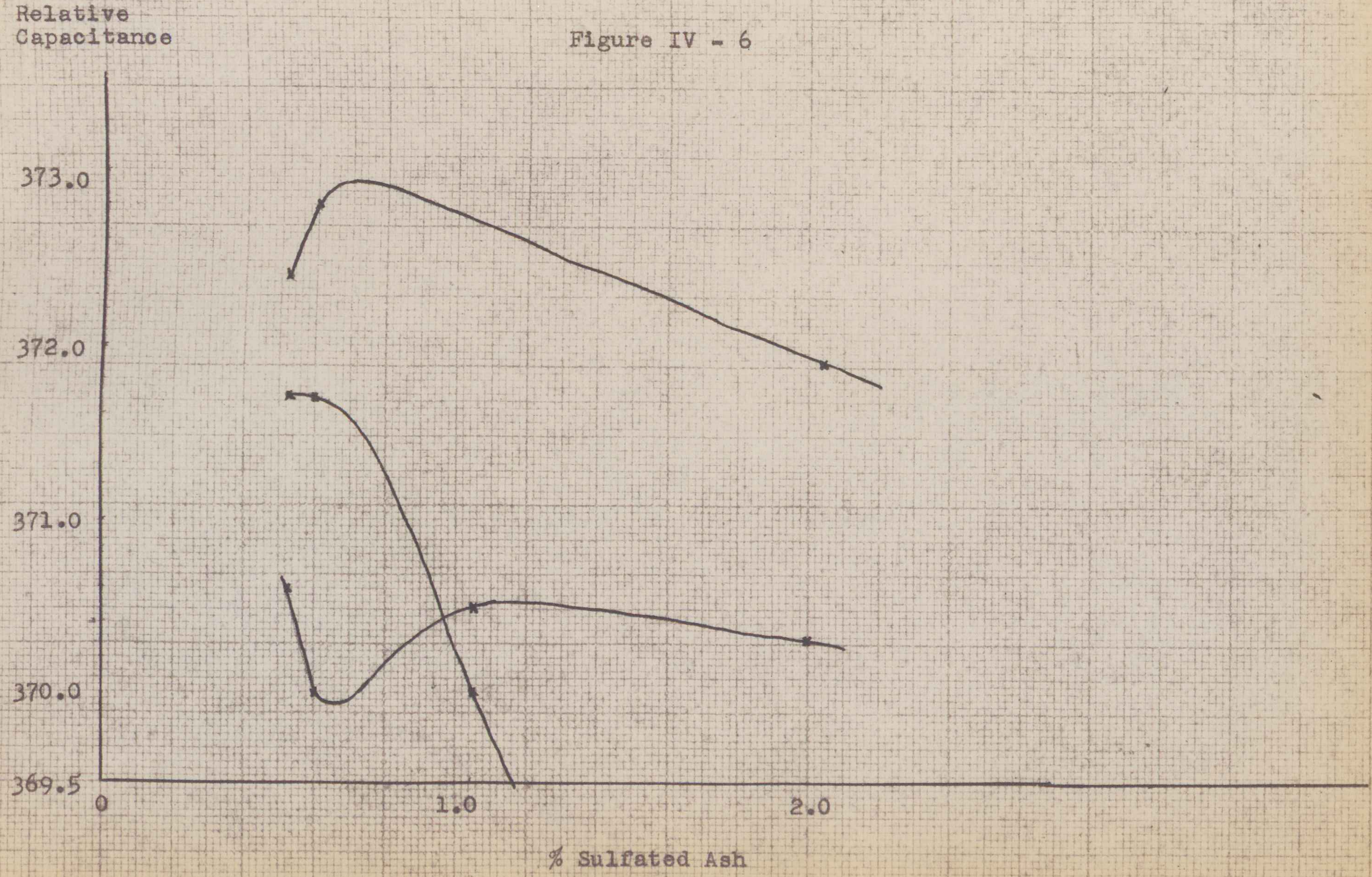
