THE DEVELOPMENT OF A COMMERCIAL PROCESS FOR THE MANUFACTURE OF DIMETHYLANILINE.

A THESIS

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CONTENTS

CHAPTER I.

INTRODUCTION.

Prior to the Great War the production of dyes in the United States was negligible. Of the total consumption only about one fifth was produced in this country, or about 3,000 short tons, and practically all of the intermediates or basis of these colors were imported from Germany.

In the year 1914 about seven companies were engaged in producing dyes employing about 600 men, and having a total capital of $3,000,000. The quantity produced was as said before, about 6,000,000 pounds with a value of $3,500,000.

In 1918 the United States produced approximately 76,802,959 pounds of different dyes with a total valuation of $83,815,746.

CHAPTER II.

DIMETHYLANALINE: ITS IMPORTANCE AND USE.

From the ten substances or "crudes" as they are commonly designated, obtained from coal tar suitable for making dyes, three hundred intermediates are manufactured. These three hundred intermediates from the bases of about nine hundred dyes of commercial importance at the present time.

The intermediates are divided into about ten different classes according to the characteristic groups which they contain. Dimethyl-aniline is a member of the Secondary Amines and their derivatives group. It is superceded only by diphenylamine in quantity used and which amounts to 4,263,458 pounds with a value of $2,412,820.

At the present time the demand far exceeds the amount produced.

It finds its main use in the manufacture of two very important dye stuffs, namely, Malachite Green and Methyl Violet. The quanity of these dyes used amounts to 290,416 pounds with a valuation of $1,626,466 for Malachite Green and 632,196 pounds with a valuation of $1,756,775 for Methyl Violet.

From the above figures it can be readily seen that this compound is of considerable commercial importance. To develop a process for its manufacture commercially was a problem thought worthy of undertaking.

CHAPTER III.

LITERATURE.

The first steps in the work of developing a commercial process for the manufacture of dimethyl-aniline was to examine the literature, and to discover if possible what work had been done on the manufacture of this intermediate.

A thoro examination revealed that while it was being manufactured in Germany in considerable quantity very little had been written regarding the type of apparatus used and the control of the process.

It was found that there were four processes of commercial value which are as follows:

ANILINE HYDROCHLORIDE PROCESS

A mixture of aniline seventy-five parts, aniline hydrochloride twenty-five parts, and methyl alcohol (free from acetone) seventy-five parts is heated in a cast iron auto clave at 230° to 270°.

METHYL CHLORIDE PROCESS.

Aniline (50 kilos) is well agitated in an auto-clave with milk of lime made from 40 kilos of

quick line and 75 litres of water. The whole is heated to 100° C. and methyl chloride pumped in at 5-6 atmospheres pressure. About 62 kilos of methyl chloride are required and the time taken about three hours. The dimethyl aniline is then distilled with steam.

THE IODINE PROCESS.

This process consists in heating aniline with methyl alcohol and iodine at 230° C for seven hours. Distilling off the dimethyl aniline with steam.

THE SULPHURIC ACID PROCESS.

Eighty kilograms of aniline, seventy-eight kilograms of methyl alcohol and eight kilograms of sulphuric acid 66° Be. are heated together in an autoclave at 230° to 235°. The pressure rises to twenty-eight to thirty-two atmospheres. This pressure remains constant for three hours after which it falls off as the reaction slows up. The product is then neutralised with caustic soda and the dimethyl aniline distilled with steam.

From these four processes the "Sulphuric Acid Process" was chosen as having the likeliest commercial

possibilities.

The aniline hydrochloride process was rejected because of the cost of aniline hydrochloride and because of the extremely high wear and tear on apparatus caused by the volatile acid.

The Methyl Chloride Process was considered unsuitable because of the excessive cost of Methyl Chloride.

The Iodine Process was also dropped because of the price of Iodine.

There is one other process which has not been mentioned before but which seems to have commercial possibilities. This is the treatment of aniline with dimethyl sulphate. At the present time nothing has been done with it, but it is a process worthy of looking carefully into.

CHAPTER IV

EXPERIMENTAL WORK.

It is thought that the reactions in the "Sulphuric Acid Process" are as follows:

$$2CH_3OH + H_2SO_4 \rightarrow (CH_3)_2\ SO_4 + 2H_2O$$

$$(CH_3)_2\ SO_4 + C_6H_5NH_2 \rightarrow C_6H_5N\ (CH_3)_2 + H_2SO_4$$

In order to carry on the work in the laboratory it immediately became necessary to develop some sort of a simple inexpensive piece of apparatus capable of standing the tremendous pressure involved in the reaction.

