ASPHALTENES **IN** LUBRICATING OILS

By

A. B. HERSBERGER

Thesis submitted to the Faculty of the Graduate School
of the University of Maryland in partial fulfillment
of the requirements for the Degree of
Doctor of Philosophy.

1936.

UMI Number: DP70397

UMI

Dissertation Publishing

ProQuest

ACKNOWLEDGMENT

Acknowledgment of Materials

The following companies contributed materials for this work:

R. T. Vanderbilt Co., Inc.

Standard Oil Company of New Jersey.

Pure Oil Company, Chicago.

The University of Maryland assumes no
responsibility for the material herein presented.

TABLE OF CONTENTS

INTRODUCTION

The action of certain substances in retarding the oxidation of drying oils has been extensively studied for years. More recently methods for prevention of deterioration of hydrocarbon oils have been investigated.

Hugh S. Taylor in discussing the problem of deterioration says

---

Hugh S. Taylor - Proc. A. S. T. M. Part II, 1932 9-42

"Control of deterioration is the inverse of the historical occupation of the chemist. Since alchemist time his prime concern has been the promotion of chemical reaction. A belated attention to the problem of preserving his synthetic achievements is not, however, without its own peculiar scientific interest and practical significance."

Fundamental reactions in deterioration are oxidation processes involving oxygen from the air as well as reactions of polymerization and decomposition.

The most logical method for retarding or preventing deterioration seems to be the addition of substances to retard the initiation or slow down the oxidation reactions. These substances are referred to as negative catalysts.

In general, most substances studied increase the time of initial oxidation after which normal or increased rate of oxidation takes place. All investigations to date indicate that the oxidation of lubricating oils is an autocatalytic reaction, resulting in sludge formation.

The rate of adsorption of oxygen by a lubricating oil varies with the nature of the oil, extent of refining, temperature, and presence of catalyst.

Most oils are used under conditions of high temperature with exposure to oxygen of the air. Deterioration takes place to a large degree by oxidation of the oil to sludges under these conditions.

The addition of suitable antioxidants to lengthen the life of a lubricating oil has been the object of oil chemist for a number of years. Thus far no entirely satisfactory inhibitor has been obtained, although there are numerous existing patents that claim such.

In studying these phenomena it must be remembered that petroleum oils are very complex in nature and the mechanism of antioxidants is not entirely understood.

Experimental data and the discussion of a new type of substance are presented in this paper. It must also be remembered that laboratory tests are not always in accord with actual engine test. Tests that approach actual conditions closely are used in this work.

Problem

"Asphaltenes in lubricating oils", and in particular "inhibitors for the prevention of their formation".

Indications

1. Sodium alcoholates have been found to act as inhibitors to oxidation of lubricating oils.

2. An optimum quantity is required for best results.

3. An empirical equation has been found to represent the data from oxidation of a simple lubricating oil.

4. Quantities of sodium alcoholates used as inhibitors, do not render the oil corrosive.

5. The longer hydrocarbon chains alcoholates disperse best with the oil and are better as inhibitors.

6. Rate of discoloration of an oil is not directly related to asphaltene formation. An oil may become very dark with little asphaltene formation, or show large amounts of asphaltene formation with little discoloration.

7. Oxygen is essential for asphaltene formation, since continued heating without oxidation does not increase asphaltene content.

8. The life of these inhibitors are limited and are probably used up in some type of reaction. Asphaltenes formed when using an alcoholate as an inhibitor are very light colored instead of the usually black or dark brown color.

LITERATURE

I. Problem

Ellis in discussing the importance of the subject says;

The Chemistry of Petroleum Derivatives by Carleton Ellis. The Chemical Catalog Company, Inc. 330 West 42nd St. New York, N.Y. p. 903.

" --Most lubricating oils are used under conditions where a temperature rise occurs, and they are nearly always in contact with the oxygen of the air. Failure in lubrication, with accompanying damage to machinery, arises to a large degree from the oxidation of the lubricant, not because of any great loss of oiliness of the lubricant itself, but rather because oxidation yields viscous or solid bodies or jelly-like emulsions with water, which interferes with the regular distribution of the lubricant at the bearing surface".

II. Cessation of Inhibitor Action

Haslam and Frolich, from their investigation of inhibitors for oils, give the following information.

R. T. Haslam and Per K. Frolich. Mechanism of Oxidation and Action of Negative Catalyst as determined by a dynamic method. Ind. & Eng. Chem. Vol. 19 #2, p. 292.

"In general, the opinion is held that the oxidation of oils is an autocatalytic process, the products being catalyst for the further oxidation of the hydrocarbons".

They further list the reasons for cessation of action of the catalyst.

1. May be oxidized and thus lose its protective power.

2. Evaporated directly without being subject to oxidation.

3. Partly destroyed by oxidation, partly removed by evaporation.

4. Lessened in activity as a result of reactions caused by heat, intermolecular condensation or polymerization of the catalyst itself or reaction between catalyst and oil.

5. Positive catalyst may be built up in the system.

Some examples of cessation of action of catalysts are:

1. p-amino phenol is a typical catalyst removed by evaporation.

2. Diphenyl amine is destroyed by evaporation and heat.

3. Diphenyl hydrazine is destroyed by heat and part by oxidation.

Frolich and Haslam also found that the addition of p-amino phenol every two hours to a sample of oil delayed its period of initial oxidation indefinitely. However, diphenyl amine did not delay the reaction after the first addition in a simular experiment.

III. Asphaltene Formation

Chernojookow points out that sludge from oxidation of refined oils may be formed in three ways,

Chernojookow - Ind. & Eng. Chem. 21, 315 (1929)

(1) "The unsaturated hydrocarbons, tars, and sulfur-containing substances, on oxidation form a sludge consisting of asphaltenes and carbenes.

(2) The saturated hydrocarbons on oxidation form acids of high molecular weight, which cannot be dissolved in petroleum ether and which have acid numbers varying between 60 and 110.

(3) Another sludge is obtained by the reaction of the metals with acids in the presence of water".

Sladnikow and Vossinskua, from their investigation showed that sulfonic acids aid polymerization.

Sladnikow and Vossinskua - Trans. Karpow Inst. Chem. 5, 109, (1926). Chem. Abstracts 22, 2049 (1928).

They found that when the refined oil was heated in an atmosphere of CO_2 with acetic acid and cyclohexanol, the reaction was one of saponification only. If, however, napthene sulfonic acids were present, resin formation took place. Glacial acetic acid itself yields resins with napthene sulfonic acids.

IV. Inhibitors and Possible Mechanisms

Smith and Wood classify inhibitors for oxidation

as follows

Otto M. Smith and Robert Erl Wood - Oxidizing Agents in the Oxidation of Unsaturated Compounds, Ind. & Eng. Chem. 18, #7, 691 (1926).

(1) Active and powerful reducers.

(2) Strong bases.

They found that the most effective inhibitors are basic

compounds of amines, aromatic phenols, and inorganic basic

reducers.

They present the following as possible theories for

action of inhibitors.

(1) "The antioxidant being basic combines with the

acidic products of oxidation and prevents them from acting

as auto-catalyst toward oxidation.

(2) The triple-bonded nitrogen atom with two partial

valences or elements with free valences forms intermediate

compounds with the easily oxidized ethenoid carbon."

Hugh S. Taylor says, in discussion of the possible

function of an inhibitor.

Hugh S. Taylor. Proc. of A. S. T. M., Part II, p. 9, (1932).

"----A chain mechanism of the type just discussed would

however, offer the possibility of such inhibitory power of

minute quantity of material, the efficiency of the inhibitor

being determined by the stage in the chain at which it
intervened, the earlier the more efficient. As we have
already pointed out, a retardation might also be achieved
by an inhibitor reducing the concentration of a powerful
accelerator of the reaction, which in the case of reactions
involving chains, might be spoken of as chain initiators.
It will emerge that a distinction between these two possible
modes of retardation can be achieved.

EQUIPMENT AND PROCEDURE

1. Methods used in determining the efficiency of the
   inhibitor.

Indiana Oxidation Test for Motor Oils.

Indiana Oxidation Test for motor oils. T. H. Rogers and
B. H. Shoemaker, Analytical Edition Ind. & Eng. Chem. Vol.
6, #6, p. 419 (1934).

Apparatus. "A thermostatically controlled oil bath
suitable for immersion of the oil tubes to a depth of 30
cm. Bright stock of good stability is used for the bath.
Temperature regulation at approximately 342° F. (172.2°C.)
within ± 0.5° F. must be maintained. Oil tubes must be
placed symetrically with reference to stirrer and heater.

Oil test tubes of heat-resistant glass of 40 to 44
mm. inside diameter, 450 to 500 mm. long, provided with a
slotted cork stopper into which is fitted an air delivery
tube of glass, of 4 to 5 mm. inside diameter.

Flowmeters, calibrated in liters of air per hour
through which air at constant pressure is supplied."

Procedure "Determine the observed bath temperature
which must be maintained in order to keep the test oil a
temperature of 341° ± 0.5° (171.7°C) corrected. Take the
temperature of the test oil with the tube in place containing

300 c.c. of oil, while passing through air at a rate of
10 liters per hour. Use a standardized thermometer,
immersing it to the approximate center of the oil, and
make appropriate stem correction. Having established
this comparison of bath and test oil temperature, the
observed bath temperature may be used for control so long
as the rate of stirring is not markedly varied and the
viscosity of the bath has not increased to more than 200
seconds furol at 210°F. $(98.9^{\circ}C.)$.

Fill the oil tube to a depth of 23 cm. (approx.
300 c.c. of oil). Place the tube in the bath, the level
of which must be at least 5 cm. above that of the test oil.
The oil bath must be up to temperature and be so maintained
that the temperature of the test oil is $341^{\circ} \pm 0.5^{\circ}$ F. The
air delivery tube is placed so that the end is within 6 mm.
of the bottom of the oil tube. One half hour after placing
the oil in the bath, start the air at a rate of 10 ± 1 liter
per hour. The start of the test period is the time of
starting the air.

For determination of sludge values withdraw a 25 c.c.
sample of test oil in a pipette. Weigh 10 gms. $(\pm 0.1$ gm.)
of this portion immediately into a 300 c.c. Erlenmeyer flask,
and dilute with 100 c.c. of A. S. T. M. precipitation naptha.
The naptha used must, by comparative test on a sample of

oxidized oil, give within 25% of the sludge value obtained with a reference sample of A. S. T. M. precipitation naptha. Stopper the flask and allow the solution to stand for three to three and one-half hours at room temperature. (20 to 25°F., 21.1 to 29.4°C)".