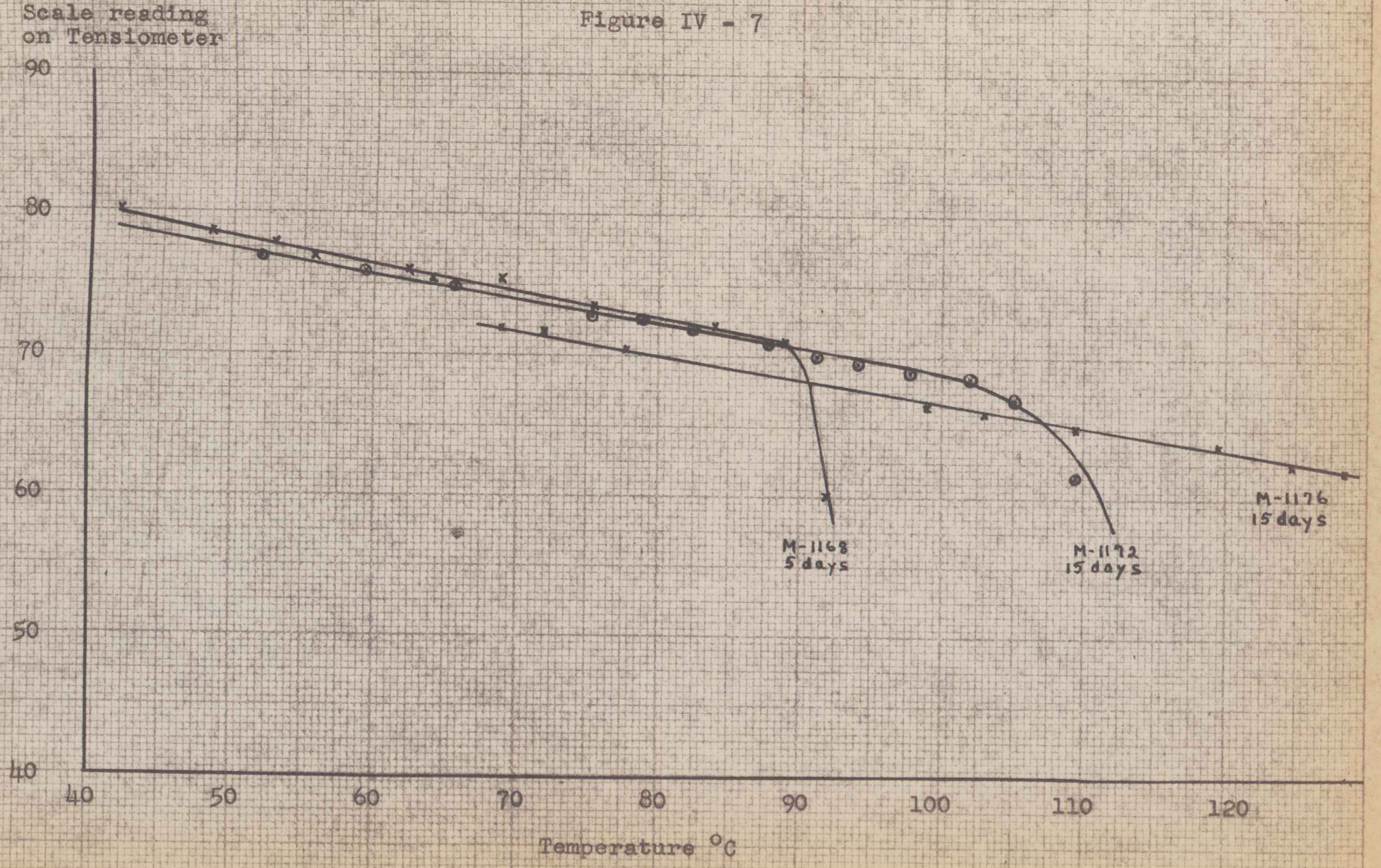