A bomb made of a piece of two inch pipe six inches long and capped at both ends which was to be heated in an oil bath was first concieved. This bomb held a charge of eighty grams of aniline, seventy-eight grams of methyl alcohol, and eight grams of sulphuric acid 66° Be. This was to give a yield of ninety six grams of di-methyl aniline.

The bomb was heated in an oil bath at 220° to 230° for five hours. It became apparent during this first run that it was going to be difficult to keep the bomb tight under the temperature and excessive

pressure conditions, and it may be said right here that this difficulty was encountered thruout all of the laboratory work and the semi manufacturing scale as well. It proved to be the hardest difficulty to surmount and one which is very important as the success of the process depends upon there being no leaks of pressure since during the time of a run even the very slightest leak will cause a loss of alcohol in the form of vapor which will prevent complete conversion and the product will be contaminated with the mono methyl compound.

The yield of di-methyl aniline from this first run was only fifty two grams and of very poor quality. A duplicate run was made with but little better success a yeild of fifty eight grams being obtained.

It was then decided to use oleum of 20% excess SO_3 in place of the 66° Be. acid. This did not prove of any benefit. In the next run the quantity of sulphuric acid was increased to 80 grams. This caused a complete decomposition with the formation of a coke like substance.

On the next run it was decided to increase the time of heating to eight hours. This seemed to be a step in the right direction for a yield of seventy six grams was obtained, altho still contaminated with mono-methyl aniline.

The next several runs were made with varying lengths of time of heating. It was found that twelve hours gave the most satisfactory results. Longer than this did not accomplish anything.

The best run obtained was a charge of 80 grams of aniline, 78 grams of methyl alcohol, and 8 grams of sulphuric acid 66° Be. heated at 230° C for twelve hours. A yield of 94 grams of dimethyl aniline was obtained containing only .25% of mono methyl. aniline.

During this laboratory work there were several runs which were absolute failures due to the impossibility of getting the bombs tight, so various other designs were tried but with little success.

The first idea that was tried in developing a new bomb was to screw the caps on the pipe as far as possible and then to run solder into the joints. This was found to be impractical because it was impossible to entirely fill the space and the gas worked underneath the solder and around the pipe until it forced an opening.

Welding the caps on to the pipe and then drilling and tapping a small hole in the top which could be closed by a plug and was used for filling and emptying was then tried but the welding proved always to be prous enough so that if the caps were not tight

the pressure was lost just the same.

Bombs of a larger size were then tried but it was found that as the size of the caps increased they very often had small pinholes in them which under such high pressure allowed the vapor to escape, so had to be discarded.

It was then decided to use a bomb constructed of smaller pipe increasing the length to maintain the same capacity. An inch pipe 12 inches long was tried but it was found that these bombs were just as difficult to make tight as those constructed of two inch.

The next idea tried was to construct a bomb of heavy steel tubing brazing a top and bottom into it. The top had a small nipple welded in it and this was closed with a cap. One of these was tried out but the brazing proved to be too weak to stand the pressure and the bottom was blown out almost resulting in a serious accident.

The results of the laboratory work are given in tabulated form as follows:

TABLE 1

No. Run	Charge	Length of Run Hr.	% Yield	% Aniline	% Mono Methyl Aniline
	80 gms. $C_6H_5NH_2$				
1	78 gms. CH_3OH	5	50%	----	----
	8 gms. H_2SO_4 66°				
2	"	5	55%	----	----
	80 gms. $C_6H_5NH_2$				
3	78 gms. CH_3OH	5	48%	----	----
	8 gms. H_2SO_4 20% SO_3				
	80 gms. $C_6H_5NH_2$				
4	78 gms. CH_3OH	5	----	----	----
	80 gms. H_2SO_4 66°				
	80 gms. $C_6H_5NH_2$				
5	80 gms. $C_6H_5NH_2$	Leak in Bomb			
	78 gms. CH_3OH				
	8 gms. H_2SO_4				
6	"	8	73%	Some	11%
7	"	Leak in Bomb			
8	"	10	86%	None	10%
9	"	12	90%	None	2.5%

TABLE 1

No. Run	Charge	Length of Run Hrs.	% Yield	% Aniline	% Mono Methyl Aniline
	80 gms. $C_6H_5NH_2$				
10	78 gms. CH_3OH	15	90%	None	3%
	8 gms. H_2SO_4 66°				
11	"	12	91%	None	.25%
	160 gms. $C_6H_5NH_2$				
12	156 gms. CH_3OH	Leaky Bomb			
	16 gms. H_2SO_4				
13	"	12	88%	None	4.5%
14	"	Leaky Bomb			
	80 gms. $C_6H_5NH_2$				
15	78 gms. CH_3OH	12	89%	None	1.5%
	8 gms. H_2SO_4-66°				

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The process was now tried out on a semi-manufacturing scale. An eight gallon antoclave manufactured by the Buffalo Foundry and Manhine Company was used for this work.

