FR-2359

REPORT NO. R-2359

DATE August 1944

SUBJECT

A Method of Analysis for Antioxidant in the New Synthetic R-O-LOO Lubricants

by

Herbert A. Pohl

NAVAL RESEARCH LABORATORY

BELLEVUE, D. C.

August 1944 NRL Report No. P-2359

NAVY DEPARTMENT

Report

on

A METHOD OF ANALYSIS FOR ANTIOXIDANT IN THE NEW SYNTHETIC B-O-100 LUBRICANTS

NAVAL RESEARCH LABORATORY
ANACOSTIA STATION
WASHINGTON, D. C.

No. of Pages: Text - 7 Tables - 2 Plates - 3

Authorization: BuShips Project Order 1121/42 of 1 July 1941; BuOrd Project Order No. 40227 of 22 September 1943.

Prepared by: Herbert A. Pohl
Herbert A. Pohl, Contract Employee

Reviewed by: W. A. Zisman
W. A. Zisman, Senior Chemist, Chief Lubrication Section

P. Borgstrom, Head Chemist, Superintendent Chemistry Division

Approved by:
A. H. Van Keuren, Rear Admiral USN, Director

Distribution:

BuShips	(5)	NDRC	(2)
BuOrd	(5)	BCSO	(2)
BuAero	(5)	ALUSNA London	(3)
SONRD	(2)	BAD	(1)

sbg

TABLE OF CONTENTS

	Page
ABSTRACT	
INTRODUCTION	
A. Authorization	1
B. Statement of Problem	1
C. Known Facts Bearing on the Problem	1
WORK OF THIS LABORATORY	
A. General Investigation of the Methods Available	2
B. Procedure for Analysis	3
(1) Discussion	3
(2) Quantitative Analytical Procedure	4
(3) Qualitative Analysis	5
(4) Precision and Limitations of the Method	5
CONCLUSIONS	7
RECOMMENDATIONS	7
BIBLIOGRAPHY	

APPENDICES

	Table
Reactions of Various Substances with the Ferric Sulfate Sulfuric Acid Reagent	I
Investigation of Used Oils	II

	Plate
Calibration Chart for Pana Analysis with Fe^{+++}	I
Light Transmission vs. Wavelength Curves	II
Correlation of Inhibitor Content with Neutralization Number	III

[redacted]

ABSTRACT

A new analytical procedure for the determination of the antioxidant content of the new B-O-100 fluids is presented. In particular, the recommended method combines simplicity, rapidity, and reliability, even when applied to severely oxidized oils. Using this procedure for analysis, a simple relation was shown to exist between the amount of antioxidant remaining in an oxidized oil and the amount of acidic oxidation products produced by the oxidation.

[redacted]

INTRODUCTION

A. Authorization

1. This investigation was authorized under Bureau of Ships Project Order No. 1121/42 and Bureau of Ordnance Project Order No. 40227.

B. Statement of Problem

2. A class of relatively new synthetic fluids is now available which give good promise of applicability as hydraulic and lubricating oils. Among these new fluids are the type B-0-100 fluids. In order to obtain optimum performance from them, an anti-oxidant is generally added, namely phenyl-alpha-naphthyl-amine, hereinafter referred to as "Pana". Information as to the nature and properties of these new fluids and their antioxidant is now classified as "CONFIDENTIAL", the patent application filed by the manufacturer having been placed under secrecy order by the U. S. Commissioner of Patents. It has become of value to have available a method for the analysis and detection of the antioxidant in studying oxidized oils, engine test samples, and the results of corrosion and aging tests. In addition, the method would be useful in the specification and analysis of new material. To be of general application it is desirable that the method be rapid, simple, and sufficiently specific to be unaffected by likely impurities such as gasoline, sludge, colored material or metal particles.