Relative
Capacitance
373.0
372.0
371.0
370.0
369.5
0
1.0
2.0
% Sulfated Ash

Figure IV - 7


Scale reading on Tensiometer
90
80
70
60
50
40
40
50
60
70
80
90
100
110
120
Temperature °C
M-1168 5 days
M-1172 15 days
M-1176 15 days

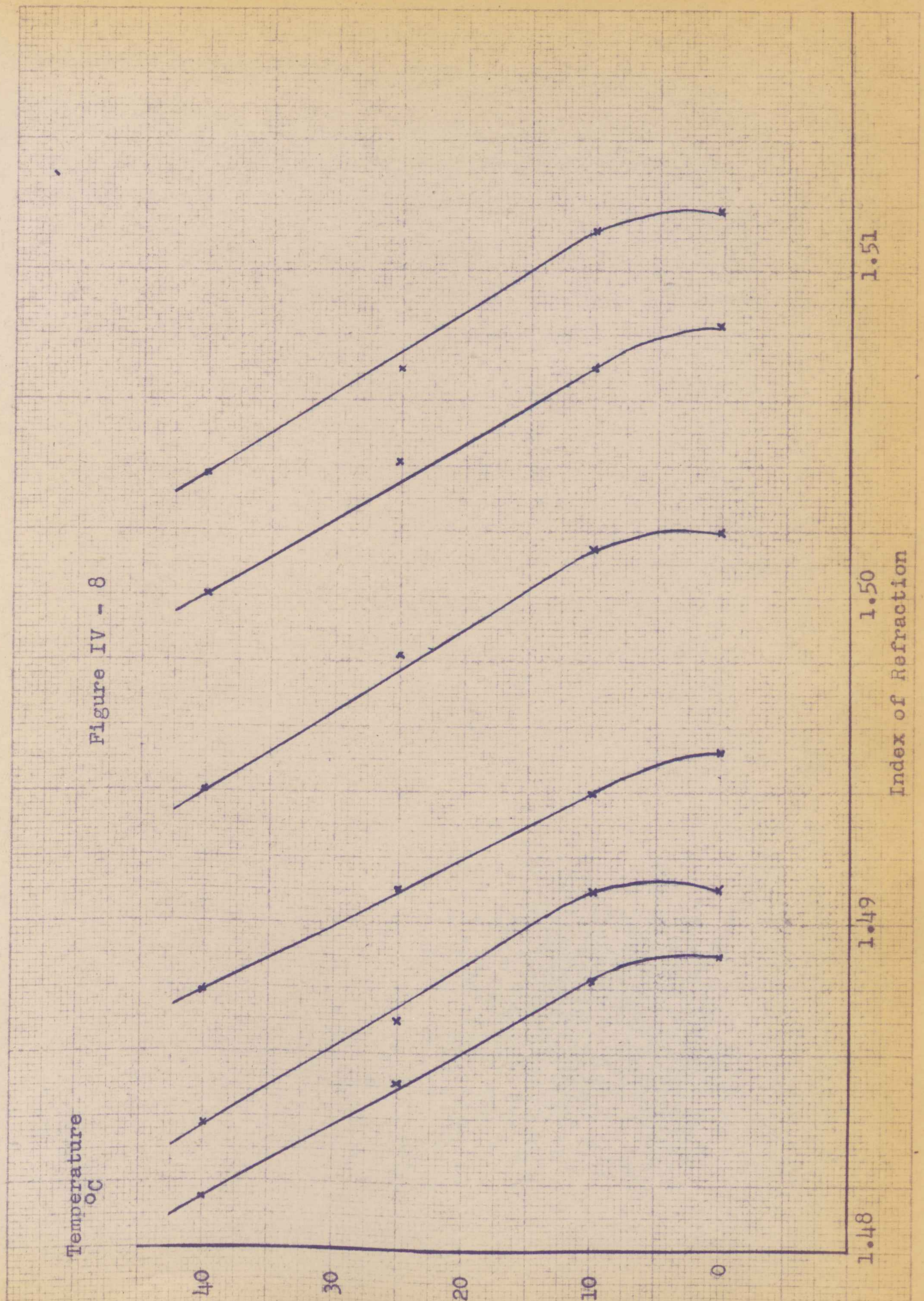

Temperature
°C
40
30
20
10
0
1.48
1.49
1.50
1.51
Index of Refraction

Figure IV - 8

C. Analysis of Ash

The purpose of this phase of the research was to find a way to improve the results obtained from spectrographic analysis of the lubricating oil ash. This analysis is being carried on at the Chemical Laboratory of the American Locomotive Company in Schenectady. The complete equipment used was purchased from Baird Associates in Cambridge, Massachusetts.

The oil ash is prepared for analysis by the following procedure:

1. 80-90 ml of the oil is burned in a vycor dish.
2. The residue is then heated at about 1100°F until the carbon is completely burned off. This usually takes an hour or two.
3. The ash is then gently brushed out of the vycor dishes, being careful not to scrape the dish, and is ground in an agate mortar.
4. .0500 g of the ash is then mixed and ground completely with .7000 g of reagent Li_2CO_3.
5. This mixture is then analyzed on the spectrograph and the results are reported in parts per million.

A microscopic examination of the ash resulting from the above procedure showed it to be distinctly non-homogeneous. Particles of different sizes and colors could be seen. The goal of our work has been to get this ash perfectly homogeneous and thus eliminate the possibility of errors in the analysis due to non-uniformity of the sample.

Fusions of the ash were made with Na_2CO_3, Li_2CO_3, Na_2CO_3-Li_2CO_3 mixtures, and with $LiHSO_4$. In all cases the fusion did not form a perfectly clear melt. Solution of the carbonate melts in dilute hydrochloric acid gave clear solutions and solutions of the $LiHSO_4$ melt in water also gave a clear solution but with a very slight precipitate.

