DECOLORIZING PROPERTIES OF OKLAHOMA BENTONITE

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By

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TABLE OF CONTENTS

SUMMARY

This study was made to determine the decolorizing properties of Oklahoma bentonite.

At the present time Fuller's earth and activated bentonite are being shipped to Oklahoma from California and Texas for the purpose of decolorizing petroleum fractions. In western Oklahoma there are large undeveloped deposits of bentonite which if utilized would represent a reduction in cost to the petroleum industry of this state.

The optimum conditions necessary to activate the Oklahoma bentonite were found to be; temperature, 185°F.; time, eight hours; acid concentration, 20% by weight concentrated sulfuric acid.

The optimum conditions of contacting oil with the Oklahoma bentonite were found to be; adsorbent concentration, ten grams of activated Oklahoma bentonite per 300 ml. oil; time, 20 minutes; temperature, 600°F.

Contacts were also made varying the adsorbent concentration for untreated Oklahoma bentonite, and for a standard brand of activated bentonite from California, Filtrol X-202.

The Oklahoma bentonite, after suitable acid treatment, proved to have a decolorizing power equal to that of Filtrol until higher adsorbent concentrations were reached. At the concentrations usually used in the refinery, between one and ten grams per three-hundred milliliters of oil, the adsorbing power of Filtrol and Oklahoma bentonite are equal. At the higher adsorbent concentrations, the Oklahoma bentonite has an efficiency of approximately 80% that of Filtrol.

The untreated Oklahoma bentonite was found to have a decolorizing power unusual to this type of clay. Compared to the Filtrol, the raw Oklahoma clay possesses a 50% efficiency in decolorizing oil. This is an even higher decolorizing power than that reported for Fuller's earth, which decolorizes one-fourth to one-third as much as an activated clay.

INTRODUCTION

All of the clays of industrial importance in decolorizing lubricating oils are composed chiefly of the mineral montmorillonite. The decolorizing clays are divided into two main classes, (1) Fuller's earth or naturally active clay and (2) sub-bentonite or activated clay. The former, Fuller's earth, is not processed except for drying and sizing and possesses a relatively low adsorbing power in decolorizing oil. The activated clays are acid leached to give them a decolorizing efficiency about four times that of Fuller's earth.

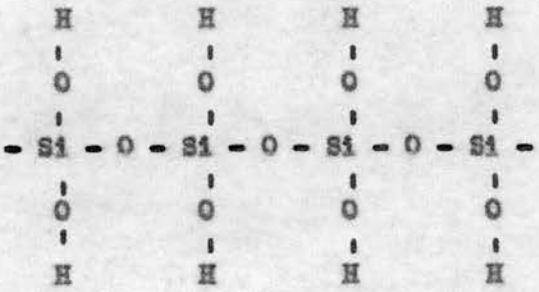
The Oklahoma bentonite used in this investigation was obtained from a deposit located five miles southwest of Woodward, Oklahoma.

The refining of lubricating oil by using clay is as old as the industry itself. The constituents which the clay is capable of removing are primarily "unsaturated compounds and next in order those that contain oxygen, nitrogen, and sulphur. The petroleum resins are strongly adsorbed and are characterized by unsaturation and a high content of oxygen."[1] The undesirable components of the oil named above include the principal color compounds, so it has become a custom to measure the extent to which the oil has been refined by the color. The use of activated clays not only produces a more saleable product but also has the advantage of removing many corrosive elements from the oil.

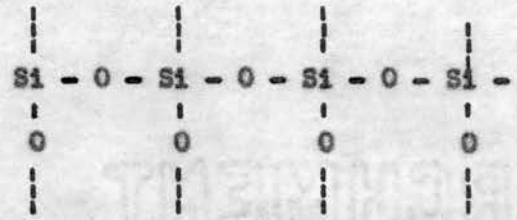
Adsorbent clays have been classed as hydrous magnesium aluminosilicates. Clays from different geological locations may contain a differnet divalent base than magnesium. The raw clay has a greasy, soapy texture, and a color ranging from coal-black to pure white.

X-ray patterns have shown that montmorillonite is composed largely of exceedingly fine plate-like crystals. "Recent X-ray work has shown that the plates themselves probably consist of alternate layers of alumina and silica, bonded together through oxygen bridges."[2] The interlattice water is present as hydroxyl groups and is not driven off until fairly high temperatures (in the range of 600°C.) are reached. Upon losing this chemically bound water, the crystal structure breaks down, leaving nothing but silica gel which will not decolorize oil.

Many theories have been presented as to the adsorbing action of the clay. The most widely accepted theory is that presented by P. G. Nutting.[3, 4, 5] The action of the clay is that of selective adsorption. During the acid treatment, certain soluble constituents are removed, including any alkaline atoms such as calcium, magnesium, sodium, etc. These basic atoms are replaced by hydrogen from the acid. The hydrogen atoms are linked by oxygen to the silicon and aluminum. This structure can be illustrated by the following sketch of a part of a hydro-silicon chain:



With mild heating the two hydroxyl groups combine with the hydrogen from the other to form a molecule of water. Thus, after heating, the structural formula would be as follows:



The open bonds produced in this way are now able to become attached to alkyl or weakly basic radicals, producing insoluble silicates.

In actual refinery practice, the activated clay is fed into the oil stream as a finely divided powder, the slurry heated to the optimum temperature and filtered in a continuous operation. The clay dosage, contact time and temperature differ for the different oil cuts. The process is easily controlled and flexible in that the same equipment can be used for different oil cuts by merely changing the operating conditions.[6, 7, 8, 9]

EQUIPMENT

The experimental work was divided into two separate operations: (1) acid treatment of the Oklahoma clay and (2) contacting the treated clay with the oil. The acid treatment was carried out in standard laboratory apparatus as shown in Figure 2. The clay-acid mixture was agitated in a three-liter beaker. An asbestos pad protected the bottom of the beaker from local over-heating. A glass stirrer which extended the full width of the beaker was so designed as to lift the clay-acid mixture up and prevent settling at any time during the acid treatment. A syphon was used to replace the water which evaporated during the treating time.