"Prepare a Gooch type crucible (approcimately 35 mm. in diameter) with a mat of 0.5 to 0.05 gm. medium asbestos fiber. During preparation of the mat, press it down before adding the last portion. Dry the crucible at approximately 300°C F. (148.9° C) for at least two hours in an oven and weigh. Filter sample, wash with precipitation naptha, heat at approximately 300°F to 0.5 hr., and weigh. Express sludge as milligrams per 10 gms. of oil.

Samples for sludge determination may be taken every 24 hours before sludging begins.------"

"The sludging time is the time required to form 10 mg. of sludge per 10 gm. of oil -----".

A modification of this method was used. The temperature of the oil bath was lowered so that the oil in the oil tubes could be kept at 300°F. ± 0.5. The reason for lowering the temperature was to slow up the rate of oxidation. Previous investigators have shown that it is hard to study the action of inhibitors if the rate of oxidation is too rapid. The air was controlled by standardized flow meters.

2. Determination of Color

The colors described in this paper are so-called "optical density colors".

Ferris and J. M. McIlvain published the construction of this colorimeter in Industrial and Engineering Chemistry.

Optical Density Color Measurement for Petroleum Oils. S. W. Ferris and J. M. McIlvain., Anal. Ed. Ind. & Eng. Chem. Vol. 6, #1, p. 23 (1934).

This colorimeter is the only one that the writer has ever used that fulfils the following six conditions.

(1) Samples should be accorded values in agreement with visual inspection.

(2) Values should be additive in the sense that the color C_m of a mixture of two oils having colors Ca and Cb will be given by equation

$$Cm = \frac{CaVa + CbVb}{100}$$

where Va and Vb are the respective percentages (by volume) of the oils whose colors are Ca and Cb.

(3) Apparatus, standards, and color values should be reproducible in any laboratory.

(4) Color values should be based on fundamental rather than arbitrary units.

(5) The method should be usable to routine work.

(6) Consistant color values should be obtainable on oils ranging from light finished products to the darkest tars and bottoms.

The principal of this colorimeter is to determine the depth of oil required to match a standard color glass in monochromatic light. Green light is used of approximately 500 to 560 mμ . The standard color glass and depth oil match when the oil and color glass adsorb the same amount of incident light.

Oils too dark to measure directly are dilute with benzene of not more than sabolt 30 color. The optical density color is calculated by the following equation:

$$\text{optical density color} = \frac{10^3 D \times 10^N}{R}$$

where D = optical density of neutral filter =

$$\frac{\log \text{ incident light}}{\text{transmitted light}}$$

R = mm. depth of oil (or solution) to match neutral filter.

N = number of dilutions (in 1 to 10 ratio).

Results on this colorimeter agree within 3% of the average.

3. Preparation of test oils.

500 gms. of the oil to be tested is weighed out to $\pm$ 0.1 gms. and the inhibitor is added. The inhibitor is weighed out to $\pm$ 0.0002 gms. and dissolved in some suitable

solvent then mixed with the oil. Benzene is sufficient for most purely organic compounds. Best results were obtained by dissolving the alcoholates in hot xylene. The particles not dissolving are very finely dispersed and when added become well dispersed in the oil. The oil and inhibitor are then divided into two equal portions, placed in the oil tubes and oxidation started after one-half hour.

4. Preparation of Inhibitors

1. Most of the organic inhibitors used were C.P. chemicals.

Aldol alpha napthylamine, phenyl beta napthylamine and s-di-beta-napthyl-p-phenylene-diamine are commercial products furnished by R. T. Vanderbilt Company, Inc., New York. They are used for antioxidants in rubber.

2. Sodium cetylate was prepared by dissolving the cetyl alcohol in dry xylene and treating with sodium. The mixture was refluxed until no further reaction was evident. After allowing to cool the sodium cetylate was filtered off and washed with dry benzene, followed by dry alcohol and ether. The product was then dried at a low temperature and placed in tightly stoppered bottles until used.

3. The sodium acetonate was prepared by treating *acetone* with sodium, filtering off the product, washing and drying as in previous preparations.

4. The sodium ethylate was prepared by treating dry ethyl alcohol with the weighed amount of sodium required to produce the desired amount of alcoholate. This sodium ethylate was not recovered, the mixture of excess alcohol and sodium ethylate being added to the oil. The excess alcohol soon evaporated off at the elevated temperature of the bath.
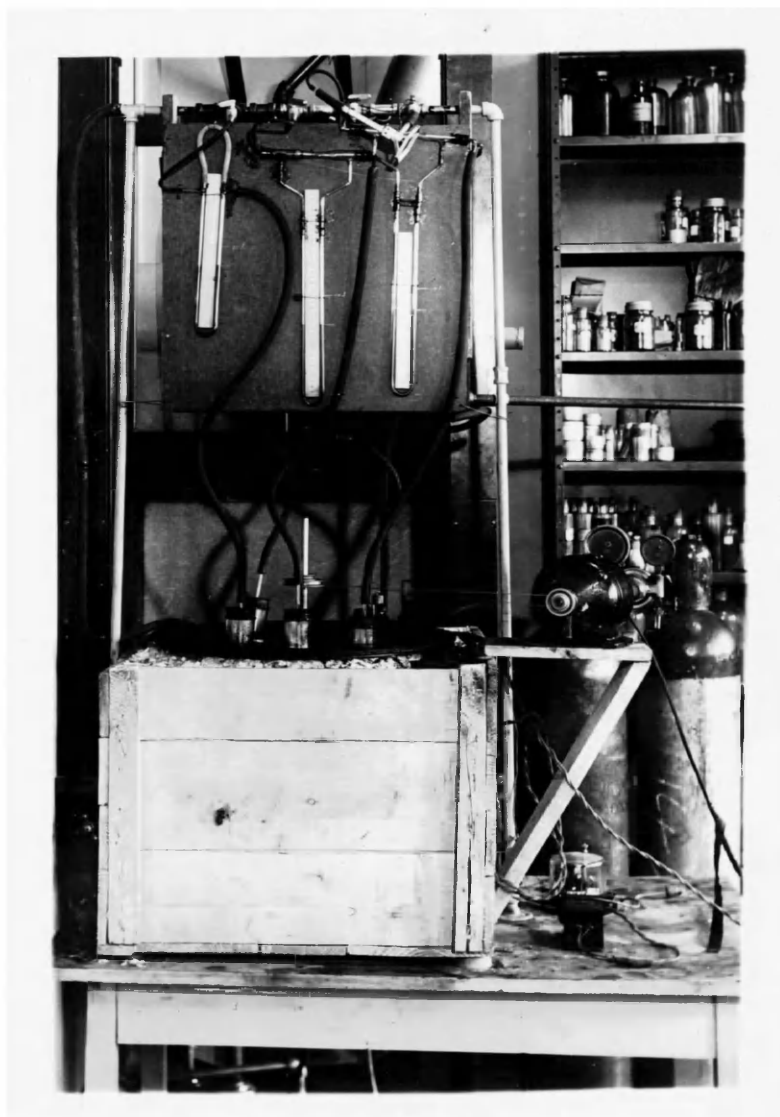
Oil Bath used in Experiments

LOLAG HEATERS.

10 LITERS OF AIR PER HOUR.

ROCK WOOL

OIL

TUBE HOLDER

45.7 CM.

40.1 CM.

53.3 CM.

63.5 CM.

THERMOMETER.

THERMOSTAT.

LOLAG HEATERS.

TUBE HOLES.
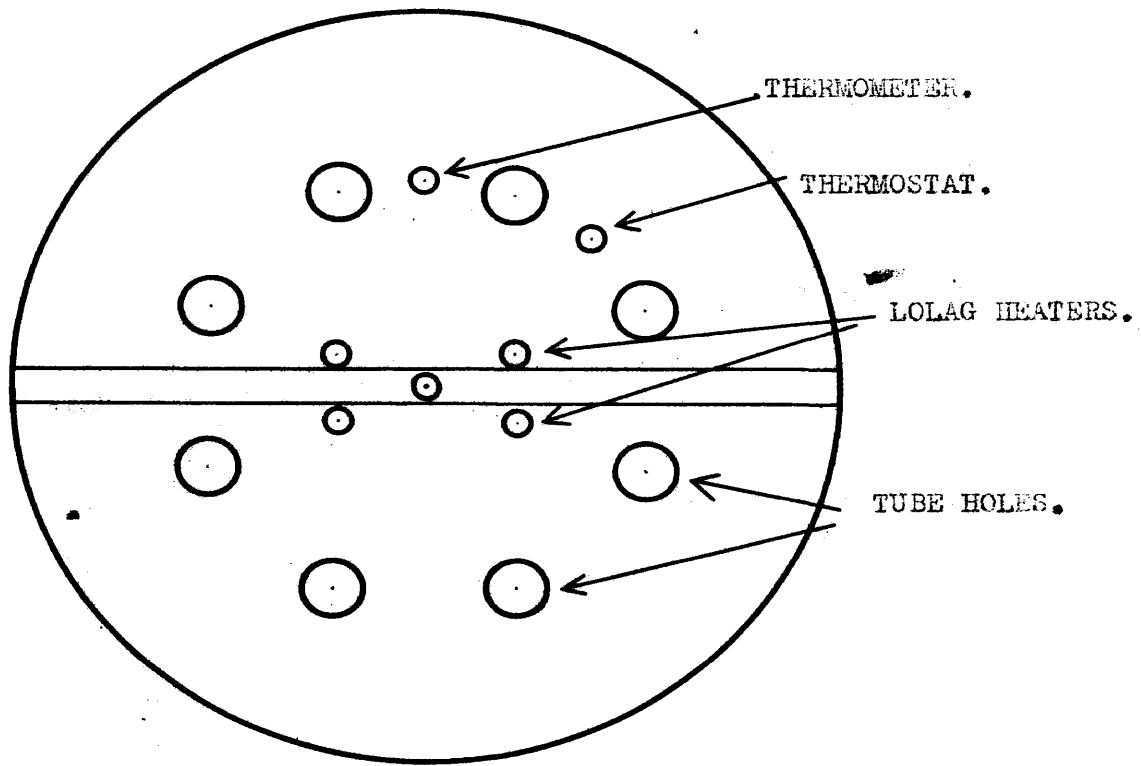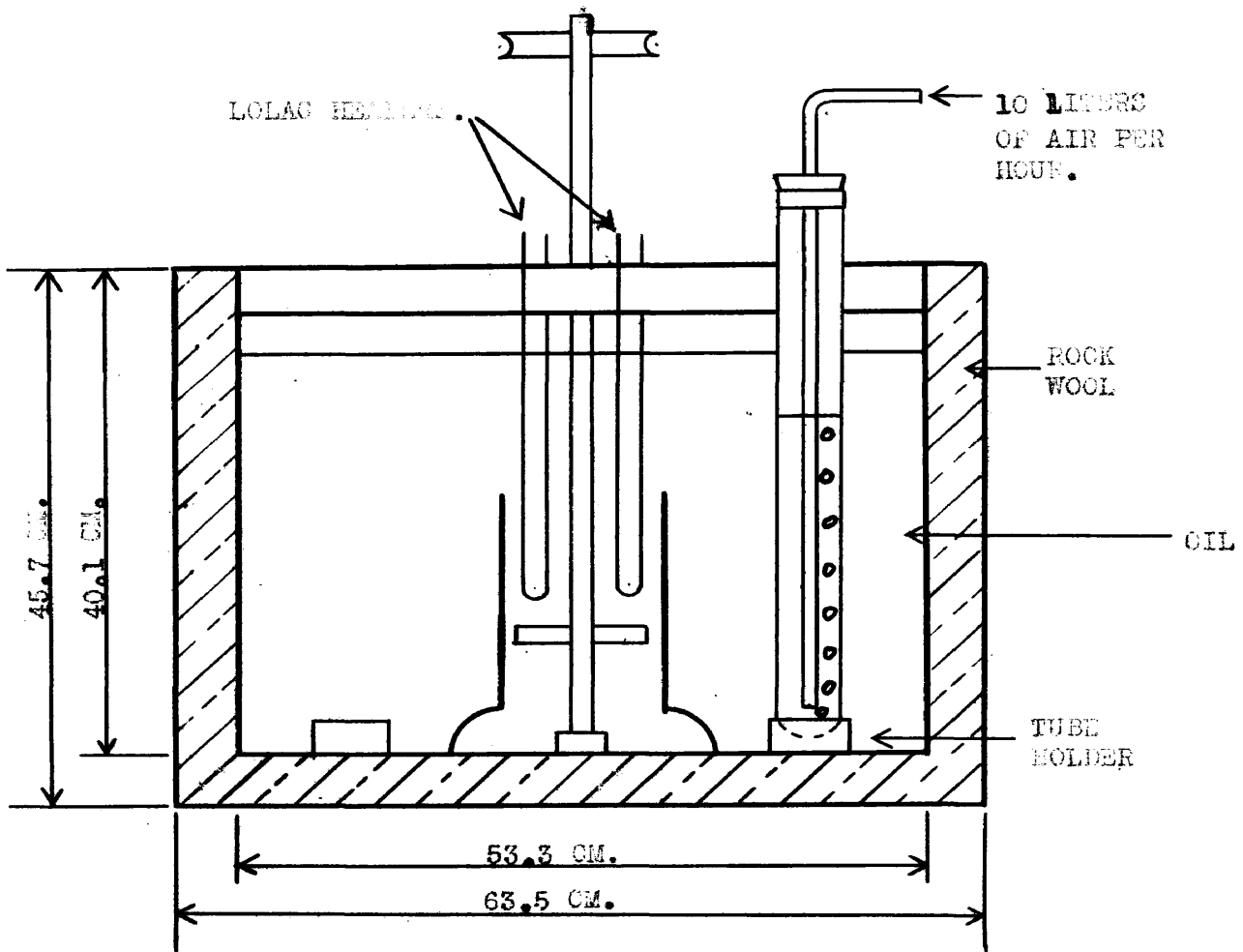
DIAGRAM OF OXIDATION BATH.