This autoclave held a charge of 6 kilogms. of aniline, 5.85 kilogms. of methyl alcohol and .6 of a kilogram of H_2SO_4- 66°. This charge yielded about 15 pounds of dimethyl aniline.

Considerable trouble was encountered in keeping this autoclave tight as it was designed with an agitator, and it was found impossible to keep the stuffing box from leaking under this high pressure.

It may be stated here that a discrepancy was noted, whether the literature was wrong or whether the pressure gauge on the autoclave recorded high is not known but the maximum pressure was found to be 700 pounds per square inch or approximately 45 atmospheres, where as it was given in the literature to be from 30 to 32 atmospheres.

To overcome the leaking of the stuffing box an oil bath was built and the agitator not used. After considerable difficulty in which several runs were spoiled, the packing of the stuffing box so that it

did not leak was accomplished. However, the autoclave was never gotten absolutely tight as the opening for the blow off valve was in rather poor shape and there was a slight leak around the threads of the nipple which fitted in there.

Various means of stopping this were tried. Filling the joint with glycerine and red lead was one thing tried. Another was calking with lead. A lead washer with a locknut was also tried, but the most successful one of all was using an asbestoes copper covered gasket with a locknut.

Gas was used for heating the oil bath which surrounded the autoclave.

The results of the work on a semi-manufacturing basis are given in tabulated form in Table 2.

TABLE 2

No. Run	Charge	Length of Run Hr.	% Yield	% Aniline	% Mono Methyl Aniline
	6 Kgm. $C_6H_5NH_2$				
1	5.58 Kgm. CH_3OH	Leaky stuffing box.			
	.6 Kgm. H_2SO_4				
2	"	11	80%	None	3.5%
3	"	Leaky stuffing box.			
4	"	12 - 13	88%	None	2.5%
5	"	12 - 13	88%	None	3%
6	"	12 - 13	90%	None	.8%

It was tried to recover Run No. 3 by adding more alcohol and sulphuric acid and heating again but it was not very successful.

Various experiments were run to see if when dimethylaniline was contaminated with mono-methylaniline whether it could be purified. Fractionating was tried first but proved unsuccessful due to the nearness of the boiling points of the two compounds.

Agitating with dilute sulphuric was tried but

this did not accomplish anything. It was found that acetic anhydride would take out the mono-methylaniline but as a commercial proposition would be too expensive.

It is believed, however, that with a properly built autoclave and a well designed plant that the product could be prepared with less than 1/2% of Mono-methylaniline.

In the following chapter is submitted a design for a plant to manufacture 1,000 pounds of dimethyl-aniline per day and a detailed outline of operation and material costs.

CHAPTER V.

DESIGN OF PLANT: OPERATION AND COSTS.

The equipment necessary for the manufacture of 1,000 pounds of dimethylaniline per day consists of (Plate 1) seven 75 gallon autoclaves (A_1 to A_7) a measuring tank for aniline (1), a measuring tank for alcohol and sulphuric acid (1'), two large steam stills (B and B_1), a steam trap (C_1), two condensers (C and D), a separating tank (E) and a sponge filter (F).

Plate number (II) shows the type of autoclave to be used. This autoclave is constructed of acid resisting iron so that an extra liner is done away with. It is set in a metal bath (K) consisting of 70% lead and 30% tin. The bath is set in a fire brick setting as shown in Plate II, and is heated by means of an oil burner.

The autoclaves are loaded from the mesuring tanks I and I' situated near the ceiling. The aniline measuring tank is constructed of sheet iron and is shown in Plate III. The alcohol and acid measuring tank is made of wood lined with sheet lead.

From the autoclaves the product is blown into the steam stills (B and B_1). These stills, the drawing of which is shown on Plate IV, are made of boiler plate, and are eight feet long and five feet in diameter. At the bottom in the front is a 2" drain. On the top at the front and back are located two 4 inch flanged openings and between them is situated a 24" manhole for cleaning purposes. On the front end an opening for putting steam into the interior is provided. The still itself is made of 9/16" boiler plate and the jacket of 1/2" boiler plate. The steam jacket has one inlet;this is thought to be sufficient. The entire still is covered with insulating material for effieiency.