C. Known Facts Bearing on the Problem

3. At the present time the only available method for the estimation of the Pana content of the B-0-100 fluids is by the combined use of refractive index and differential adsorption. It is of limited application because of its lack of specificity for Pana.[1] Because of this, it was necessary to find a more specific method in order to be able to extend the investigation of the antioxidant content to other than unoxidized or unused oils. For this reason, many of the methods of analysis for amines were looked into. Outstanding among the available methods were the following:

(1) Potentiometric titration with perchloric acid in an anhydrous acetic acid medium.[2]

(2) Steam distillation of the acidified unknown followed by a bromination of the distillate and weighing of the precipitate.[3,4,5]

(3) Nitration.[6]

(4) Steam distillation of the acid medium followed by gravimetric determination of the amine precipitated from the distillate by anhydrous hydrochloric acid in hexane solution.[7]

(5) Selenious acid - sulfuric acid treatment yielding a colored product.[8]

(6) Extraction of the amine with acid followed by direct determination of the amine.[9]

(7) Grignard reaction yielding colorimetric possibilities.[10]

(8) a. Titration with nitrite ion using external indicator.[11]

b. Titration with nitrite ion using potentiometric method.[12]

(9) Development of color using oxidation by ferric ion in sulfuric acid solution, followed by a colorimetric determination.[13]

(10) Development of color using oxidation by benzoyl peroxide.[14]

(11) Development of color using oxidation by nitrous acid in concentrated sulfuric acid.[15]

(12) Color reaction with sodium nitroprusside in acetone.[16]

WORK OF THIS LABORATORY

A. General Investigation of the Methods Available

4. A number of the available methods of analysis were tried and the results, positive and negative, are entered here because of their general interest.

(1) Extraction of the amine from the B-O-100 fluid by an acid solution was found impractical because the B-O-100 fluids, although only slightly soluble in water, are completely soluble in hydrochloric or sulfuric acid solutions of moderate or high concentration (from 4 M to 5 M and higher). The

[redacted]

temperature coefficient of solubility in the acid solutions is like that in water, negative.[17] The amine seemed inappreciably soluble in hydrochloric acid of any concentration less than 7 M.

(2) Direct titration of the oil-amine mixture in an acidified alcoholic solution using sodium nitrite was found impractical because of the sluggish and indefinite nature of the reaction with the amine. Evidence for the presence of peroxides in the original fluid was found.

(3) Attempted precipitation of the amine as the hydrochloride from hexane solutions of the B-O-100 fluids and amine using gaseous hydrogen chloride gave a precipitate four to ten times too large in weight indicating considerable co-precipitation of the B-O-100 fluid with the amine hydrochloride. The method was abandoned.

(4) The color developed with the amine in concentrated sulfuric acid upon the addition of nitrous acid was too transient to be used quantitatively in analyzing for the amine.

(5) An acetone solution of the amine gave no visible reaction with sodium nitroprusside.

(6) An intense, moderately stable red-brown color was developed by heating the oil plus amine dissolved in an alcohol with an excess of benzoyl peroxide. The optimum heating was found to be about five minutes in a boiling water bath. It is possible to determine Pana quantitatively in this fashion by diluting the resultant colored mixture to a constant volume and measuring the depth of color by a suitable means, but chloroform, benzene, or deep coloration in the original oil interfere, thus materially decreasing the value of the method.

(7) The reaction of ferric sulfate in 18 N sulfuric acid with Pana proved capable of quantitative application. The procedure was standardized and adapted to colorimetric analysis of B-O-100 fluids, since they are soluble in sulfuric acid of this concentration.

B. Procedure for Analysis

(1) Discussion

5. The oxidation of Pana by ferric ion in 50% sulfuric acid produces a compound of a very intense blue-purple color. The color develops completely within two minutes at room

temperature and remains unchanged in intensity for at least 30 minutes. It does not markedly disappear in samples kept 90 days. The color produced by this reagent is so intense that the usual oil sample must be diluted one thousand fold before it is of low enough intensity to measure conveniently. This is a valuable attribute of the method for it allows the determination of Pana even in samples originally of deep color.

(2) Quantitative Analytical Procedure

6. One ml. of the oil sample is slowly and carefully pipetted into a 100 ml. volumetric flask and diluted to 100 ml. with pure ethyl alcohol (95%). After shaking and, if necessary, centrifuging or decanting to remove sediment from the alcoholic solution, a one ml. sample of this first dilution is again diluted to exactly 10 ml. with the reagent. The characteristic blue of the colorized Pana, if present, develops quickly and completely at room temperature within 2 to 3 minutes from the moment of mixing. The colored solution is transferred to the colorimeter or photelometer and its light transmission compared with that of pure water. In the present investigations a Cenco photelometer was employed. A Photovolt B-590 filter was used although any similar filter passing only a narrow band of the spectrum in the region 5500 to 6400 A° will suffice. The water cell was 5.0 cm. through and the sample cell was 1.0 cm. through. The observed percent transmission on comparison with the calibration curve established using standards may be read off as percent Pana in the original oil.