DATA

Table I

Physical Characteristics of Test Oil

Oil A
Western Base Oil

A.P.I. Gravity 60°F.	26.2
Flash Point	405°F
Fire Point	465°F
Viscosity 100°F (Saybolt)	224
Viscosity 210°F "	49
Optical Density Color	32

Oil B
Pennsylvania Base Oil

A. P. I. Gravity 60°F.	29.1
Flash Point	440°F
Fire Point	485°F
Viscosity 100°F (Saybolt)	467
Viscosity 210°F "	63
Optical Density Color	19

Table II

Physical Characteristics of Precipitation Naptha

A.P.I. Gravity 60°	71.3
Analine Point	58.5°C
Distillation Range	
Initial B.P.	37°C
10% Distilled over	54°C
20% "	60°C
30% "	66 "
40% "	72 "
50% "	78 "
60% "	85 "
70% "	92 "
80% "	99 "
90% "	109 "
Max. B.P.	135.5"

Table III

Time in hrs.	Asphaltenes mg. per 10 gm. of oil	$(Asphaltenes)^{\frac{1}{2}}$
Pure Oil A		
0		
24	2.3	1.52
48	14.5	3.80
72	34.6	5.87
95	65.6	8.10
118	104.0	10.20
140	154.0	12.40
Pure Oil B		
0		
48	1.2	1.1
72	1.9	1.39
96	5.9	2.44
120	12.3	3.50
144	23.4	4.73
168	34.5	5.87
192	47.8	6.90

Table IV

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	$(\text{Increase in})^{\frac{1}{2}}$ (asphaltenes)
Inhibitor 0.1% alpha napthylamine			
0	4.0	0	
24	5.9	1.9	1.37
47	8.0	4.0	2.00
71	13.5	9.5	3.07
96	23.3	19.3	4.40
120	34.6	30.6	5.51
144	50.9	46.9	6.82
168	68.0	64.0	8,0
Inhibitor 0.1% aldol-alpha napthylamine			
0	4.0		
24	5.2	1.2	1.09
48	6.7	1.7	1.30
72	12.7	8.7	2.95
96	23.0	19.0	4.35
118	38.3	34.3	5.85
140	57.2	53.2	7.3
Inhibitor 0.1% beta napthylamine			
0	4.0	0	
24	8.1	4.1	2.02
48	12.5	8.5	2.92
72	18.4	14.4	3.78
96	27.0	23.0	4.80
120	35.9	31.9	5.63
144	47.5	43.5	6.60
Inhibitor 0.1% phenyl beta napthylamine			
0	6.0	0.0	
24	8.5	2.5	1.58
48	15.6	9.6	3.09
72	25.7	19.7	4.42
96	29.6	33.6	5.8
118	58.8	52.8	7.23
140	74.5	68.5	8.25
166	118.4	112.4	10.60

Table IV (Cont'd.)

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
Inhibitor 0.1% phenyl-alpha napthylamine			
0	6.0		
24	8,2	2.2	1.48
48	14.7	8.7	2.92
72	30.4	24.4	4.92
96	48.8	42.8	6.52
117	70.0	64.0	8.00
144	100.2	94.2	9.70

Table V

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
Inhibitor 0.1% S-Di-Beta-napthyl-p-phenylenediamine			
0	7.6	0	0
2	10.6	3.2	1.8
5	12.9	5.3	2.3
10	13.7	6.1	2.45
22	18.6	11.0	3.31
46	25.5	17.9	4.22
70	41.2	33.6	5.80
94	59.4	51.8	7.20
118	78.0	70.5	8.40
140	109.0	93.3	9.65

Table VI

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
	Inhibitor 0.025% sodium cetylate		
0	2.0		
24	2.3	0.3	0.54
40	2.9	0.9	0.95
62	8.3	6.3	2.52
84	21.8	19.8	4.45
109	47.1	45.1	6.7
135	29.9	67.9	8.65
157	109.0	107.0	10.35
	Inhibitor 0.05% sodium cetylate		
0	3.8	0	
24	3.9	0.1	0
48	4.1	0.3	0.54
62	8.2	4.4	2.11
84	18.2	14.4	3.8
109	38.6	34.8	5.9
135	64.8	61.0	7.8
157	96.1	92.3	9.6
	Inhibitor 0.1% sodium cetylate		
0	7.8	0	
24	8.1	0.3	0.54
40	10.7	2.9	1.7
62	23.2	15.4	3.92
84	39.2	31.3	5.6
109	65.9	58.1	7.62
135	102.3	94.5	9.7
157	136.8	129.0	11.4
	Inhibitor 0.2% sodium cetylate		
0	12.2	0	
24	13.4	1.2	1.1
48	18.9	6.7	2.6
62	31.6	19.4	4.4
84	49.4	37.2	6.1
109	77.8	65.6	8.1
135	110.5	98.3	9.9
157	153.8	141.6	11.9

Table VII

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{3}}$ (asphaltenes)
Inhibitor 0.025% sodium ethylate			
0	2.0	0	
24	1.9	0	
48	7.9	5.9	2.44
72	16.6	14.6	3.82
97	34.5	32.5	5.7
142	79.1	77.1	8.78
173	120.2	118.2	10.85
Inhibitor 0.05% sodium ethylate			
0	3.9	0	
24	3.9	0	
48	7.9	4.0	2.0
72	18.7	13.8	3.7
97	33.2	29.3	5.4
142	75.0	71.1	8.4
173	116.4	112.5	10.6
Inhibitor 0.1% sodium ethylate			
0	7.7	0	
24	7.5	0	
48	16.7	9.0	3.0
72	28.9	21.2	4.6
97	35.7	38.0	6.15
142	92.8	85.1	9.2
173	135.9	123.2	11.3
Inhibitor 0.2% sodium ethylate			
0	12.2	0	
24	12.3	0.1	0
48	16.2	4.0	2.0
72	23.1	10.9	3.3
97	31.6	19.4	4.4
142	44.6	42.4	6.5
173	78.3	66.1	8.1

Table VIII

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
Inhibitor 0.025% sodium acetonate			
0	2.1	0	
24	3.5	1.4	1.2
48	5.7	3.6	1.9
74	13.0	10.9	3.3
96	23.4	21.3	4.6
124	41.7	41.6	6.45
147	63.3	61.2	7.81
Inhibitor 0.05% sodium acetonate			
0	4.1		
24	5.1	1.0	1.0
48	7.0	1.9	1.4
74	12.5	8.4	2.9
96	22.3	18.2	4.3
124	41.5	37.4	6.1
147	60.4	56.3	7.5
Inhibitor 0.1% sodium acetonate			
0	7.8	0	
24	9.7	1.9	1.4
48	13.5	5.7	2.4
74	23.8	16.0	4.0
96	36.0	28.2	5.3
124	54.2	46.4	6.8
147	73.9	66.1	8.1
Inhibitor 0.2% sodium acetonate			
0	12.0	0	
24	16.8	4.8	2.2
48	27.2	15.2	3.9
74	31.2	29.2	5.4
96	56.5	44.5	6.66
124	80.0	68.0	8.25
147	104.3	92.3	9.6

Table VIII (Cont'd.)