The laboratory contacting apparatus, as shown in Figure 1 and 1-A, was similiar to that used by the Filtrol Corporation. It consists of a wrought iron pot made from two four-inch collars welded together. (An inch of threads at the top permits the pot to be attached to a fixed head in the contactor assembly). A wrought iron plate welded to the bottom completes this part of the apparatus. Attached to the fixed head are a steam inlet tube, thermometer well, mechanical stirrer, and a water-cooled condenser. The steam is used to keep a non-oxidizing atmosphere above the oil in the pot. The condenser provides a steam outlet and a means of regulating the steam flow by the overhead condensate. The steam must be absolutely dry when it enters the pot to prevent the oil charge from foaming and coming out the condenser tube. Two burners with wing tips were used to super heat the steam. A blow-off valve, located just before the super heated section, was kept open during runs to guard against any

condensate getting into the pot. The oil was filtered in a buchner funnel using vacuum.

The color of the oil was determined by using a Cenco Sheard Sanford Photelometer, shown in Figure 3. The photelometer scale reads from 0 to 100. The adsorption cells used were standard 1 cm-12 cc capacity. A standard orange filter was used on all readings. The color scale used was an arbitrary one, the standard being a setting of 100 on the photelometer with distilled water and the orange filter before each color determination.

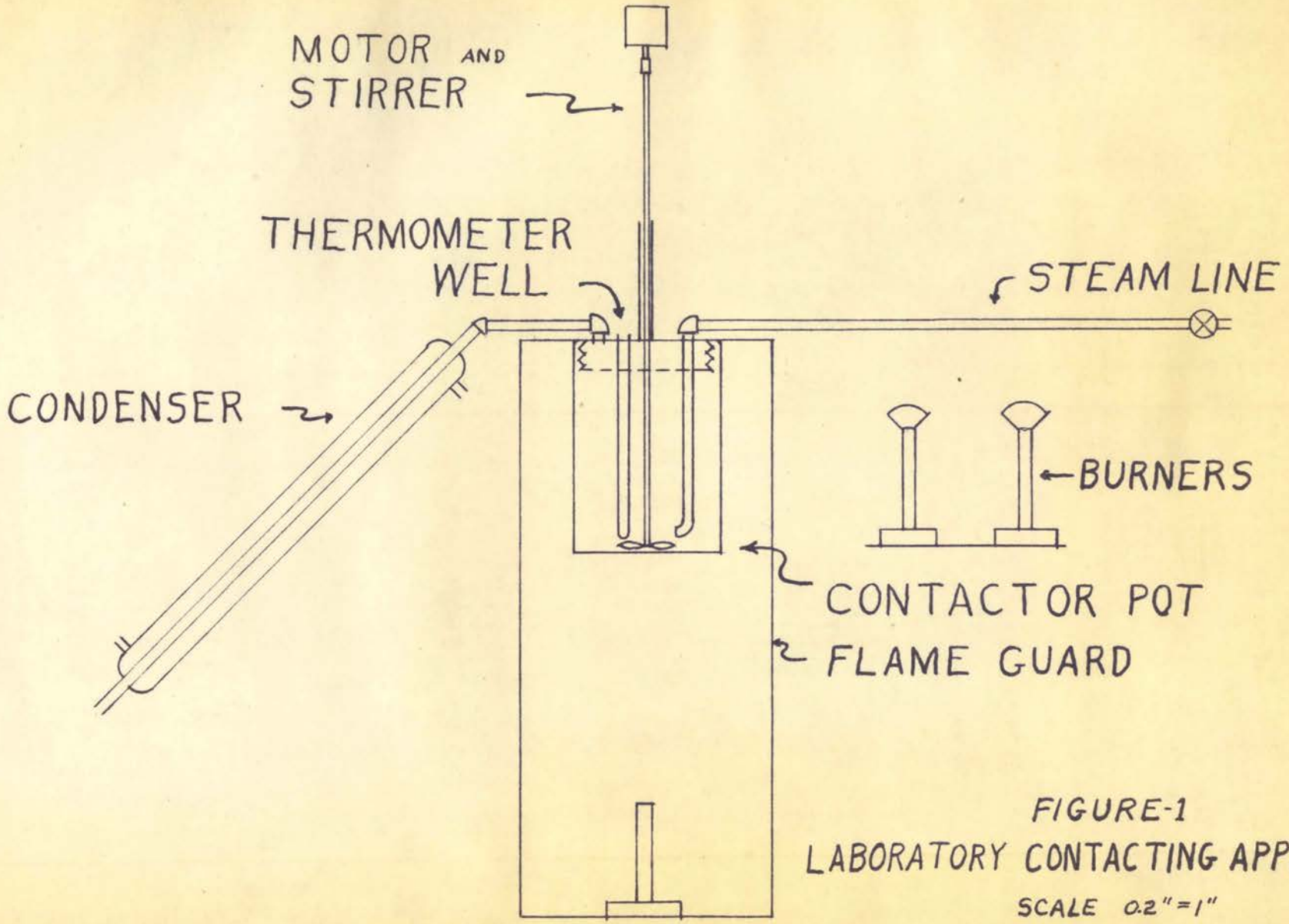


FIGURE-1
LABORATORY CONTACTING APPARATUS
SCALE 0.2" = 1"