The vapours from the still are conducted first to the steam separator C_1; here any overflowing liquid is separated and returned to the still. This is just an ordinary type steam separator. The vapours then go into condenser C Plate V, which consists of 20' of 1" lead pipe, and from here into condenser D Plate VI, which consists of 60' of 1" lead pipe. From C the condensate flows thru a siphon tube back into the still. Condenser C can be entirely cut off by means of valves as it is only used at the beginning for the recovery of methyl alcohol. It is necessary to use quite an excess of

alcohol in the autoclaves and costs make it desirable to recover this. It amounts to about 2,000 pounds a month.

The condensed steam and dimethyl aniline now flow into the separator E, Plate VII. This separator is constructed of 1/4" wrought iron plate and is so designed as to be continuous in its operation. The mixture flows into the perforated tube in the center. At the end of every operation water is drawn off from Z until dimethyl-aniline flows from P. Then at the beginning of the next run valves p, p_1 and z are closed, the mixture collecting separates the water flowing off at z_1 and the dimethyl-aniline at p_2 into the sponge filter, Plate VIII.

The sponge filter consists of a tank which is partly filled with a bag of sponges. The sponges take up what little water is left in the dimethyl aniline and it is ready for shipping.

After steam distillation dimethyl-aniline should not come in contact with copper, bronze or brass as it is discolored by these metals. This same will occur in glass bottles when exposed to

light and especially with simultaneous addition of air.

Cast or sheet iron drums are to be used as containors when shipping.

DETAILS OF OPERATION.

Work is started at six in the morning. The autoclaves are charged from the measuring tanks with 80 kilograms of aniline, 78 kilograms of methyl alcohol and 8 kilograms of sulphuric acid in each. It is thot desirable to prepare the alcohol and sulphuric acid a head of time as this tends to speed up the reaction. Half of the aniline is run in and then the alcohol and sulphuric acid and then the rest of the aniline. It is figured that the loading ought to be completed by 10 o'clock at which time heating is begun and the temperature held at 230° to 235° C. as shown by a thermometer placed in the metal bath. At about 2 o'clock in the afternoon the maximum pressure ought to be reached. This pressure remains constant for about three hours and recedes slightly there after. At 11 o'clock at night the heating is completed and the autoclaves allowed to cool until the next morning.

In the morning the blowing off is started; the blow off valves in the autoclaves are slowly opened, these are connected to a system of pipes which convey the issuing gases and steam to a condenser in which the methyl alcohol condenses. The gases which pass thru the condenser consisting mainly of methyl ether

are passed thru a water scrubber before being released into the air. This scrubber will also keep back any methyl alcohol that passes thru the condenser.

After all the pressure is released, the blowing off of the product into the steam still is commenced. This is accomplished by means of compressed air.

A little water and sufficient Caustic soda to neutralize the excess acid are placed in the still. As soon as the dimethyl-aniline is all in, a little steam is turned into the inside to mix the contents, then the steam is turned into the jacket. Water and methyl alcohol distill off first and are condensed. After most of this alcohol is out, steam is turned into the inside of the still. The steam carries out the dimethyl-aniline and also a little alcohol which remains. This passes into the first condenser where the steam and dimethyl-aniline are condensed and returned to the still; the methyl alcohol passes on to the second condenser where it is condensed and collected. The distillation is carried on slowly until drops of dimethyl-aniline separate rapidly from the mixture in the still. The vapours are now conducted directly into the large condenser. The condensate which is a mixture of water and dimethyl-aniline is then run

into the separating tank where the dimethyl-aniline is drawn off and the water flows away. From the separating tank the dimethyl-aniline is run into a sponge filter which removes all of the water. The dimethyl-aniline is now placed in containers for shipping.

There is little more to say in regard to details of operation. Three men on each shift ought to be sufficient to run the entire plant.

STEAM REQUIREMENTS.

During the maximum distillation period the condensate consists of 1 part dimethyl-aniline and 6 parts water added as steam. However, before and after this period more steam is required, further the jacket of the still is steam heated and steam is used for the compressing of air. Therefore, six fold weight is not sufficient and it is figured that 15 parts of steam to 1 part of dimethyl-aniline will be required. At the present time it is impossible to figure the cost of this as the price of coal is so variable.

TESTING OF DIMETHYL-ANILINE.

For the determination of mono-methyl-aniline

the acetic anhydride test is used. Acetic anhydride added to pure dimethyl-aniline causes a lowering of the temperature of almost 1 degree. In the best commercial grades about 1/2 degree. If the mono-methyl-aniline content is not too high 1° increase in temperature corresponds to about 1/2% of mono-methyl-aniline (exact .815° for 1% mono methyl-aniline according to the Chemiker Zeitung 1889 S387).