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
	Inhibitor 0.4% sodium acetonate		
	24.5	0	
0	24.2	0	
24	25.7	1.2	1.1
48	29.0	4.0	2.0
74	36.4	11.9	3.45
96	44.9	20.4	4.5
124	59.2	34.7	5.8
147	70.9	46.4	6.8

Table IX

Oil B

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
Inhibitor 0.025% sodium cetylate			
0	1.6	0	
24	1.6	0	
47	1.7	0.1	
72	1.9	0.3	0.54
97	3.3	1.7	1.33
120	9.4	7.8	2.78
143	14.0	12.4	3.52
167	32.2	20.6	4.53
192	35.0	33.4	5.75
215	49.2	47.6	6.9
Inhibitor 0.05% sodium cetylate			
0	3.0	0	
24	3.1	0.1	
47	3.0	0	
72	3.1	0.1	0.4
97	4.1	1.1	1.05
120	7.0	4.0	2.0
143	13.3	10.3	3.2
167	20.8	17.8	4.2
192	32.4	29.4	5.4
215	43.1	41.1	6.4
Inhibitor 0.1% sodium cetylate			
0	6.4	0	
24	6.6	0.2	0
47	6.3	0	0
72	6.9	0.5	0.7
97	9.6	3.3	1.8
120	15.1	8.7	2.95
143	22.4	16.0	4.0
167	32.5	26.1	5.1
192	46.4	40.0	6.3
215	59.6	53.2	7.3

Table IX (Cont'd.)

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
	Inhibitor 0.2% sodium cetylate		
	11.7	0	
	11.5		
	11.9	0.2	
	12.8	1.1	1.05
	15.8	4.1	2.02
	22.3	10.6	3.25
	40.3	18.6	4.3
	41.7	30.0	5.5
	58.1	46.4	6.7
	74.2	62.5	7.9

Table X

Inhibitor 0.1% sodium hydroxide

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
0	8.6		
24	11.8	3.1	1.8
48	16.9	8.3	2.88
72	24.0	15.4	3.92
96	36.7	28.1	5.3
120	49.6	40.5	6.35
144	64.6	58.0	7.6

Inhibitor 0.1% aluminum ethylate

0	8.6	0	
24	10.0	1.4	1.2
40	15.0	6.4	2.53
62	31.8	23.2	4.82
84	54.1	47.5	6.89
109	77.5	68.9	8.30
135	145.6	137.0	11.70

Inhibitor 0.1% cetyl alcohol

0	0	0	
24	4.0	4.0	2.0
48	15.0	15.0	3.87
72	35.0	35.0	5.92
99	63.5	63.5	7.96
122	92.0	92	9.60

Table XI

Time in hrs.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
Inhibitor 0.05% sodium cetylate			
0	3.7		0
24	3.9	0.2	
48	4.9	1.2	1.1
72	12.7	9.0	3.0
96	26.5	22.8	4.77
air turned off 24 hrs.			
120	24.0	20.3	4.50
144	51.2	47.5	6.90
168	77.7	74.0	8.60
192	112.7	109.0	10.45

Table XII

Oil A Containing 0.05% sodium cetylate and 0.01 gms. of
sodium cetylate added every 24 hrs.

Time in hrs.	Estimated wt. inhibitor in ppt.	Asphaltenes mg. per 10 gm.of oil	Increase in asphaltenes	(Increase in)$^{\frac{1}{2}}$ (asphaltenes)
0	3.8	3.7		
24	6.8	6.9		
48	9.8	9.7		
72	12.8	10.1		
96	15.8	10.2		
120	18.8	10.1		
144	10.1*	10.0	0	
168	10.1	18.4	8.3	2.88
192		25.7	15.6	3.94
216		38.5	18.4	4.23

* Taken as amount of inhibitor thrown out in asphaltene
determination after last addition of inhibitor.

Table XIII

Time in hrs.	Optical Density Color	Increase in Density color
Pure oil A.		
0	32	0
24	175	143
48	504	472
72	835	803
95	1063	1031
118	1606	1574
140	2045	2018
Pure oil B.		
0	19	0
24	380	361
48	910	891
72	1445	1426
96	1849	1820
120	2491	2480
144	3010	2991
168	3540	3521
Oil A 0.1% NaOH		
0	32	0
24	112	80
48	181	147
72	289	257
96	368	336
120	495	463
144	690	658
Inhibitor 0.1% sodium cetylate in Oil A.		
0	32	0
24	175	143
48	413	381
72	645	613
99	1175	1143
122	1495	1463

Table XIV

G = milligrams of asphaltene formed per 10 gms. of oil.
t = time in hrs.; k = constant characteristic of the rate
    of asphaltene formation
n = constant characteristic of the oil or the inhibitor
    added. Increasing negative values are a measure of the
    effectiveness of the inhibitor

$$G^{\frac{1}{2}} = kt + n$$

Inhibitor	k	n	T when G = 10
Oil A	0.094	-0.76	47.0
Pure Oil B	0.046	-1.90	112.1
alpha napthylamine	0.050	-0.40	71.2
aldol alpha napthylamine	0.067	-1.8	74.0
phenyl alpha napthylamine	0.067	-0.1	48.7
beta napthylamine	0.038	0.2	77.8
phenyl beta napthylamine	0.059	1.08	47.5
S-Di-beta-napthyl-p-phenylenediamine	0.055	1.9	22.9
0.025% sodium cetylate	0.073	-1.5	63.9
0.05% sodium cetylate	0.077	-2.6	75.0
0.1 " " "	0.072	-1.3	58.0
0.2 " " "	0.078	-0.4	41.7
0.025% sodium ethylate	0.068	-0.9	59.8
0.05% " "	0.068	-1.2	64.1
0.1 " "	0.066	-0.15	50.2
0.2 " "	0.048	-0.3	71.0
0.025 sodium acetonate	0.061	-1.2	72.3
0.05 " "	0.062	-1.7	78.5
0.1 " "	0.057	-0.2	59.0
0.2 " "	0.051	1.6	30.6
0.4 " "	0.056	-0.4	63.5
0.025% sodium cetylate oil B	0.049	-3.45	135.0
0.05 " "	0.046	-3.45	143.5
0.1 " "	0.047	-2.85	128.0
0.2 " "	0.049	-2.75	120.5
0.1% sodium hydroxide	0.049	+0.6	52.2

Table XV

Corrosion Tests

% Inhibitor	Effect Copper Test	100 cc oil standing with 100 cc water 24 hrs.
Sodium Cetylate		
0.025%	negative	neutral
0.05%	"	"
0.1%	"	"
0.2%	"	"
Sodium Acetonate		
0.025	negative	neutral
0.05	"	"
0.1	"	"
0.2	"	"
0.4	positive	slight alkalinity

Table XVI

Inhibitor	Color of asphaltenes	White Scale formed in bottom of oil tubes
0.025% sodium cetylate		none
0.05% " "	medium brown	"
0.1% " "	" "	"
0.2% " "	" "	"
0.025% sodium ethylate	" "	"
0.05% " "	" "	"
0.1 " "	" "	"
0.2 " "	light yellow	white scale formed
0.025 sodium acetonate	medium brown	none
0.05 " "	" "	"
0.1 " "	" "	"
0.2 " "	light brown	very slight scale
0.4 " "	light yellow	white scale formed
0.1% NaOH	very light yellow	scale formed
no inhibitor	black	none

INCREASE IN ASPHALTENES.
MG. PER 10 GMS. OF OIL.
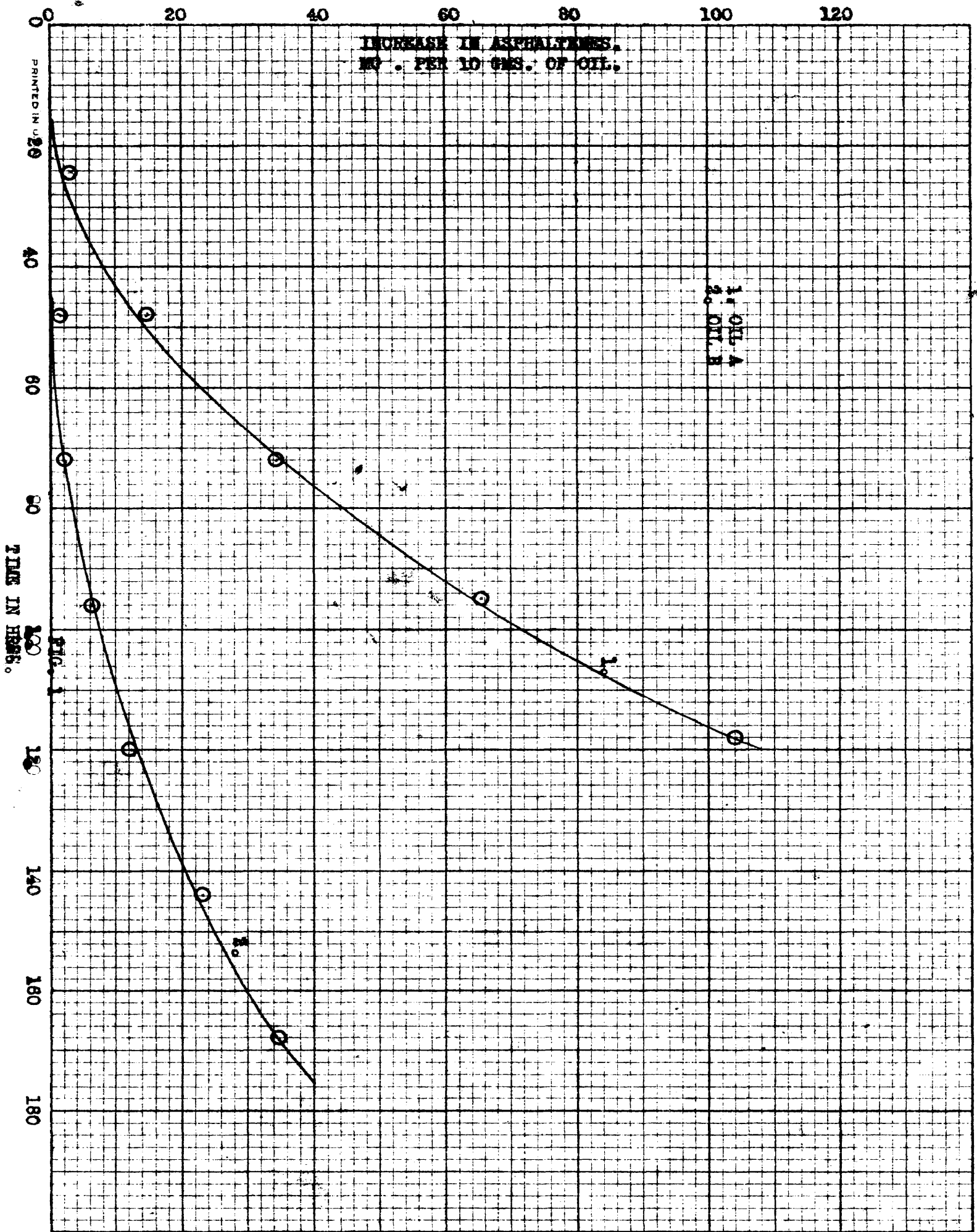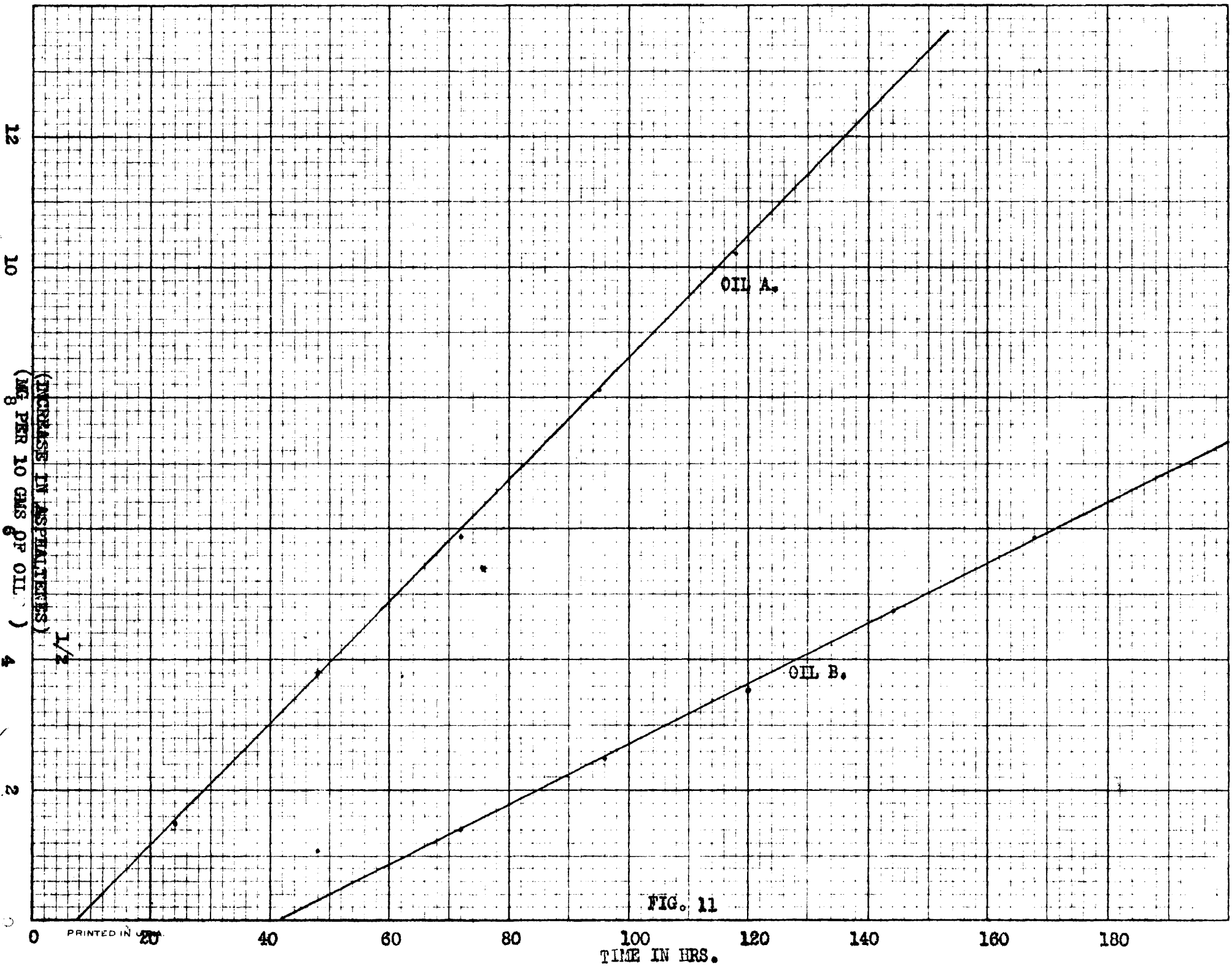
TIME IN HRS.