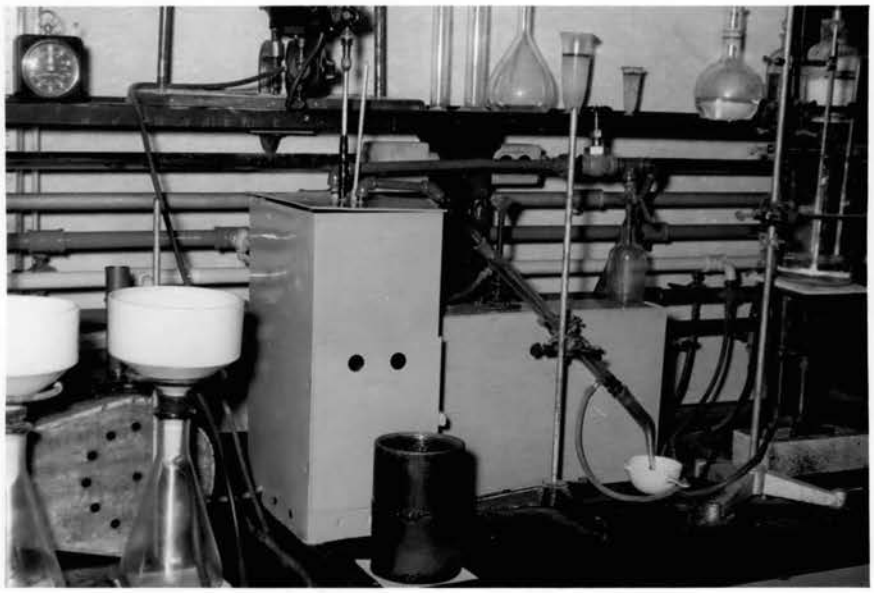


Figure 1-A

Laboratory Contacting Apparatus

Figure 2

Acid Treating Apparatus

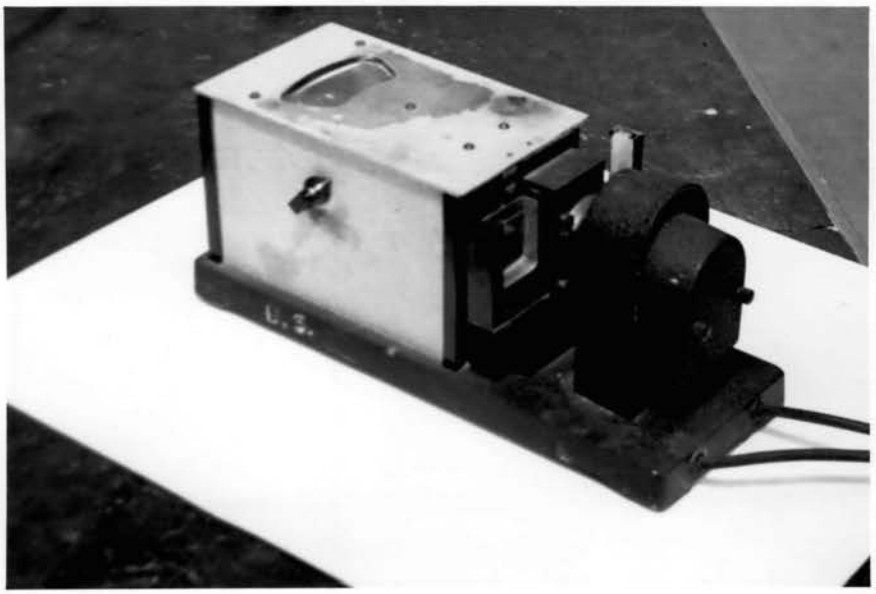


Figure 1

Cenco Sheard Sanford Photelometer

PROCEDURE

I. Activation of bentonite.

The bentonite was crushed to approximately one-quarter inch size particles and dried at 220°F. in a constant temperature oven for one hour. It was then ground with a mortar and pestle to pass a 200-mesh screen. Each batch consisted of 200 grams of bentonite and 500 grams of dilute sulfuric acid. A constant stirring rate of 90 r.p.m. was used.

The optimum temperature of acid treatment was found by making treatments at six different temperatures over the range of 110°F. to 210°F. An acid concentration of 20% by weight and a time of eight hours was used for each of the treatments.

To determine the optimum time of acid treatment, activation was carried out at 210°F. using an acid concentration of 20% by weight for time intervals ranging from two hours to twelve hours.

Treatments were then carried out using acid concentrations varying from 10% by weight, to 25% by weight. The temperature and time were held constant at 210°F. and eight hours.

After each acid treatment, samples were filtered and washed four times, using one liter of distilled water for each wash. The samples were then dried at 220°F. for two hours.

II. Contacting Process.

Each of the 24 samples of activated bentonite was used to decolorize oil samples in the following manner: 8.55 grams of bentonite was added to 300 ml. of No. 5291 Continental bright stock.

These proportions are representative of those used in an oil refinery. The contacting cycle used was that recommended by the Filtrol Corporation[10] for contacting bright stocks, and is as follows:

Preliminary: Turn superheated steam on to blow the line free of condensed water. The contactor pot with the oil-adsorbent mixture is screwed in place and the stirrer is adjusted to give a uniform rate of 400 r.p.m. throughout the entire cycle.

Beginning of the Run: Heat is applied at a uniform rate, the average rate of temperature rise being approximately 50°F. per mimute.

300°F.: The superheated steam is admitted and regulated to give a condensed steam overhead of approximately one ml. per mimute.

25 Mimutes at 550°F.: The fire is turned off, and the door of the flame guard is opened.

22 Mimutes (approximately) at 440°F.: Turn off superheated steam from oil-adsorbent mixture.

25 Mimutes (approximately) at 350°F.: Stop stirrer, remove contactor pot, and filter contacted oil immediately through a suction funnel.

After filtering, the oil sample was placed in a bottle, stoppered, and allowed to cool to room temperature. Color of the treated oil was then determined using a photelometer. The photelometer was first set to read 100, using distilled water and an orange filter. A reading was then taken through the treated oil.

The optimum conditions of acid treatment were determined by plotting the color of the oil produced by each of the samples against the variable for that sample. A sample of clay was then activated using the optimum conditions of time, temperature, and acid

concentration. This final sample of clay was then used to determine the optimum conditions of contacting the clay with the oil.

First, a series of contacts was made varying the weight of clay per 300 ml. of bright stock using the Filtrol contacting cycle. Contacts were made using weights ranging from five to thirty grams of clay.