The specifications for de-methyl-aniline at the present time are that it must have a boiling point within 4° of its true boiling point, which is 192° C. allowing a variation of 2°- or 2°+ and must not contain more than 1/2% of mono-methyl-aniline, this last is very important.

The mono-methyl aniline test is carried out as follows 10 c.c.of dimethyl-aniline are pipetted into a test tube and 3 c.c. of acetic anhydride into another. A thermometer graduated to 0.1° is placed in the first, both test tubes are placed in water for about a 1/4 of an hour until the temperatures are the same. The andydride is then added to the dimethyl-aniline. The mixture is stirred with the thermometer and the rise in temperature observed. With a small content of mono-methyl aniline the temperature at first falls slightly and then gradually rises.

The boiling point determination is carried out as in the usual manner for aniline.

If it is found necessary to analyse to analine or alcohol any of the standard methods may be used. However, it is not likely that this will be necessary as both of these compounds may be obtained in pure enough form for this process.

MATERIAL COSTS.

Based on a yield of 92% of the theory.

80 kilogms. - 176#	$C_6H_5WH_2$	at 36¢	= $63.36
78 kilogms. - 171.6#	CH_3OH	at 54¢	= $92.66
8 kilogms. - 17.6#	H_2SO_4	at .0105	= .19
65 kilogms. - 14.3#	NaOH	at .059	= .84
		TOTAL	$157.05

93:122::176:X

93 X = 21472

X = 231# Dimethylaniline

92% yield = 212.5#

$157.05 ÷ 212.5 = 73.9¢ per #

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To Mr. H. S. Reed, Professor of Industrial Chemistry, I wish to extend my sincerest thanks for his help and advice and under whose supervision this work was preformed.

The End.

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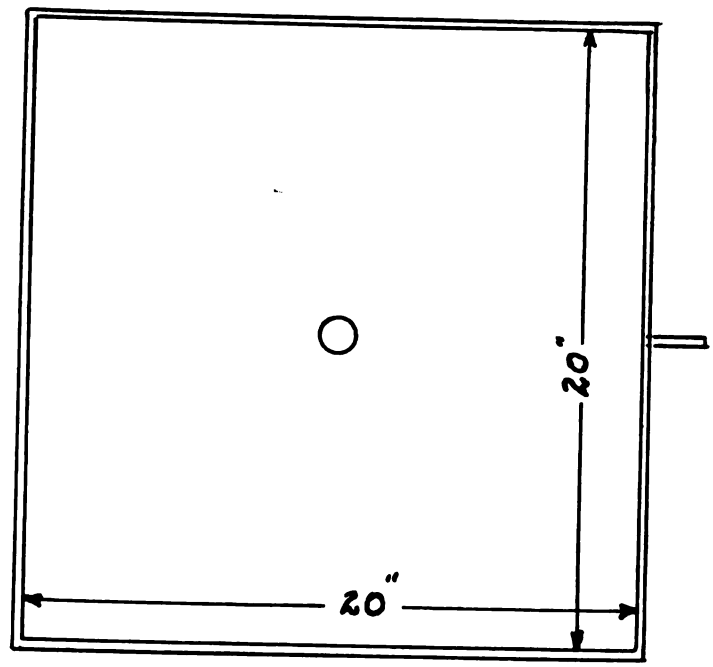
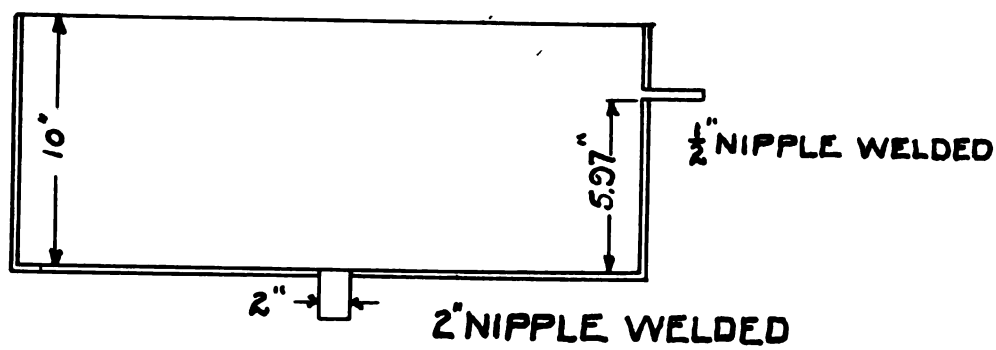
AUTOCLAVE

?- REQUIRED

PLATE II.