FIG. 1

1. OIL A
2. OIL B

FIG. 11

(DECREASE IN ASPHALTENES)
(MG PER 10 GMS OF OIL)

OIL A.

OIL B.

TIME IN HRS.

FIG. 111

1. Pure oil A
2. 0.1% Cetyl Alcohol
3. 0.1% Phenyl beta napthyl amine
4. 0.1% Aldol alpha napthyl amine
5. 0.1% Beta napthyl amine
6. 0.1% Alpha napthyl amine.

INCREASE IN ASPHALTENES.
MG. PER 10 GMS. OF OIL.

TIME IN HRS.

FIG. 1V.

TIME IN HRS.

1. Oil A.
2. Phenyl beta napthyl amine   0.1%
3. Aldol alpha napthyl amine   0.1%
4. Alpha napthyl amine   0.1%
5. Beta napthyl amine   0.1%

(INCREASE IN ASPHALTENES)
(MG. PER 10 GMS. OF OIL)

FIG. V.

1. Oil A.
2. 0.1% S-D-Beta-napthyl-para-phenylene-diamine.

(INCREASE IN ASPHALTENES)^{1/2}
(MG. PER 10 GMS. OF OIL)

TIME IN HRS.

(INCREASE IN ASPHALTENES)
(MG. PER 10 GMS. OF OIL)

FIG. VI.

TIME IN HRS.

1. Oil A.
2. 0.1% Octyl alcohol.
3. 0.2% Sodium cerylate.
4. 0.1%   "
5. 0.025%   "
6. 0.05%   "

FIG. VII

TIME IN HRS.

INCREASE IN ASPHALTENES.

1. 0.1% Sodium ethylate.
2. 0.025% "   "
3. 0.05%   "   "
4. 0.2%   "   "

FIG. V111

Y-axis: (INCREASE IN ASPHALTIZATION (MG. PER 10 GMS. OF OIL))

X-axis: TIME IN HRS.

Legend:
1. Oil A.
2. 0.1% Sodium ethylate.
3. 0.025%   "   "
4. 0.05%   "   "
5. 0.2%   "   "

PRINTED IN U

FIG. LX

Y-axis: $\left\{ \begin{array}{c} \text{INCREASE IN ASPHALTENES} \\ \text{MG. PER 10 GMS. OF OIL.} \end{array} \right\}^{1/2}$

X-axis: TIME IN HRS.

Legend:
1. Oil A.
2. 0.2% Sodium acetate
3. 0.1%   "   "
4. 0.025%   "   "
5. 0.05%   "   "
6. 0.4%   "   "

PRINTED IN U.S.A

INCREASE IN ASPHALTENES.

1. 0.2% Sodium cetylate. oil B
2. 0.1%   "   "   "
3. 0.025% "   "   "
4. 0.05%   "   "   "
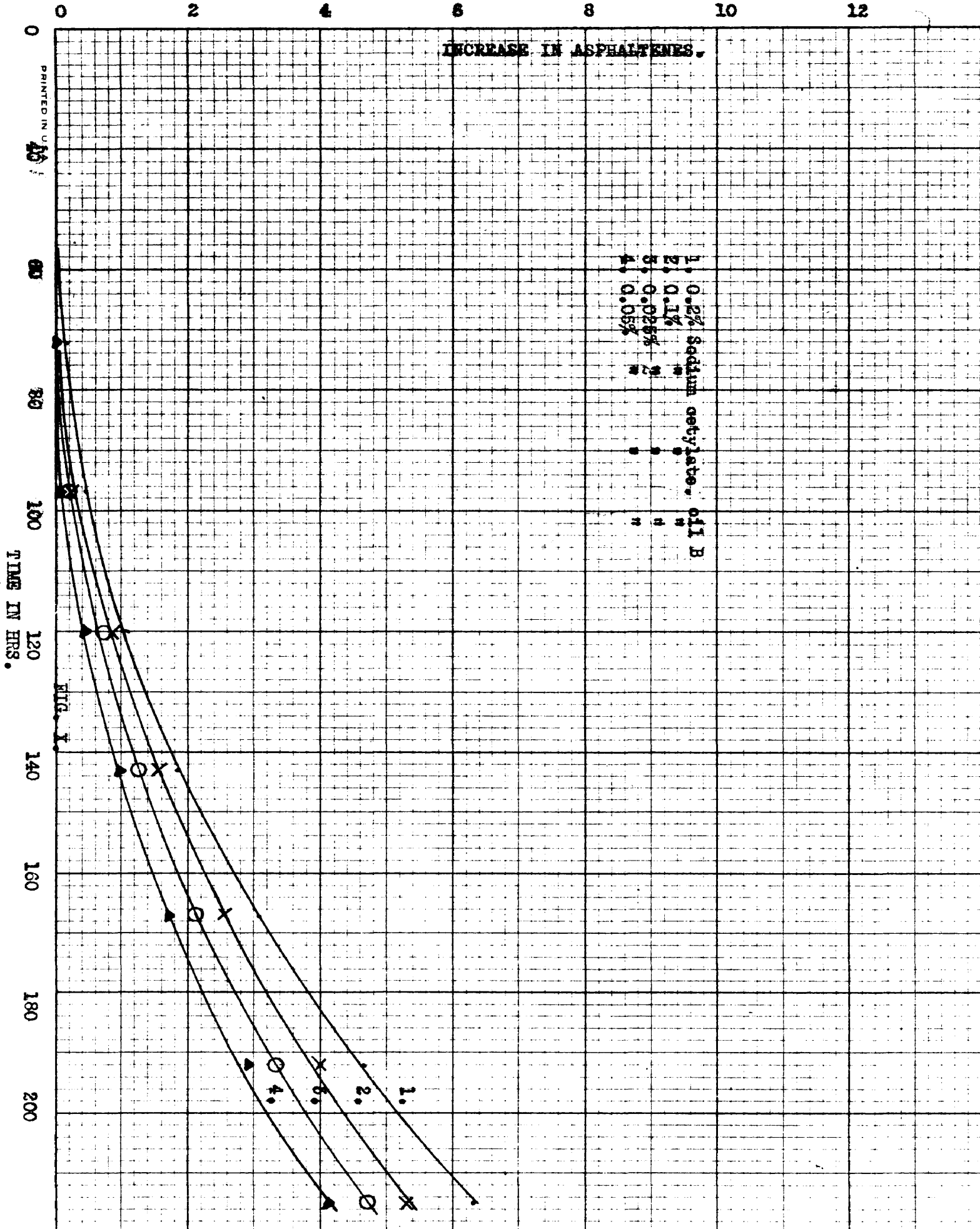
TIME IN HRS.

FIG. I.

FIG. XI

TIME IN HRS.

INCREASE IN ASPHALTENES. MG. PER 10 GMS. OF OIL.

5. 0.05% " "
4. 0.025% " "
3. 0.1% " "
2. 0.05% sodium copylaite.
1. Pure oil B.