7. The calibration curve obtained using the above procedure is given in Figure I.

8. Preparation of the Reagent. Chemically pure concentrated sulfuric acid is diluted with an equal volume of distilled water, and about 3% by weight of ferric sulphate is added to the solution. The mixture is shaken violently and then filtered using suction and a sintered glass filter crucible. It was found convenient to add 2% by volume of "Celite Filter Aid" as this speeds up filtration markedly. The nearly colorless filtrate is usable immediately and is practically of the same transmissivity as pure water. Upon standing several days a white crystalline deposit may form in the reagent. This must be filtered off, but otherwise does no harm to the quality of the reagent. The reagent contains several hundred times more ferric ion than is necessary to oxidize the Pana normally present.

(3) Qualitative Analysis

9. One very small drop of the oil to be examined is mixed in a test tube with 5 to 10 ml. of the reagent. The tube is shaken and the color developed by the end of one to two minutes is noted. If no color develops no Pana is present; if a pale color develops a trace may be present (usually less than 0.1%). If a readily discernible blue develops the amount of Pana present in the oil probably lies in the neighborhood of 0.1 to 0.5%, and a deep blue indicates that the Pana content is high, probably in the order of 2%.

(4) Precision and Limitations of the Method

10. The reproducibility of individual measurements of the Pana content in oils may be judged from the scatter of points in Figure I. The plot of the log of the percent transmission against concentration shows a linear relationship, in agreement with Beer's law.

11. The effect of substances other than Pana upon the analysis has also been investigated. The results in Table I show that relatively few compounds, even of similar type such as aliphatic or primary amines, interfere with the test. Blue colors were developed only by very similar compounds, i.e., diphenyl amine and triphenyl amine; compounds which probably have some value as oxidation inhibitors in any case. From these qualitative tests it was concluded that the present procedure was sufficiently specific for Pana to be of rather general use.

12. An interesting result of these experiments came in the development of intense, stable, and very characteristic colors by benzidine and di-anisidine with the reagent. This means that new and delicate quantitative colorimetric methods of analysis can be made using this reagent on these compounds. Further experiments would doubtless yield new uses for this reagent.

13. In addition to ascertaining the specificity of the analytical procedure it is necessary to show the limits of application in used engine oils or in oils degraded by other means. Table II gives the data for several oils which had been oxidized at elevated temperature and the data on an uninhibited oil which had been run in an Onan engine for a considerable period of time during which the viscosity had dropped 21%. Also given are the original added Pana content and the present apparent Pana content as judged by the procedure outlined in this report. There is an indication that the products

of decomposition of Pana as they occur in used oils interfere to a slight extent with the test. The amount of interference seems proportional to the amount of Pana originally present causing a slightly high reading roughly equivalent to 1/20 of the original amount of Pana present.

14. A comparison of the transmission curves (Fig. II) for the colors generated by the reagent on pure Pana as present in an unused oil and on the oil sample III-1, which presumably contains 0.11% Pana, showed that the colored compounds produced in the oxidized oil by the reagent are probably a complex mixture and not due entirely to pure Pana, for the absorption curve although similar to that of Pana is dissimilar in some respects. The total amount present of all the material capable of producing color with the reagent at this stage of oxidation of the oil is so small, however, that further work on this point was not undertaken (see paragraph 17).

15. The analyses of the used oils were supplemented by analyzing for known amounts of Pana added to them after the oil was oxidized. This was done to determine if possible the effect of any disturbing influences on the analysis. The results (Table II) show that precise measurements were obtained, despite the background of used oil products.

16. As a further check on the reasonableness of the results obtained by this method of analysis, Figure III was constructed and compares the percent remaining of the original Pana as obtained by this analysis with the observed change in neutralization number. There seems to be a good correlation between the two sets of data making the otherwise unchecked results of the Pana analysis seem reasonable. The data seem to approximate an equation of the form

$$\log \Delta N = A(C_o/C) + B$$

where ΔN is the observed change in the neutralization number; A and B are constants; C_o is the original concentration of Pana; C is the final observed concentration of Pana.