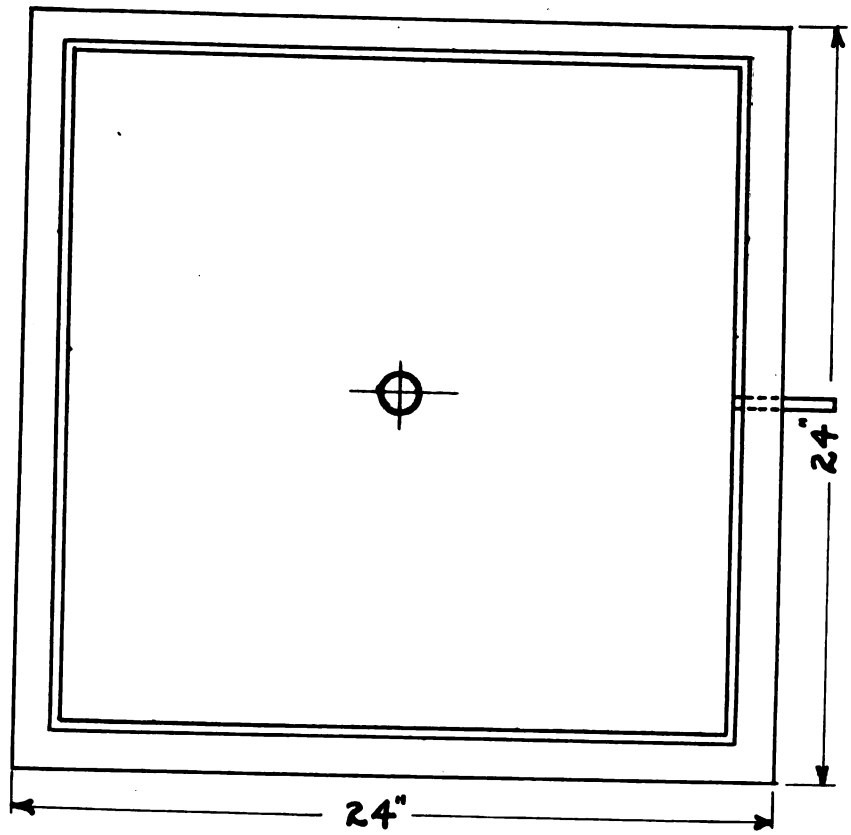


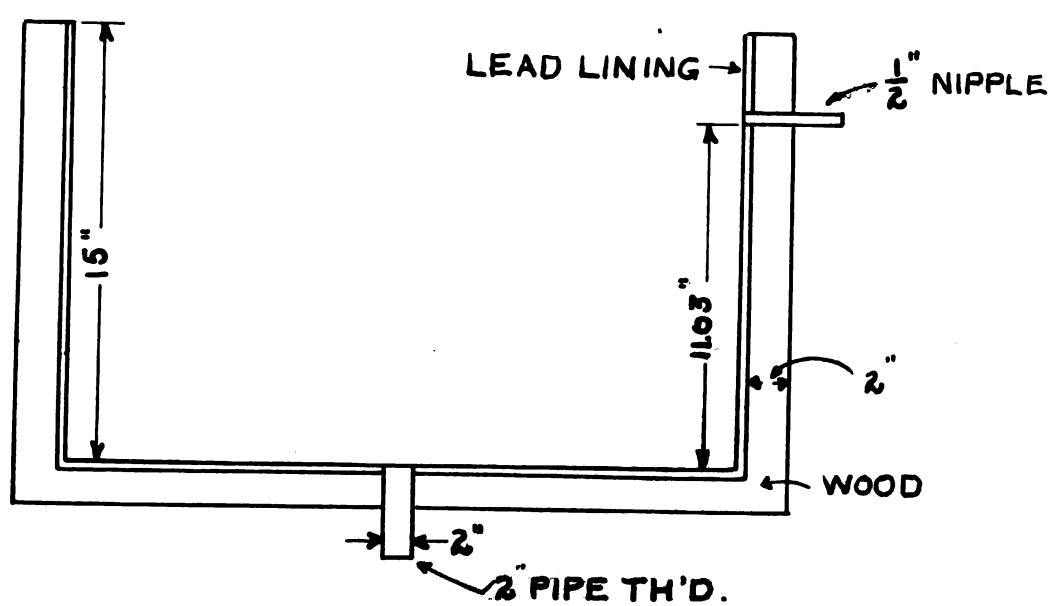
12 GAUGE SHEET IRON