FIG. X11
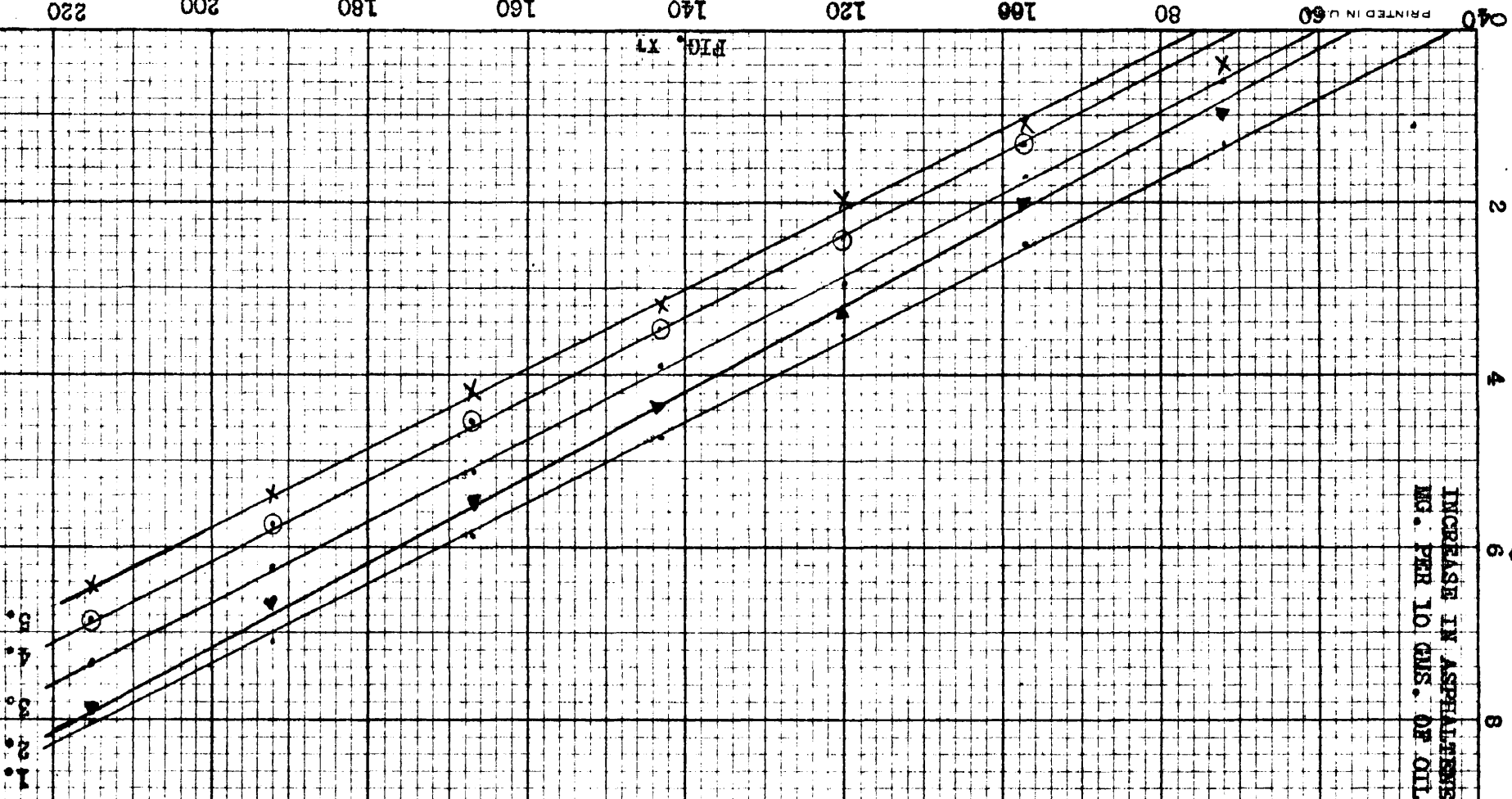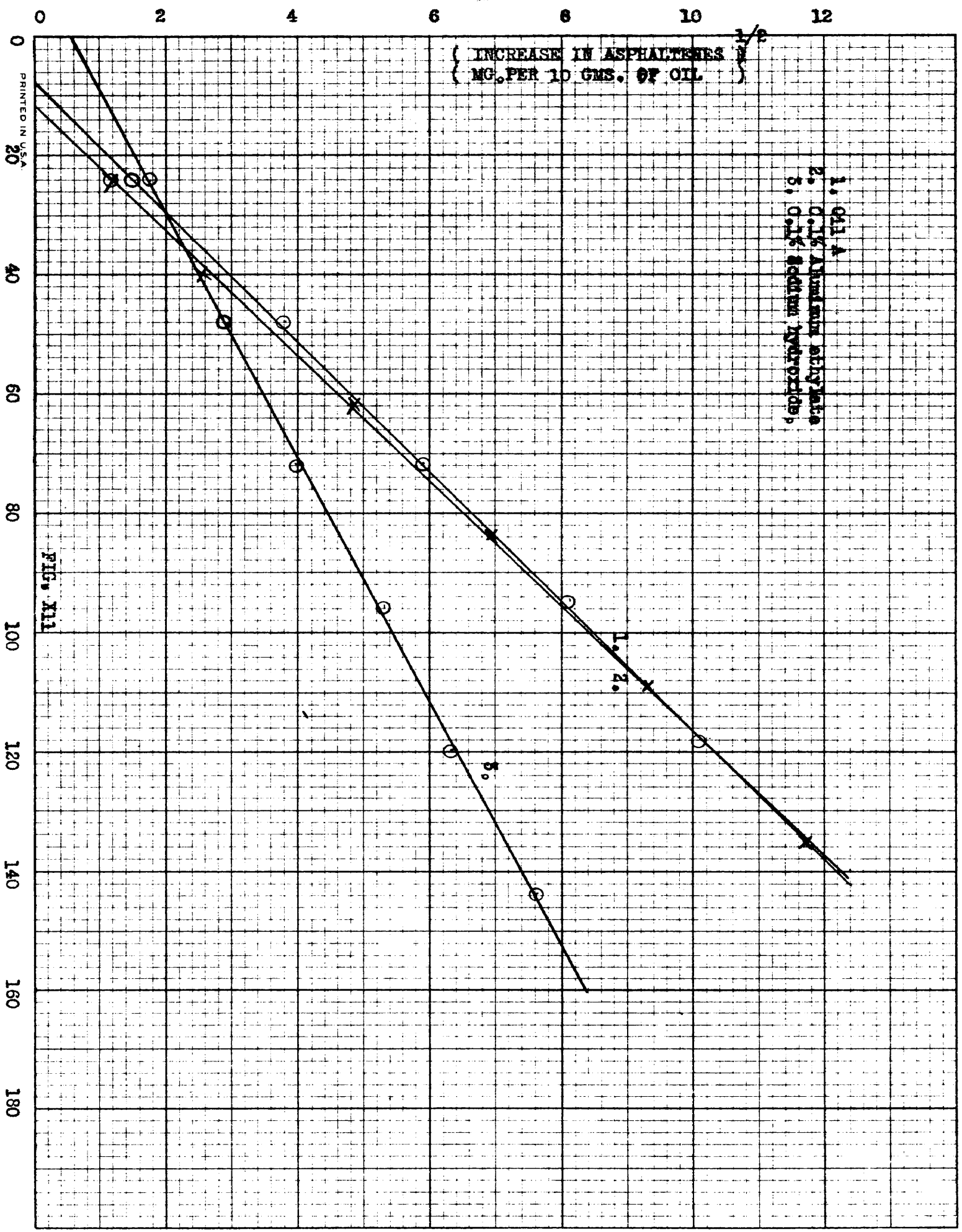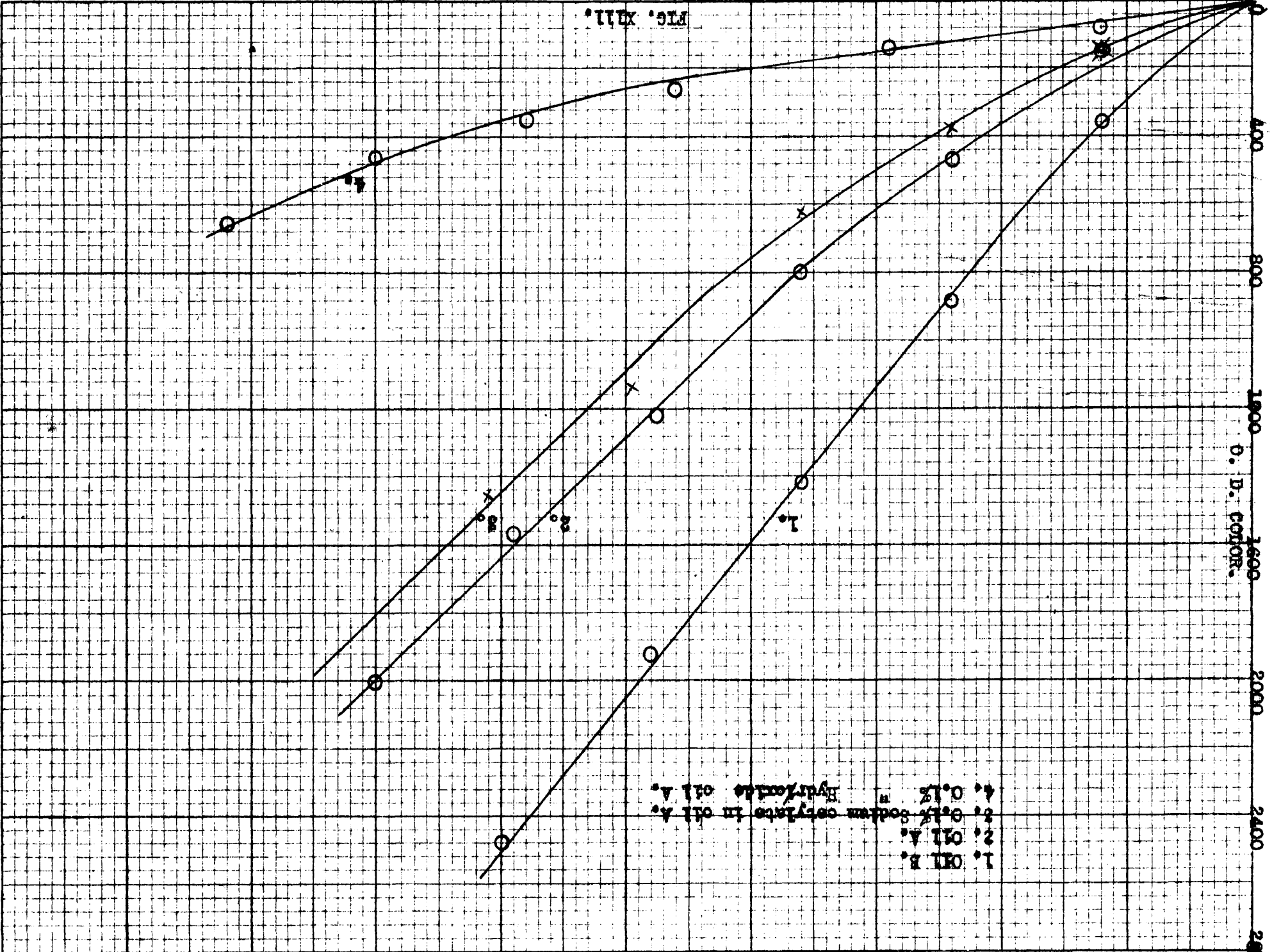
INCREASE IN ASPHALTENES
MG. PER 10 GMS. OF OIL

1. Oil A
2. 0.1% Aluminum stearate
3. 0.1% Sodium hydroxide.

0 20 40 60 80 100 120 140 160 180

FIG. XLII.