CONCLUSIONS

17. a. Several methods for the detection or analysis of the antioxidant content in the B-O-100 fluids have been developed and described. The new and preferred method, oxidation with ferric ion, is simple, specific and not greatly interfered with by color or sludge in oils being analyzed. The precision of the new method compares well with that of the earlier differential adsorption-refraction method which was applicable only to virgin oils. Its application to qualitative tests is very simple and requires only a very small drop of sample.

18. b. The new method is applicable even to severely oxidized oils, although the precision of the determination near the point of disappearance of antioxidant is interfered with to some extent by oxidation products of the antioxidant. This error amounts roughly to 1/20 of the original amount of Pana present.

19. c. The results of the analysis allow a correlation of the antioxidant content and the change of neutralization number during oxidation of the oil. There is systematic change in the neutralization number with the drop in antioxidant content due to oxidation.

RECOMMENDATIONS

20. It is recommended that the procedure described above using ferric ion reagent for the analysis of the antioxidant content be used for the investigation and specification of new or used B-O-100 fluids.

21. It is recommended that this procedure for the determination of phenyl-alpha-naphthyl-amine be considered where needed for the analysis of other lubricants.

BIBLIOGRAPHY

1. NRL Report No. P-2273 of February 1944 "Properties of the Carbide and Carbon Synthetic Polymer B-0-100 Fluids of interest in Lubrication and Hydraulics".
2. Blumrich & Bandel, Angew. Chem. 54 374 (1941).
3. Becker & Hunold, Zt. ges. Shiess und Sprengstoffwesen 28 233, (1933), 28 284 (1933).
4. Bresser ibid, 30 42 (1935).
5. Ellington & Beard, J. Soc. Chem. Ind. 50 151T (1931).
6. Cook, S. G. Ind. Eng. Chem. (Anal Ed.) 7 250 (1935).
7. Craig, D., ibid 9 56 (1937).
8. Dewey & Gelman, ibid. 14 361 (1942).
9. Hodgson & Marsden, J. Soc. Chem. Ind. 58 154 (1939).
10. Meade, J. Chem. Soc. 1939 1808.
11. Craig, D., Ind. Eng. Chem. Anal. Ed. 12 345.
12. Singh & Ahmed, J. Ind. Chem. Soc., 15, 416 (1938).
13. Thiel, A. Z. Electrochem., 35, 274 (1929).
14. Merck's Index, 5th Ed., Test #915.
15. Sidgwick, N. V., Organic Chemistry of Nitrogen (1937) p. 62.
16. Merck's Index, 5th Ed., Test #2115.
17. NRL Report No. P-2273, Section (h) of February 1944.