ANILINE MEASURING TANK

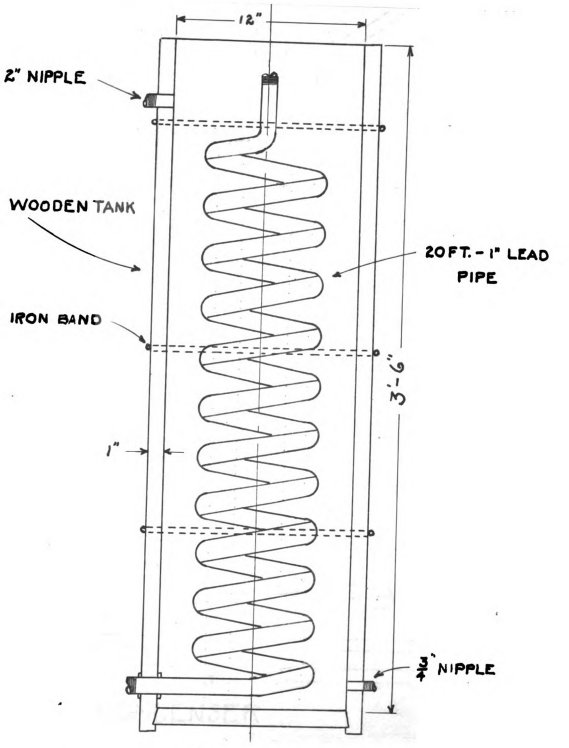
PLATE III





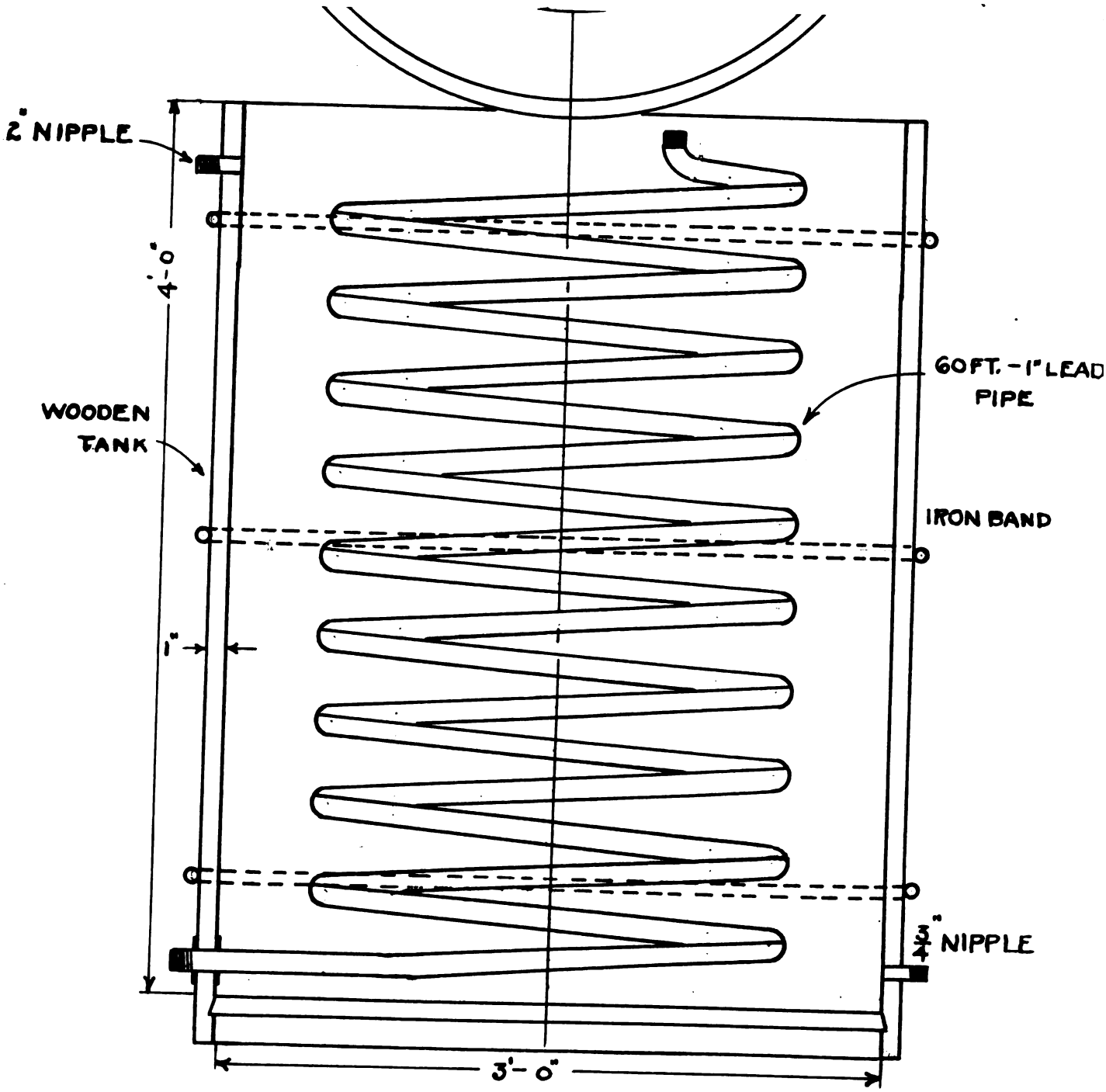