Another method of preparing the ash sample was tried. This consisted of digestion of the oil with sulfuric acid and metallic Se as a catalyst, thus getting rid of all the carbon. Subsequent evaporation of the sulfuric acid gave the ash as a residue.

Two test samples were prepared for analysis. The first sample (Seaboard 1405, Sample 2-1-53, Tampa, Florida, reclaimed oil) was prepared as follows:

1. An ash was obtained by the procedure outlined before which is used by the American Locomotive Company.
2. .0500 g of this ash was fused with .7000 g of Li_2CO_3 in a platinum crucible using a meker burner.
3. The fused melt was then completely dissolved in dilute HCL.
4. The solution was evaporated to dryness and the residue was ground in an agate mortar.

The analysis of this is given in Table IV.

The second sample (Dieseltex oil #2 can, Gulf, Mobile and Ohio Railroad, Loco. No. 705) was prepared as follows:

1. 30-40 ml of oil were burned off in an evaporating dish until about 5 ml remained.
2. The burner was removed and the flames were allowed to extinguish themselves. Then 50 ml of concentrated H_2SO_4 was added and heated slightly.
3. The resulting solution was poured into a 250 ml erlen-

meyer flask and a small amount of Se metal, on the end of a spatula was added.

4. This was boiled until a clear yellowish solution was obtained.

5. The H_2SO_4 was evaporated off in an evaporating dish and the ash residue was collected by brushing.

6. .0500 g of the ash was then ground with .7000 g of Li_2CO_3 in an agate mortar.

The analysis of this is given in Table IV also.

From Table IV it can be seen that the problem of getting reproducible results is not solved yet. Further attempts at obtaining perfect homogeniety of the sample as well as an investigation of possible malfunction of the instrument should probably be carried out in order to solve this problem.

TABLE IV

Sample	Pb	Si	Fe	Cr	Al	Cu	Ag
Seaboard 1405)	3	30	63	284	17	2	Tr.
Sample 2-1-53)	2	50	67	312	18	2	Tr.
Tampa, Florida)	4	63	71	384	19	2	Tr.
Reclaimed Oil)	2	54	65	387	20	2	Tr.
	2	63	68	357	23	2	Tr.
	2	68	56	249	15	2	Tr.
	4	68	68	230	15	2	Tr.
	3	59	59	171	10	2	Tr.
	4	63	75	333	17	2	Tr.
	3	63	66	450	27	2	Tr.
	2	54	55	221	12	2	Tr.
	2	59	62	257	16	2	Tr.
Dieseltex oil)	51	20	62	63	23	8	Tr.
#2 can, Gulf,)	49	20	55	63	26	8	Tr.
Mobile & Ohio)	81	16	54	63	24	8	Tr.
Railroad)	53	10	49	54	21	7	Tr.
Loco. No. 705)	82	12	54	54	15	7	Tr.
	56	11	47	50	16	9	Tr.
	63	14	46	50	15	8	Tr.
	98	17	58	64	23	7	Tr.
	73	12	48	50	15	3	Tr.
	85	23	66	68	31	9	Tr.
	70	14	69	63	23	6	Tr.
	50	21	64	68	32	7	Tr.

SUMMARY

The oxidation stability of the lubricating oils was determined by a test devised at the American Locomotive Company in Schenectady. This test, called the Dipping Light Bulb Test, was used on a large number of lubricating oils of widely varying composition.

Separation of the oil constituents by chromatographic analysis, using a succession of various solvents was also tried, and proved very promising. This may prove useful for tracing the reactions occurring in the oxidation of lubricating oils as well as for determining their base stock or composition.

Two physical constants, the index of refraction and the density of some of the oils, were measured. An attempt was made to then correlate these with stability. Although no exact relation was found, general trends were observed. In some Monsanto oils of the same base stock, the relations held quite well.

Other miscellaneous investigations were carried out on the lubricating oils. Among these were an investigation of the ultraviolet spectra, the change of surface tension with temperature, and the change of the index of refraction with temperature.

An improvement in the results of spectrographic analysis of the ash of lubricating oils was also attempted. This was done by investigating the fusion of the ash with lithium and sodium carbonates, and lithium acid sulfate in an attempt to get a more homogeneous mixture of the constituents of the ash. Analysis of the ash did not show improvement in the results. Other possible causes of errot should also be investigated before anything conclusive can be said.

In general this work has been an exploration of the possibilities available for increasing the accuracy of predicting the success of lubricating oils in actual use.

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