Using the optimum clay dossage, the optimum contact time and temperature were determined by making a series of contacts using specific times at different temperatures. Contacts were made for 10, 20, 30, and 40 minutes at each of the temperatures 300, 400, 500, and 600°F. The contacting cycle was as follows:

Preliminary: Turn superheated steam on to blow the line free of condensed water. The contactor pot with the oil-adsorbent mixture is screwed in place and the stirrer is adjusted to give a uniform rate of 400 r.p.m. throughout the entire cycle.

Beginning of the Run: Heat is applied at a uniform rate, the average rate of temperature rise being approximately 50°F. per minute.

300°F.: The superheated steam is admitted and regulated to give a condensed steam overhead of approximately one ml. per minute.

Specified Time at Specified Temperature: After the specified time has elapsed, the fire is turned off and the door of the flame guard opened. The oil-adsorbent mixture is allowed to cool to 350°F., superheated steam is turned off, and the oil is filtered.

The treated oil was then bottled, stoppered, and allowed to cool to room temperature, and the color determined using the photelometer. The color plotted against the variables of weight of clay,

time and temperature gave the optimum conditions of the contacting process.

Series of runs were made with Filtrol X-202, activated bentonite, and untreated Oklahoma bentonite for comparison. The standard Filtrol cycle was used, and the weight of both the Filtrol and untreated clay was varied from 5 to 30 grams.

RESULTS

ACTIVATION OF THE BENTONITE.

Each of the three variables of acid treatment was plotted against the color of oil produced in the contacting process.

Figure 4 is a plot of temperature of acid treatment versus photelometer reading. The curve rises, levels off at a maximum reading of 62.5 on the photelometer scale at a temperature of 185°F. of acid treatment, and drops to a lower value of 60 at 210°F. The lower reading of 60 at 210°F. probably resulted for the reason presented by P. G. Nutting. "Removal of all soluble bases by long leaching in hot acid destroys the crystal lattice, leaving only iso-tropic silica gel, highly adsorptive for water but of low adsorbing power for oils."[5] The optimum temperature of acid treatment was found from Figure 4 to be 185°F.

Figure 6 shows a plot of photelometer readings versus time of acid treatment. A maximum reading of 60 was obtained at a time of eight hours. The lower values obtained by acid treatment of longer than eight hours were caused by the destruction of the crystal lattice with long leaching in hot acid as shown by the temperature curve previously mentioned.

The third variable of acid treatment, acid concentration, is shown plotted versus photelometer readings in Figure 5. This curve shows a maximum value of 60 at 20% by weight of concentrated sulfuric acid.

The optimum values of acid treatment were thus found to be 185°F., 8 hours acid treatment, and 20% acid concentration. These values

compare well with those reported in the literature for activation of bentonites from other localities. E. W. Zublin[11] gives average values of 210°F., 8 hours and an acid concentration of 20% by weight.

CONTACT PROCESS.

Figure 7 shows the decolorizing power of different weights of acid treated Oklahoma bentonite. The photelometer readings increase linearly with weight of clay until ten grams is reached, at which point the curve tends to flatten out. This is an indication that the clay has removed from the oil all of the colored constituents it is capable of removing. P. G. Mutting[5] states, "The decolorizing power of both naturally active and acid-activated adsorbent clay approaches a fixed upper limit." Ten grams of bentonite per three hundred milliliters of oil was taken as the optimum adsorbent concentration.

The optimum time and temperature are shown in Figure 8. Time of contact was plotted versus photelometer readings with temperature as the parameter. The curve representing the contact at 600°F. produced the optimum color. There was slight loss of oil at this temperature, but it was so small as to be considered negligible. The optimum temperature and time of contacting are therefore 600°F. and 20 minutes.

Figure 7 also has plotted on it adsorbent concentration curves for Filtrol X-202 and untreated Oklahoma bentonite. The curves show that the Filtrol possesses an adsorbing power equal to that of activated Oklahoma bentonite until an adsorbent concentration of 10 grams per 300 ml. of oil is reached. At this point both curves tend to flatten out. The Filtrol, however, decolorizes to a greater extent

at the higher concentrations.

The adsorbent concentration curve for the untreated bentonite proves that the clay is naturally active to a certain extent. Using 20 grams of untreated clay per 300 ml. of oil, a decolorizing efficiency of 70% is obtained, compared to the decolorizing power of the optimum value of 10 grams of treated Oklahoma clay per 300 ml. of the same oil.