Table I

Reactions of Various Substances with the Ferric Sulfate-Sulfuric Acid Reagent

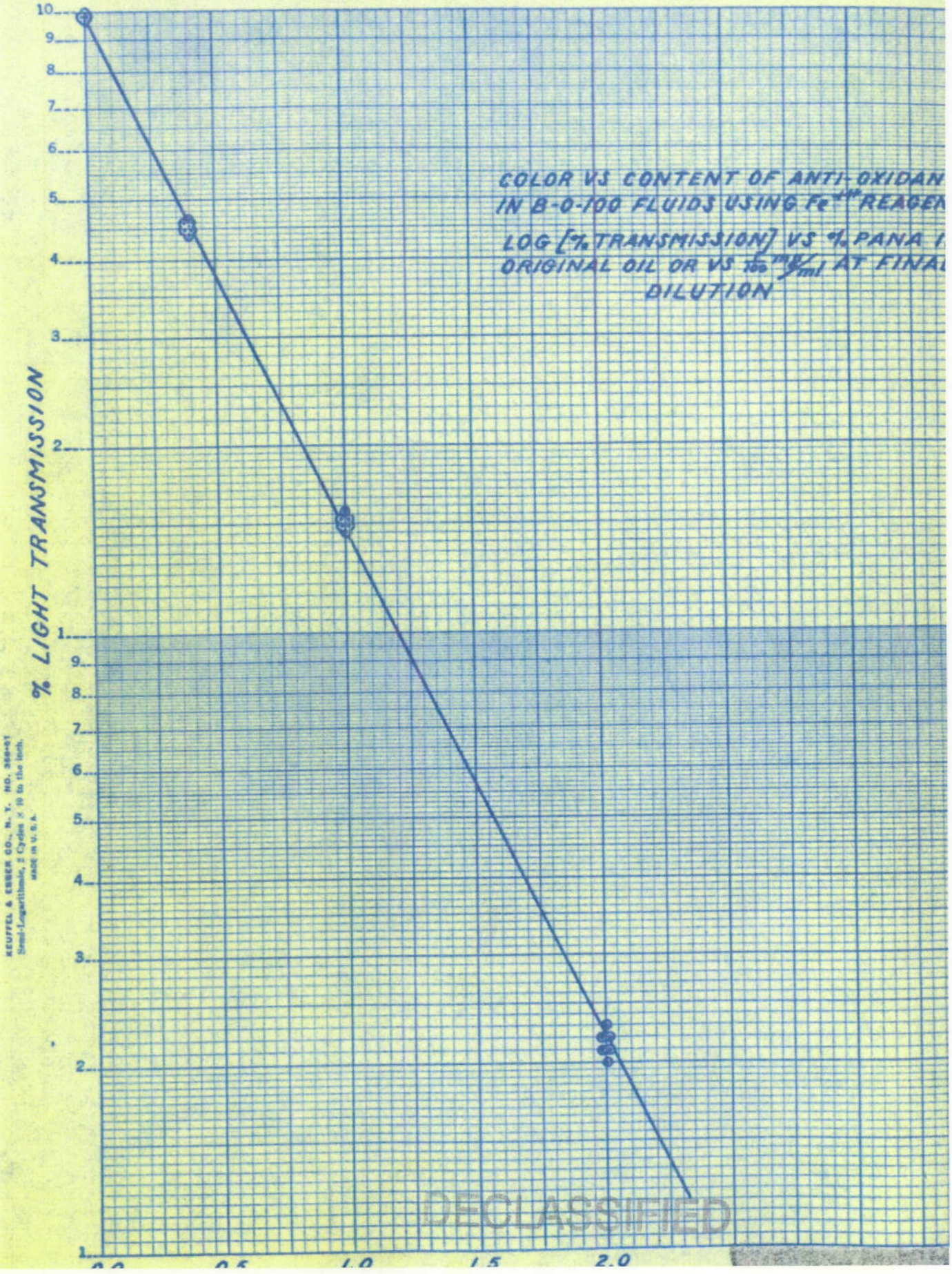
Substance	Color developed at end of test	Depth of color developed
aniline	none	none
methyl aniline	"	"
dimethyl aniline	"	"
p-toluidine	"	"
xylidine	"	"
dipicrylamine	yellow	pale
diphenylamine	blue-purple	deep (very stable)
phenyl-alpha-naphthyl-amine (Pana)	" "	" " "
triphenylamine	green-blue	" " "
benzidine	yellow	" (stable)
dianisidine	red	" "
2-4-dimethyl quinoline	yellow	pale
dimethyl glyoxime	"	very pale
methylene blue	blue-green	moderate
morpholine	yellow	very pale
beta naphthol	"	" "
p-nitro phenyl hydrazine	"	pale
di-phenyl hydrazine HCl	green	pale
alpha-benzyl, alpha-phenyl, hydrazine HCl chlorides	yellow-green	"
	" "	"
aviation gasoline containing U.O.P. #4 inhibitor	none	none