O. D. COLOR.

0
400
800
1200
1600
2000
2400
2800

1.
2.
3.
4.

1. OIL B.
2. OIL A.
3. 0.1% Sodium oxylate in oil A.
4. 0.1% Hydroxide oil A.

PRINTED IN U.S.A.

Data from table XI

FIG. XIV

TIME IN HRS.

(INCREASE IN ASPHALTENES)

(MG. PER 10 GMS. OF OIL)·¹/²
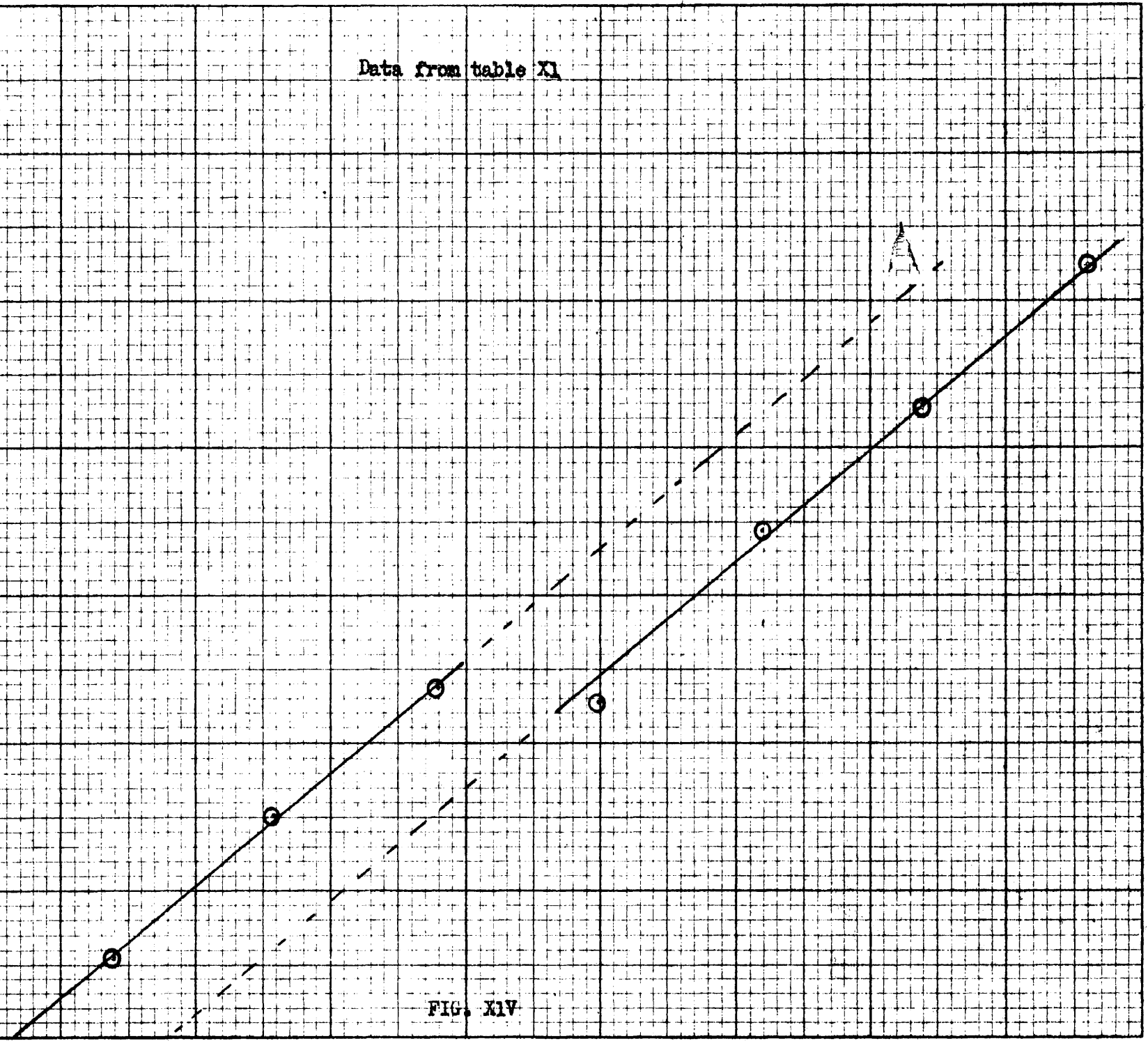
CALCULATIONS

Curve Calculations

Values of k and n (Table XIV) were made by taking values off the curves for $G^{\frac{1}{2}}$ when t equals 50 and 100 hours. Two simultaneous equations were set up and values for k and n were calculated. The equation is $G^{\frac{1}{2}} = kt + n$.

G = asphaltenes in mg. per 10 gms. of oil.

t = time in hours.

k = constant characteristics of the rate of
reaction.

n = constant specific to the oil or inhibitor added.

Color

Optical density colors were calculated from the following equation.

$$O.\ D.\ C.\ = \frac{10^{3}\ D \times 10^{N}}{R}$$

D = optical density of neutral filter.

R = depth of oil or solution in mm. required to
match the neutral filter.

N = number of dilutions in the ratio of 1 to 10.

DISCUSSION OF PLOTTED RESULTS

Oxidation Curves and Empirical Equation

Figures I, III, VII, IX are time vs. asphaltene concentration curves. The oxidation curves are typical of autocatalytic reactions. The curves for the organic inhibitors are similar in shape to those obtained for the sodium alcoholates. This indicates that the function of sodium alcoholates is similar to that of the organic inhibitors.

R. W. Dornte, working on the total oxygen adsorption mechanism for white oils, found the following information.

Ind. & Eng. Chem. Vol. 28, #1, p.27 (1936). Oxidation of white oils by R.W. Dornte.

In discussing total oxygen adsorption vs. time curves he says, " It has been found these curves can be represented by the equation

$$V^{\frac{1}{2}} = kt + n$$

where V = total oxygen adsorbed in c.c.

t = time in hrs.

k = constant characteristic of rate of oxidation reaction.

n = specific constant.

"---This empirical equation has been found to represent the

oxygen adsorption data over the entire range of
temperature and total adsorption which were possible to
investigate.

He further says "--- It is difficult to assign
physical significance to the constant n (in equation given
above). The value of n is probably related to the
inhibition of the reaction by unavoidable foreign materials
and natural inhibitors in the oil."

A similar equation has been found to represent the
asphaltene time curves. These data give straight lines in
all cases. The equation holds well for both the organic
inhibitors tested and the sodium alcoholates investigated.
Some disagreement of the data at the lower concentrations
occurs. However, the general agreement is very good. This
can be observed from Figures II, IV, VI, VIII,IX, XI.

## Discussion of Equation $G^{\frac{1}{2}} = kt + n$

Values of k are a measure of the rate of the
reaction. Negative values of n are a measure of inhibition
of the reaction. The oxidation reaction is delayed for some
period of time depending on the inhibitor and thus a negative
value of n is obtained.

Positive values of n are more difficult to explain.
A positive value of n means some asphaltene concentration at

zero time which is not the actual case. A possible explanation is thus.

The first increment of oxygen along with the inhibitor and some constituent of the oil react to form a new substance which is thrown out as alphaltenes in the asphaltene determination. This new substance then acts as an inhibitor for further oxidation and thus gives a small value of k for the reaction. A marked example of this is S-Di-Beta-napthyl-para-phenylene diamine. This phenomenon is readily understood by examination of Figure V. To substantiate this theory, asphaltene determination were made at shorter interval of time than the previous first test taken at 24 hours. Determination at 1, 5 and 10 hours were made and it can be seen from Fig. V that there is considerable asphaltene content one hour after oxidation is started.

This mechanism can be represented thus.

1. Inhibitor + O_2 + oil $\xrightarrow{\text{very fast}}$ B.

oil + O_2 $\xrightarrow[\text{slow}]{\text{B(catalyst)}}$ asphaltenes
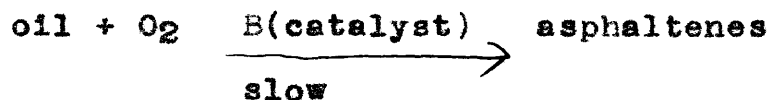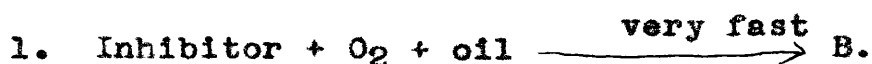
B is asphaltic in nature also.

This reasoning is also supported by the observations of A. M. Wagner and J. C. Brier in their study of inhibitors for drying oils.

Influence of antioxidants on the Rate of Oxidation of Linseed Oil. A. M. Wagner & J. C. Brier, Ind. & Eng. Chem. 23,41,662 (1931).

"---The peculiar behavior of m and p phenylene
diamine in abruptly transforming phenylene diamine-
linseed oil systems from a characteristic green color to
one of tary black soon after oxidation was started at
100°C. led to the belief that these compounds had been
decomposed under the conditions of the experiment and the
decomposition products and not the original compounds were
acting as antioxidants.

"---at 100°C paragallol and alpha napthylamine like
hydroquinone did not influence the rate of reaction
oxidation of linseed oil when added after the conclusion of
the induction period. Meta and p-phenylene diamine, on the
other hand, interrupted the oxidation of linseed oil under
the same conditions. At 30°C, however, p-phenylene diamine
was not able to inhibit the oxidation of linseed oil, whereas
hydroquinone did so very effectively. This fact with the
peculiar behavior of the phenylene diamine during the
experimental work indicates that it is their decomposition
products and not the phenylene diamines themselves that
exercise the antioxygenic influence at 100°C".

The products from the S-Di-Beta napthyl-para phenylene
diamine undoubtedly form some second product B as indicated in
the above mechanism, since the asphaltene concentration at
zero times is greater than the weight of inhibitor added.
This would not be the case if S-Di-Beta napthyl phenylene

diamine simply decomposed.