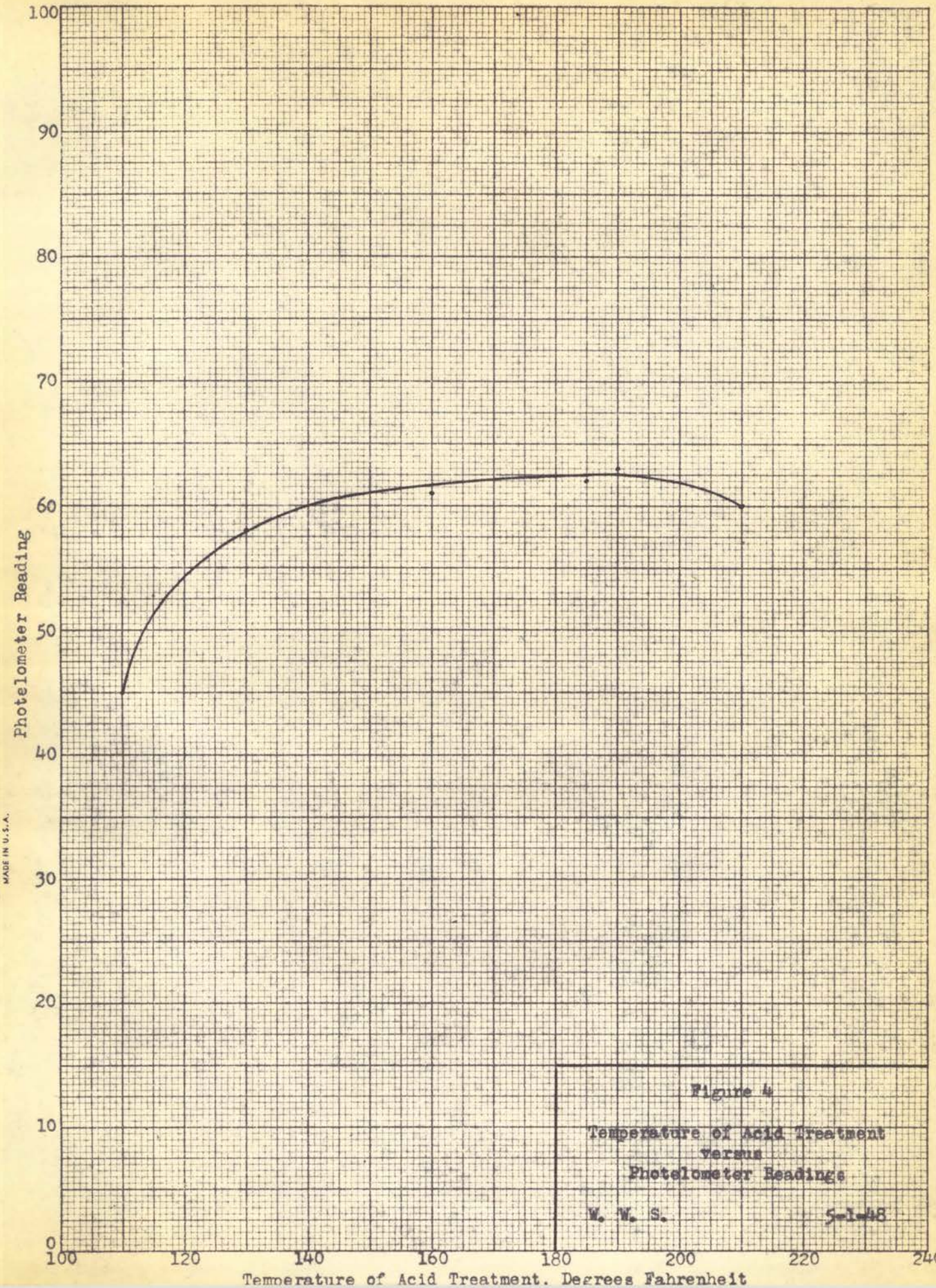


Figure 4

Temperature of Acid Treatment
versus
Photelometer Readings

W. W. S. 5-1-48