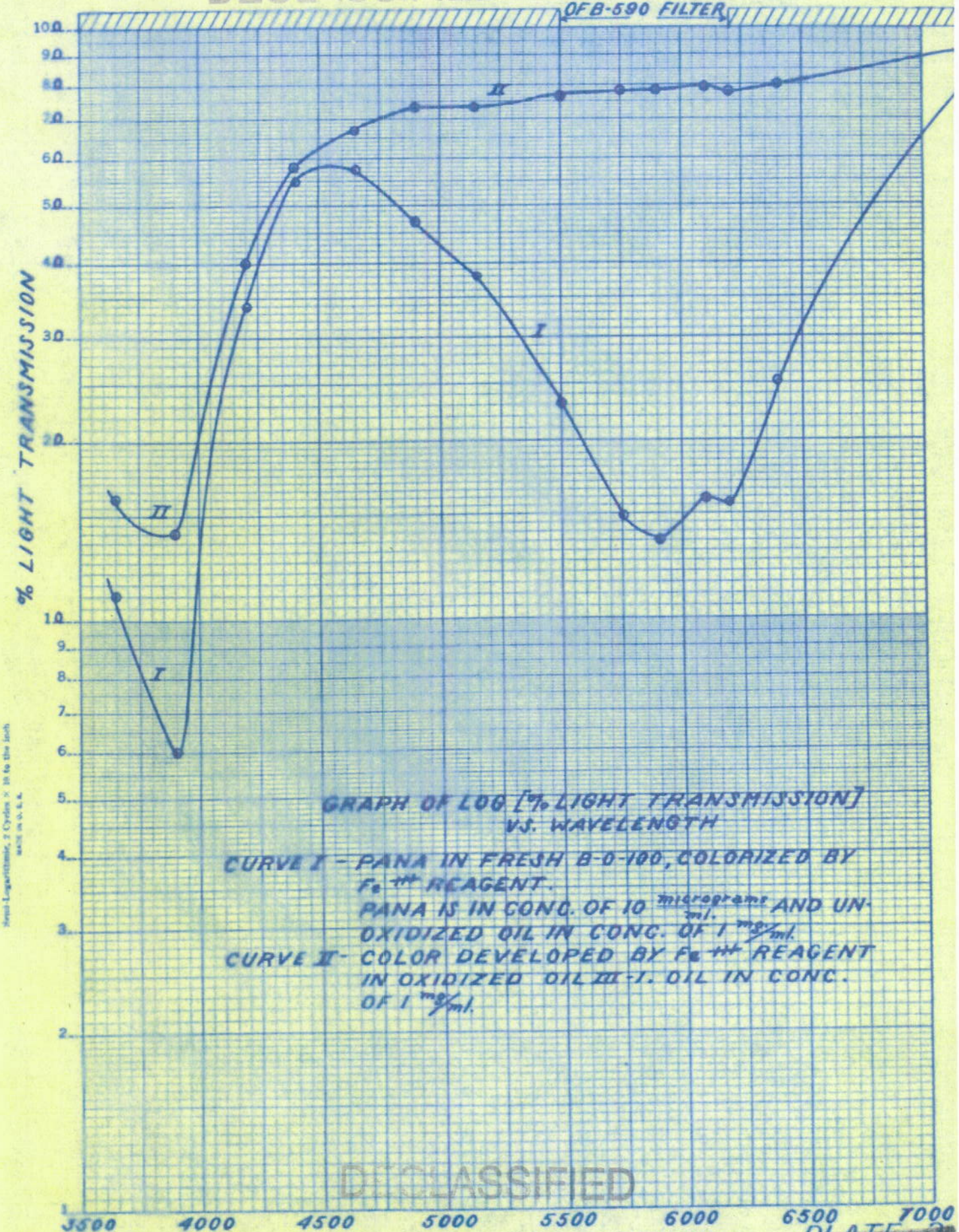
Table II

Investigation of Used Oils

Type no. of B-O-100 fluid	135	250	250	135	250	250	250	400
Run number	XIII-1	III-1	III-2	XI-1	IV-1	XIV-1	B-401*	4
Temperature (°F) of run	300	200	200	250	200	250	--	300
Time of run (hrs.)	200	211	211	208	208	215	72	187
Original neutralization number	0.2	0.78	0.2	0.1	0.1	0.20	--	--
Final neutralization number	100	1.3	60	1.5	0.16	0.28	--	--
Change in neutralization number	100	0.5	60	1.4	0.06	0.08	--	--
Materials added, other than Pana	none	1/4% copper naphthenate	1/8% copper naphthenate	Pb, Fe, Cr, and bronze	1/2% acid palmitic	none	none	none
Total percent Pana in original	2.0	1.0	0.5	2.0	2.0	2.0	0.0	0.25
Total percent Pana found at end of run	0.11	0.13	0.03	0.13	1.78	0.99	0.00	0.01
Percent of original Pana found	5.5	13	6	6.5	89	50	--	4
Percent Pana added to oxidized oil (as measured by weighing in)	0.40	0.40	0.40	0.40	0.40	0.40	0.40 1.00 2.00	--
Percent Pana added to oxidized oil as measured by analysis	0.38	0.40	0.39	0.39	0.37	0.45	0.39 0.98 1.97	--

* Run in Onan engine for 72 hrs. at end of which time the viscosity had dropped 21.3%.