Discussion of Sodium Alcoholates

Table XIV shows the various values of n and k as
calculated from the equation $G^{\frac{1}{2}} = kt + n$. It can be seen
that sodium cetylate gives the larger negative values of
n. 0.05%. Sodium Cetylate gives the largest negative
value of n for all the sodium alcoholates tested. 0.05%
is the quantity of sodium ethylate and sodium acetonate giving
the best results. The disagreement of 0.2% sodium ethylate
and 0.4% sodium acetonate with the general results is
explained as follows: 0.2% sodium ethylate gives a larger
negative value of n than does 0.1%. By inspection of Table
XVI it can be seen that this quantity of inhibitor showed
a tendency to settle out and produce a hard white scale in
the bottom of the oil tube. Also, the color of the oil
remained a light brown during the entire period of oxidation.
This is quite different from the results observed for 0.025,
0.05 and 0.1% sodium ethylate. Dispersed sodium hydroxide
had a similar effect upon the oil as did 0.2% sodium ethylate.
This white scale formed on the bottom of the oil tube by the
addition of too large a quantity of sodium ethylate is
probably sodium oxide or hydroxide. It is quite soluble in
hydrochloric acid. This white scale formation took place
approximately 12 hours after oxidation of the sample was started.

To determine if a similar effect would be produced with
sodium acetonate, a sample containing 0.4% of sodium
acetonate was oxidized since 0.2% sodium acetonate had
shown a normal effect. As can be seen by examination of
Table XIV 0.4% sodium acetonate acted very similar to 0.2%
sodium ethylate. After about 12 hours a hard white scale
formed on the bottom of the oil tube. The color of the oil
remained a light brown during the period of oxidation and a
larger negative value of n was obtained than for 0.2% sodium
acetonate. A similar effect was noted for sodium cetylate
during the experiment where successive additions of sodium
cetylates were made. After the fifth addition 0.01 gm. of
sodium cetylate a scale formed on the bottom of the test
tube and the oxidation proceeded similar in nature to the
sample containing 0.1% dispersed sodium hydroxide.

Effect of Sodium Hydroxide

As referred to above a sample of oil containing 0.1%
of dispersed NaOH was carried through the oxidation tests.
Figure XII and Table XIV show the results. The sodium
hydroxide soon formed a hard white scale on the bottom of
the oil tube. The color of the oil remained transparent
throughout the oxidation period while the asphaltenes formed
were light yellow in color compared to the usual dark brown
and black asphaltenes usually obtained. As stated above too
large an amount of the sodium alcoholates would produce the

same effect. 0.1% sodium hydroxide gave a value of

m = +0.6 and a low rate or k = 0.049. It is thus seen

that the effect of NaOH decreases the rate of oxidation

markedly.

Results of Successive Additions of Sodium Cetylate

An experiment was carried out to see if the period

of initial oxidation could be delayed indefinitely by

making successive addition of sodium cetylate instead of

the addition of the inhibitor all at once. As shown in

Fig. VI 0.05% sodium cetylate gave the best results. It

can be seen the oxidation apparently starts after about 34

hours. It was decided to make additions of 0.01% gm. every

24 hours to a sample initially containing 0.05% sodium

cetylate. The results of this experiment are shown in Table

XII. It can be observed that the addition of successive

amounts of sodium cetylate delayed the period of initial

oxidation. This same effect has been observed for some

organic inhibitors by Haslam and Frolich.

Mechanism of Oxidation and Action of Negative Catalyst as
Determined by a Dynamic Method. H. T. Haslam & Per K. Frolich,
Ind. Eng. Chem. Vol. 19 #2, p. 292.

They found that by making successive additions of

p-amino-phenol oxidation of a sample could be delayed

indefinitely, while successive addition of diphenylamine to

another sample had no noticeable effect.

Results Using Oil B

Another oil was tested to make sure that the
effect of sodium cetylate as an inhibitor was not specific
to oil A. Oxidation test on oil B using various amounts
of sodium cetylate showed that the best result was obtained
using 0.05%. It can be noted from Fig. XI and Table XIV
that oil B is much more resistant to oxidation than oil A.
Quite large negative values of n are obtained for oil B
using sodium cetylate as an inhibitor.

Relation of Asphaltene Formation and Color Formation

It was believed that it might be possible to
correlate asphaltene formation with increasing discoloration
of the oil. This was soon shown not to be the actual case.
Fig. XIII shows that the curves for color formation and
asphaltene formation do not take place at the same rate.
A sample containing 0.1% NaOH showed rather rapid asphaltene
formation with a very slow rate of discolorization, and vice
versa. Oil B becomes discolored quite rapidly and asphaltene
formation is very slow. Oil A is much less discolored than
oil B but asphaltene formation is much more rapid.

It must be concluded from this that the asphaltic
bodies produced are not always the colored constituents of
the oil, and that the dark coloring matter formed in an oil

from oxidation is not necessarily asphaltic in nature.

Necessity of Oxygen for Asphaltene Formation

A sample of oil A containing 0.05% sodium cetylate was oxidized for 96 hours, then the oxidation stopped with continued heating for another 24 hours. Oxidation was then started again. Fig. XIV represents the results of this experiment. It is readily seen that oxygen is a necessary constituent of asphaltene formation, since no increase in asphaltene formation was noted after oxidation was stopped. Asphaltene formation took place normally after oxidation was started again.

DISCUSSION OF RESULTS

Methods and Material

Oil A is a western base oil in contrast to oil B,
which is a paraffin base oil. All experiments were made
using oil A. Oil B was used as a check to make certain
that the effects observed were not specific to oil A.

The method used for determining the amount of
asphaltene present in a given sample is that set forth
by the "Indiana Oxidation Test". Results by different
operators using the test are shown to check within 10%
of an average. However, duplicate results of a single
observer agree much better. Duplicate determinations
within 5% were consistently obtained in this work. Usually
the agreement was much better. Care was taken to standardize
the procedure as to time of standing before filtering,
washing of precipitate, drying of the precipitate and the
method of preparing the crucible. Better results in this
type of a determination are practically impossible to obtain
due to the unknown nature of the material being tested. A
blank determination was made after the addition of each
inhibitor. Part of most inhibitors were found to be thrown
out as a precipitate in the asphaltene determination.

The colors used in these experiments are known as

optical density colors. The method of determining is described under equipment and procedure. Duplicate results are readily obtained within 3%. This is much better than other colorimeters for determining the color of petroleum oils.

Original test of the effect of sodium alcoholates were made with a mixture of hexal and heptal alcoholates. After the effect was observed pure substances were used.

The sodium cetylate and sodium acetonate were prepared in large enough quantities so that all of it used as inhibitors would have the same constancy of purity. This was done because any slight variation in purity would make the results incomparable.

Ethyl alcohol, xylene, benzene, etc. used as solvents for inhibitors were shown to be inactive as inhibitors themselves. Cetyl alcohol used as such produces an inhibiting effect. This is shown in Fig. VI.0.1%.was used, since that is the amount claimed most efficient by B. W. Story.

U. S. Patent, 1,841,070. Jan. 12, 1932.

It can be noted that sodium cetylate is much more efficient.

Test for Corrosion

Tests were run to determine if the addition of sodium cetylate to the oil would render it corrosive. The results of these tests are shown in Table XV. Addition of sodium

cetylate of 0.025, 0.05, 0.1 and 0.2% showed no effect upon the copper strip in the standard A. S. T. M. method for corrosion. 0.4% of sodium acetonate did show a slight positive corrosion test.

Samples of oil were then allowed to stand with water for 24 hours to see if the inhibitor would be destroyed if an oil containing it came in contact with water. Tests of the water for free bases after 24 hours were negative except in the case where 0.4% sodium acetonate had been added. However, this quantity is far above the amount of inhibitor showing best results as an antioxidant.

Possible Mechanism of Inhibitor Action

The mechanism by which these sodium alcoholates inhibit oxidation may be one of several. First it may destroy a powerful positive catalyst present in the oil. Second it may prevent the initiation of the oxidation mechanism by being oxidized itself. Third, it may interrupt somewhere in the chain the oxidation of hydrocarbons to asphaltenes.

The experimental data show that the initial oxidation of the oil is delayed, also the rate by which the oil is oxidized after it has started is considerably less. Sodium alcoholates undoubtedly interrupt the chain of oxidation reactions of the hydrocarbons. This is substantiated by the fact that the asphaltenes produced while using sodium

alcoholates as inhibitors are much lighter in color than those normally produced. This would indicate that their make-up is also different.

A possible explanation is that the sodium alcoholates acting as basic substances react with the acidic constituents formed and prevent them from acting as autocatalyst toward oxidation.

It also must be noted that there is an optimum amount of these type substances that produce the most inhibiting effect. This phenomenon has also been noted for some organic inhibitors, one being di-phenyl amine. A possible explanation of this is that these substances are converted themselves to positive catalysts. Also it was found that by successive additions of sodium cetylate to a sample being oxidized, produced a much longer delay in the time of initial oxidation. The previous addition being used up or poisoned before another addition of the inhibitor. If a large amount is added at once it is oxidized, destroyed or converted to a positive catalyst before acting as a negative catalyst in the mechanism of retarding oxidation.

$Al(OC_2H_5)_3$ was tried as an inhibitor to determine if other metal alcoholates showed a similar effect. Practically no effect at all was noted for $Al(OC_2H_5)_3$. This would further indicate that inhibiting power of the sodium alcoholates is related to their action as a base. They may be called a "reserve" base.

CONCLUSION

1.   Sodium alcoholates have been shown to act
as inhibitors to oxidation of lubricating oils. Their
action seems most likely one of interruption of the
chain reaction producing asphaltenes. They probably react
with the acidic constituent produced and prevent them from
acting as autocatalyst for further oxidation or prevent them
from polymerizing and forming asphaltene bodies. 0.05% seems
to be the most efficient.

2.   The longer hydrocarbon chain alcoholates
disperse best with the oil and produce the greater effect.

3.   The data representing the asphaltene formation
from oxidation of a sample lubricating oil fit the empirical
equation $G^{\frac{1}{2}}$ = kt + n very nicely.

4.   An explanation has been offered for a large
positive value of n in equation $G^{\frac{1}{2}}$ = kt + n. It was shown
that a large positive value of n indicated that the inhibitors
had combined with oxygen and some constituent in the oil to
produce a new substance but acted as an inhibitor after its
formation.

5.   The rate of discoloration of a lubricating oil
cannot be taken as a measure of the asphaltene formation.
Thus one oil may be discolored very rapidly with little
asphaltene formation, while another may show rapid asphaltene

formation with only moderate discoloration.

6. An ideal inhibitor may be designated as substance producing a very large negative value of n and a small value k in equation $G^{\frac{1}{2}} = kt + n$.

From experimental data obtained in these experiments an ideal inhibitor may be a substance possessing the following characteristics:

1. Large reserve basicity.

2. Soluble in oil.

3. Unaffected by oxidation and heat.