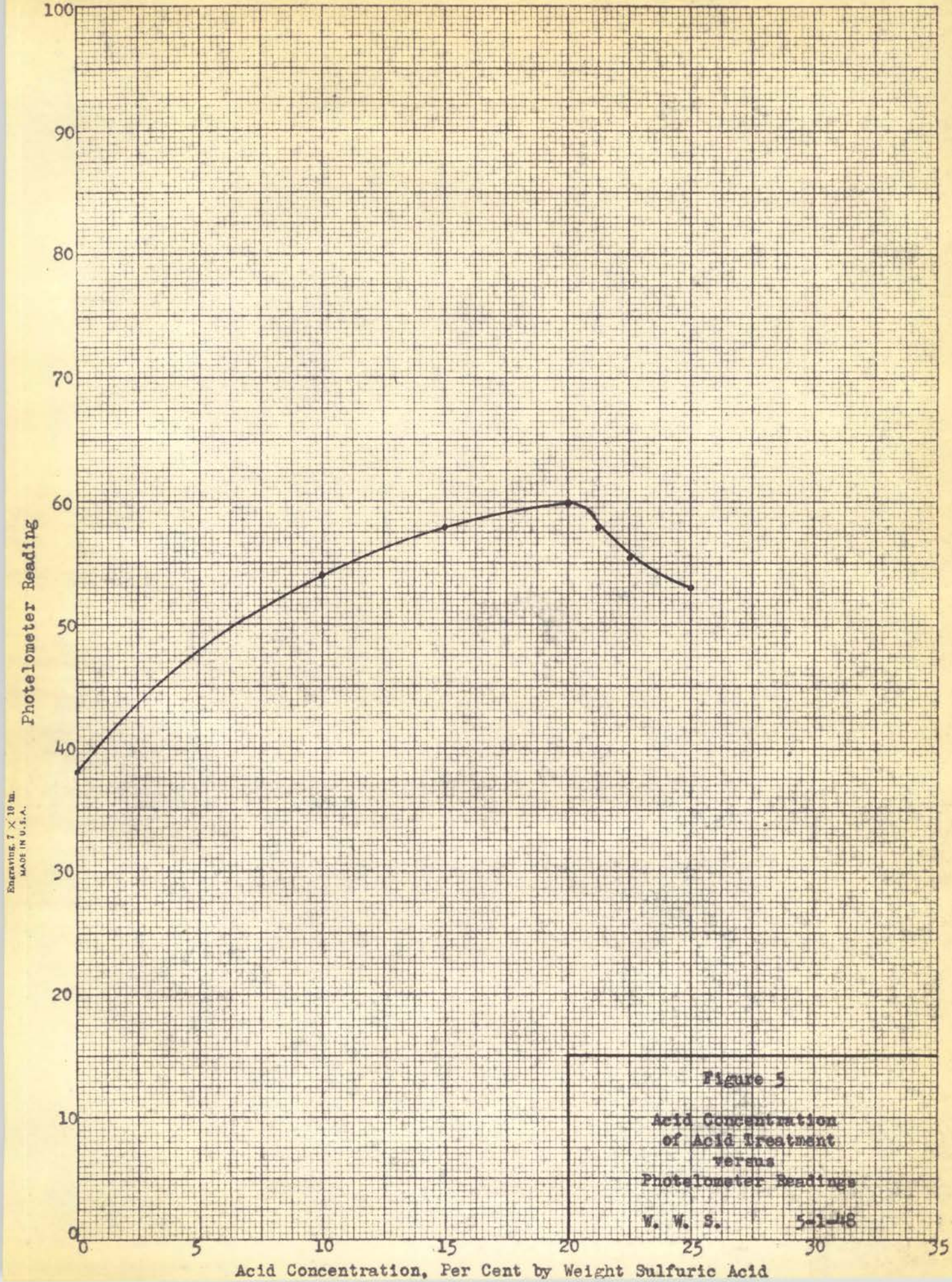


Figure 5

Acid Concentration of Acid Treatment versus Photelometer Readings

W. W. S. 5-1-48