GRAPH OF LOG [% LIGHT TRANSMISSION]
VS. WAVELENGTH

CURVE I - PANA IN FRESH B-0-100, COLORIZED BY Fe^{+++} REAGENT.
PANA IS IN CONC. OF 10 micrograms/ml. AND UNOXIDIZED OIL IN CONC. OF 1 mg%/ml.

CURVE II - COLOR DEVELOPED BY Fe^{+++} REAGENT IN OXIDIZED OIL III-1. OIL IN CONC. OF 1 mg%/ml.

PLATE 2

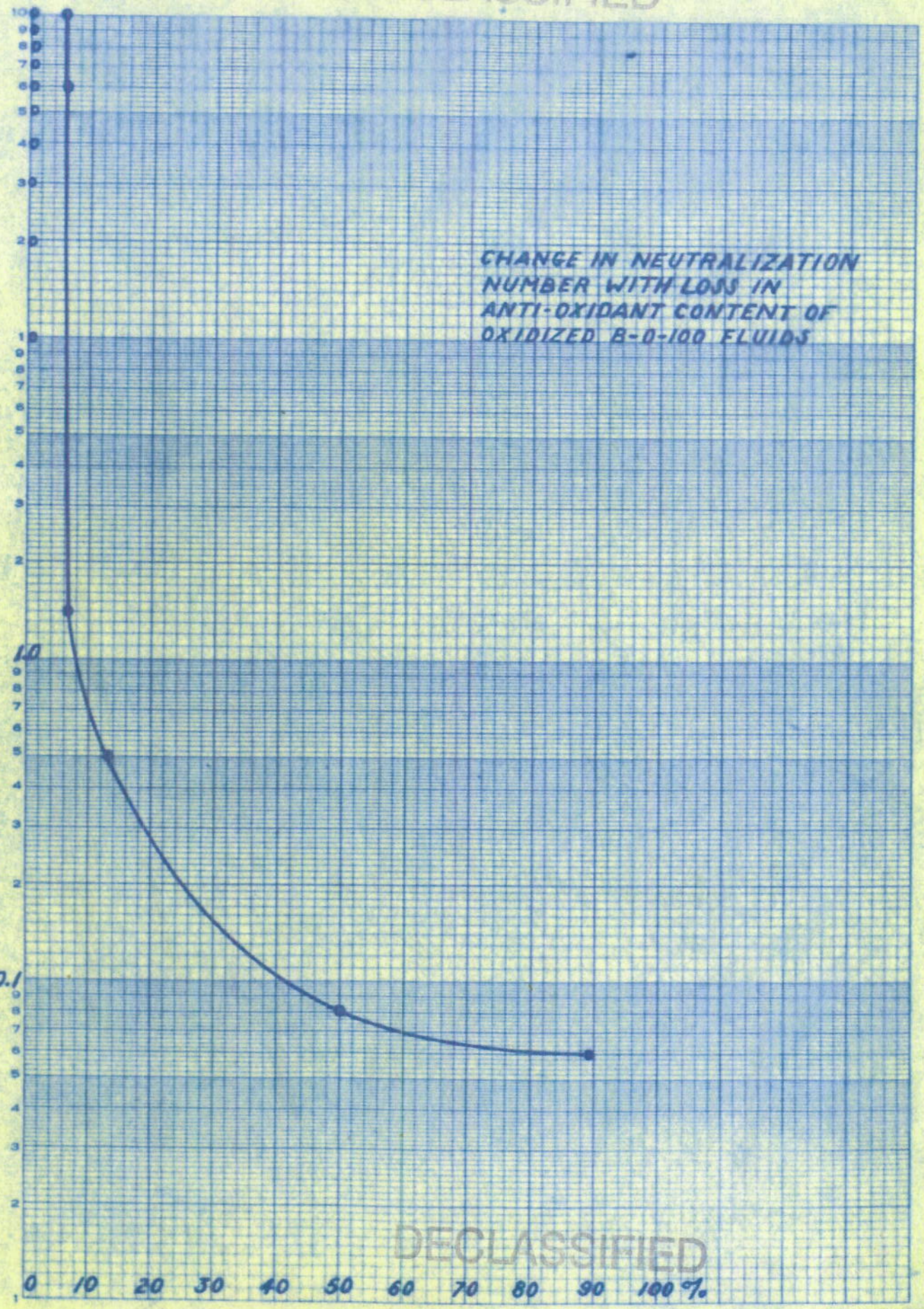
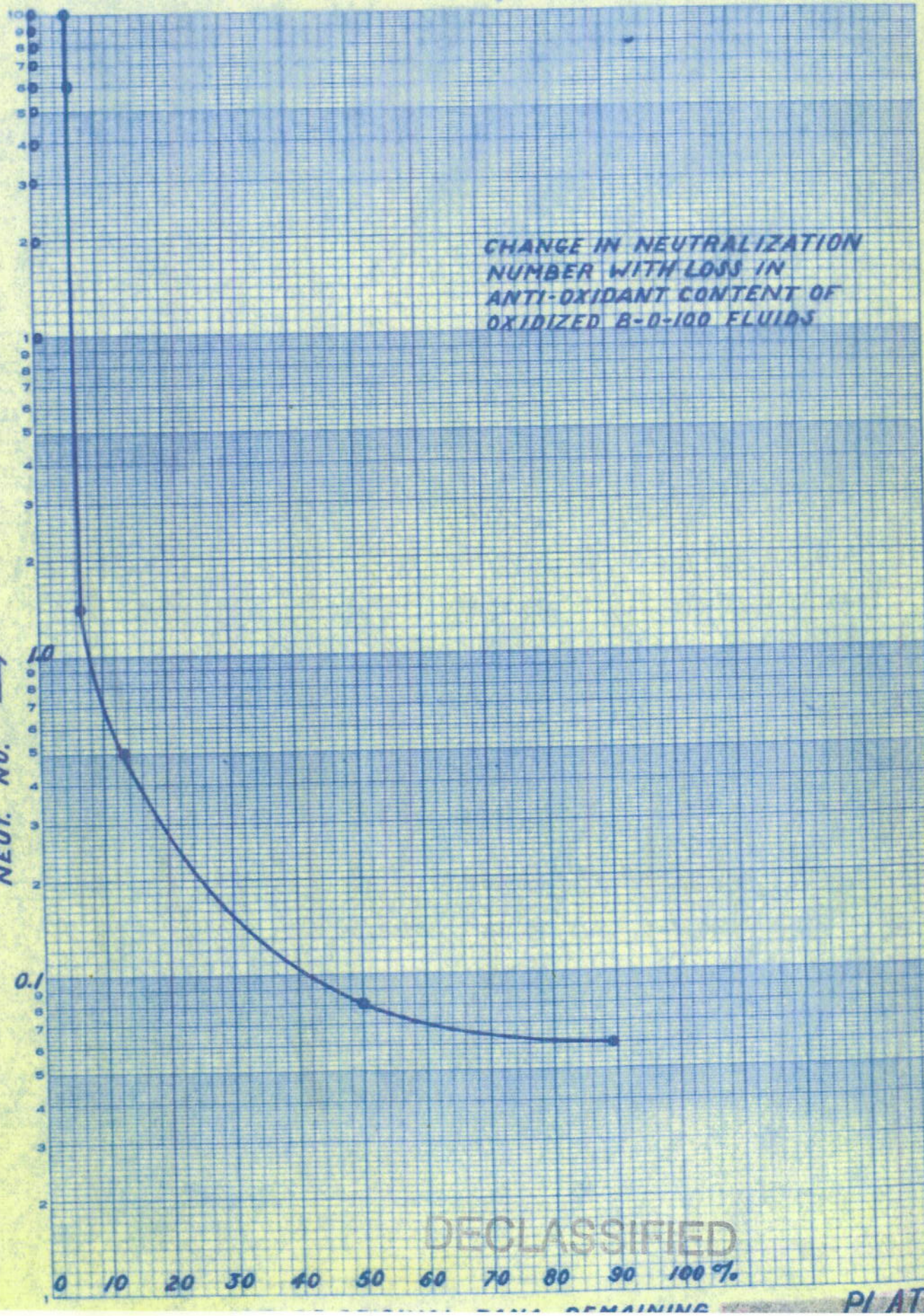


PLATE 3



PLATE