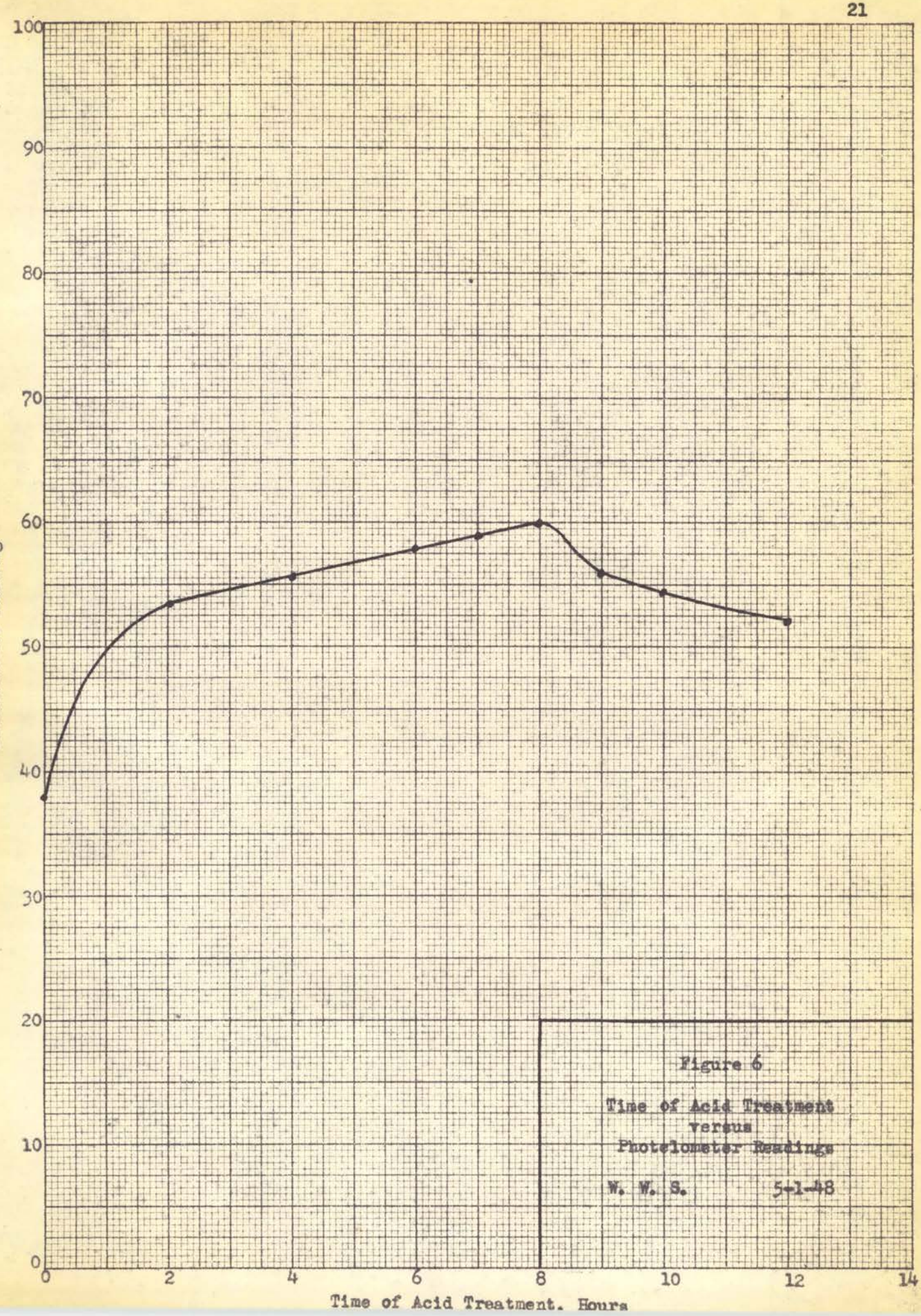
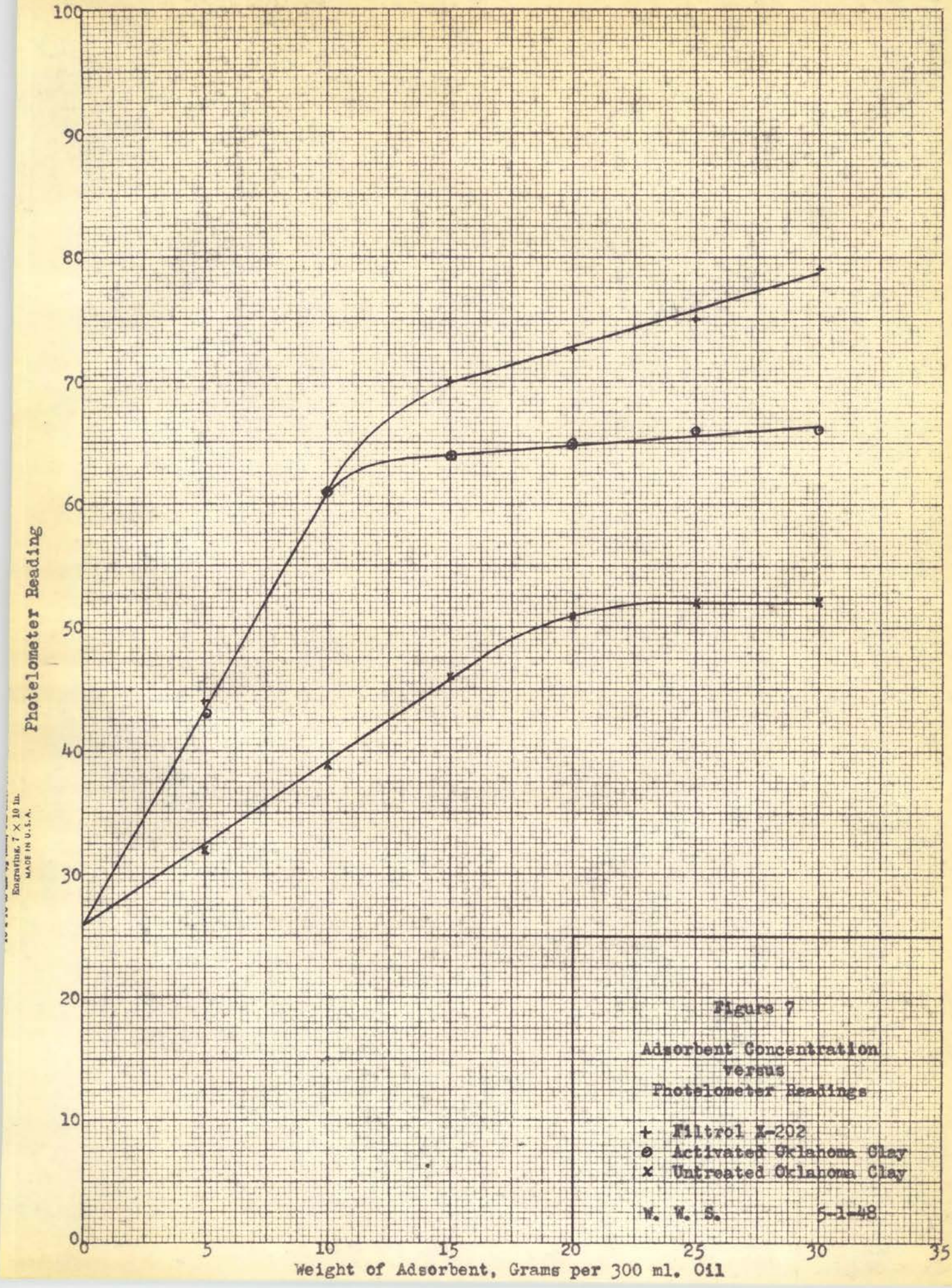
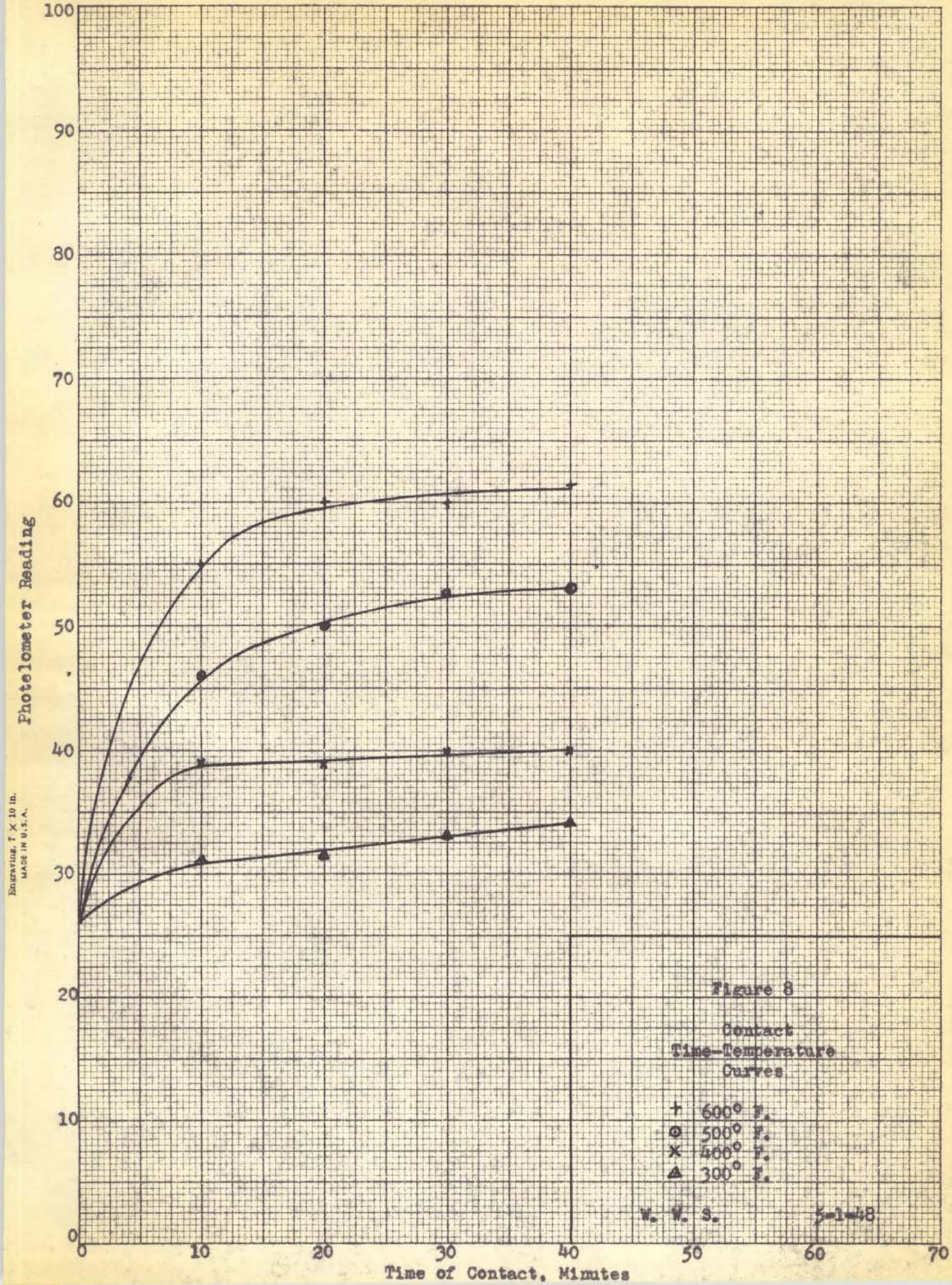


Figure 6

Time of Acid Treatment
versus
Photelometer Readings

W. W. S. 5-1-48


Photelometer Reading
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
Weight of Adsorbent, Grams per 300 ml. Oil
Figure 7
Adsorbent Concentration
versus
Photelometer Readings
+ Filtrol X-202
⊘ Activated Oklahoma Clay
× Untreated Oklahoma Clay
W. W. S. 5-1-48


Photelometer Reading
Time of Contact, Minutes
0
10
20
30
40
50
60
70
80
90
100
Figure 8
Contact
Time-Temperature
Curves
+ 600° F.
⊙ 500° F.
× 400° F.
△ 300° F.
W. W. S. 5-1-48
ENGRAVING 7 × 10 in.
MADE IN U.S.A.

CONCLUSION

The decolorizing power of activated Oklahoma bentonite is equal to that of Filtrol X-202 for adsorption concentrations up to ten grams per 300 ml. of oil. Above this value the efficiency is 80% that of Filtrol.

The untreated Oklahoma bentonite is found to have a decolorizing power unusual to this type of clay. Compared to the Filtrol, the raw Oklahoma clay possesses a 50% efficiency in decolorizing oil. This is an even higher decolorizing power than that reported for Fuller's earth,[12] which decolorizes one-fourth to one-third as much as an activated clay.

The optimum conditions for acid treating the Oklahoma bentonite are: temperature, 185°F., time, eight hours, and acid concentration, 20% by weight concentrated sulfuric acid.

The optimum conditions for contacting the activated Oklahoma bentonite with oil are: adsorbent concentration, 10 grams per 300 ml. oil, temperature, 600°F., and a time of 20 minutes.

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APPENDIX

Table I

Effect of Temperature on Activation

Oklahoma Bentonite

Sample No.	Temperature °F.	Time Hours	Acid Concentration Wt. % Sulfuric Acid	Photelometer Reading	Average Reading
11	110	8	20	45	45
1-A	130	8	20	58	
1-B	130	8	20	58	58
2	160	8	20	61	61
12	185	8	20	62	62
3-A	190	8	20	63	
3-B	190	8	20	63	63
4-B	210	8	20	60	
4-C	210	8	20	60	
4-D	210	8	20	60	60

Table II

Effect of Time on Activation

of

Oklahoma Bentonite

Sample No.	Temperature °F.	Time Hours	Acid Concentration Wt. % Sulfuric Acid	Photelometer Reading	Average Reading
7-A	210	2	20	52	
7-B	210	2	20	55	53.5
6-A	210	4	20	54	
6-B	210	4	20	57	55.5
5-A	210	6	20	58	
5-B	210	6	20	58	58.0
17	210	7	20	59	59.0
4-B	210	8	20	60	
4-C	210	8	20	60	
4-D	210	8	20	60	60.0
18	210	9	20	56	56.0
8-A	210	10	20	52	
8-B	210	10	20	57	54.5
14	210	12	20	52	52.0

Table III

Effect of Acid Concentration on Activation of Oklahoma Bentonite

Sample No.	Temperature °F.	Time Hours	Acid Concentration Wt. % Sulfuric Acid	Photelometer Reading	Average Reading
13	210	8	10	53	54.0
9	210	8	15	58	58.0
4-B	210	8	20	60	
4-C	210	8	20	60	
4-D	210	8	20	60	60.0
16	210	8	21.25	58	58.0
15-A	210	8	22.5	55	
15-B	210	8	22.5	56	55.5
10	210	8	25	53	53.0

Table IV

Effect of Adsorbent Concentration

on

Contacting Untreated Oklahoma Bentonite

Sample No.	Adsorbent Concentration Grams per 300 ml. Oil	Photelometer Readings
19	5	33
20	10	38
21	15	46
22	20	51
23	25	52
24	30	52

Table V

Effect of Temperature and Time

on

Contacting Activated Oklahoma Bentonite

Sample No.	Temperature °F.	Time Minutes	Photelometer Readings
38	300	10	31
39	300	20	32
40	300	30	33
41	300	40	34
42	400	10	39
43	400	20	39
44	400	30	40
45	400	40	40
46	500	10	46
47	500	20	50
48	500	30	52
49	500	40	53
50	600	10	55
51	600	20	60
52	600	30	60
53	600	40	61

Table VI

Effect of Adsorbent Concentration

on

Contacting Filtrol X-202

Sample No.	Adsorbent Concentration Grams per 300 ml. Oil	Photelometer Readings
26	5	44
27	10	61
28	15	70
29	20	72
30	25	75
31	30	79

Table VII

Effect of Adsorbent Concentration

on

Contacting Activated Oklahoma Bentonite

Sample No.	Adsorbent Concentration Grams per 300 ml. oil	Photelometer Readings
32	5	43
33	10	61
34	15	64
35	20	65
36	25	66
37	30	66

RECOMMENDATIONS FOR FURTHER STUDY

The adsorbent clays and their action in decolorizing oil have not been studied to any great extent. As yet there is no definite correlation between the physical or chemical properties of a clay and its decolorizing efficiency on oil.

The Oklahoma bentonite has been produced commercially for drilling mud only. The preceding study has shown that Oklahoma bentonite is capable of decolorizing oil. Research should now be made to study the physical and chemical properties of the Oklahoma clay. A study should also be made to determine the effect of decolorization upon the physical and chemical properties of the oil.

An important point brought out in the preceding paper is the decolorizing power of the untreated Oklahoma clay. Further study should be made to determine the decolorizing power of the clay as a percolation grade Fuller's earth.

Typist: Mary Wallace Spohn