ALCOHOL-ACID MEASURING TANK

PLATE III



CONDENSER

PLATE V



CONDENSER

PLATE VI

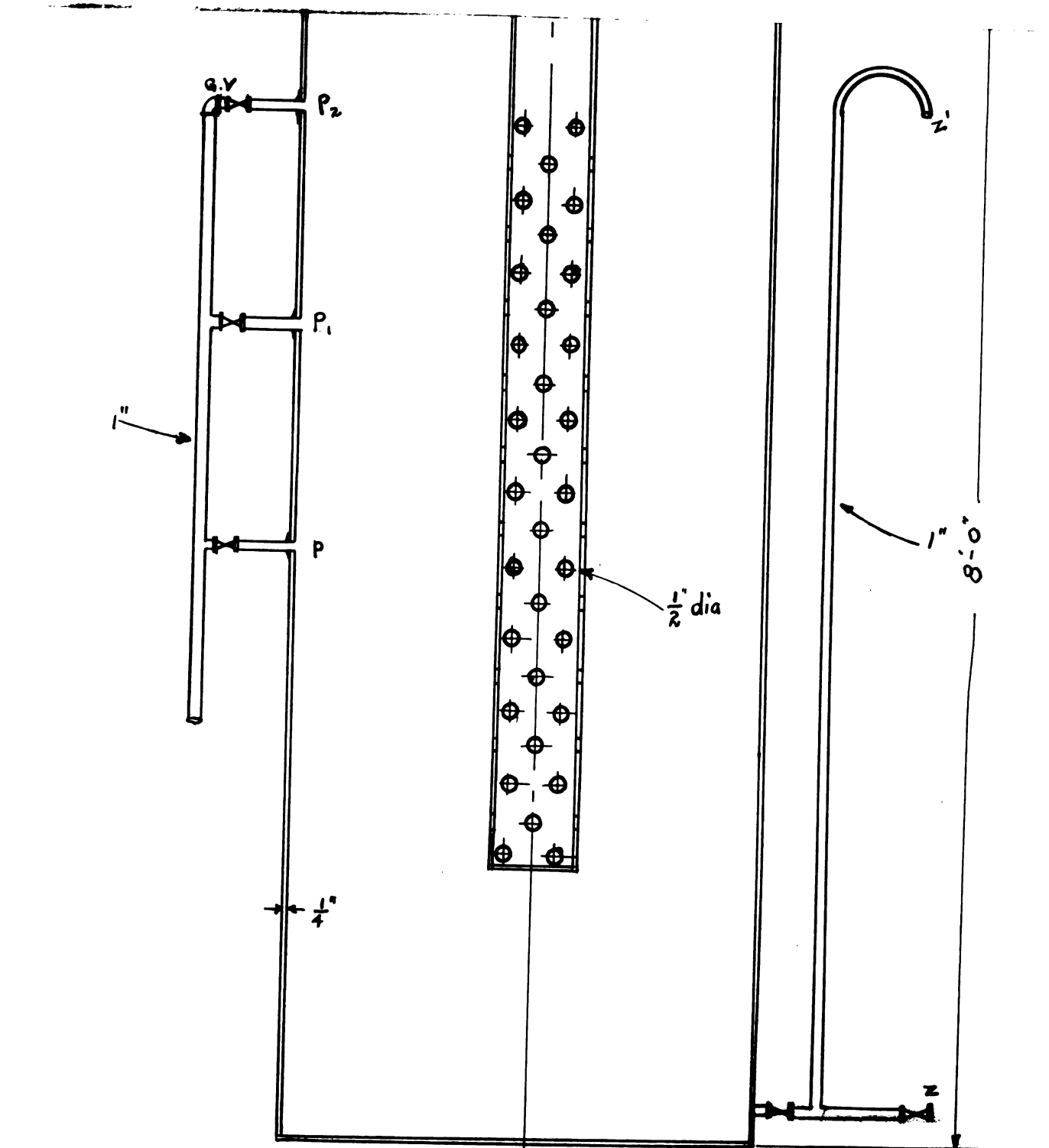
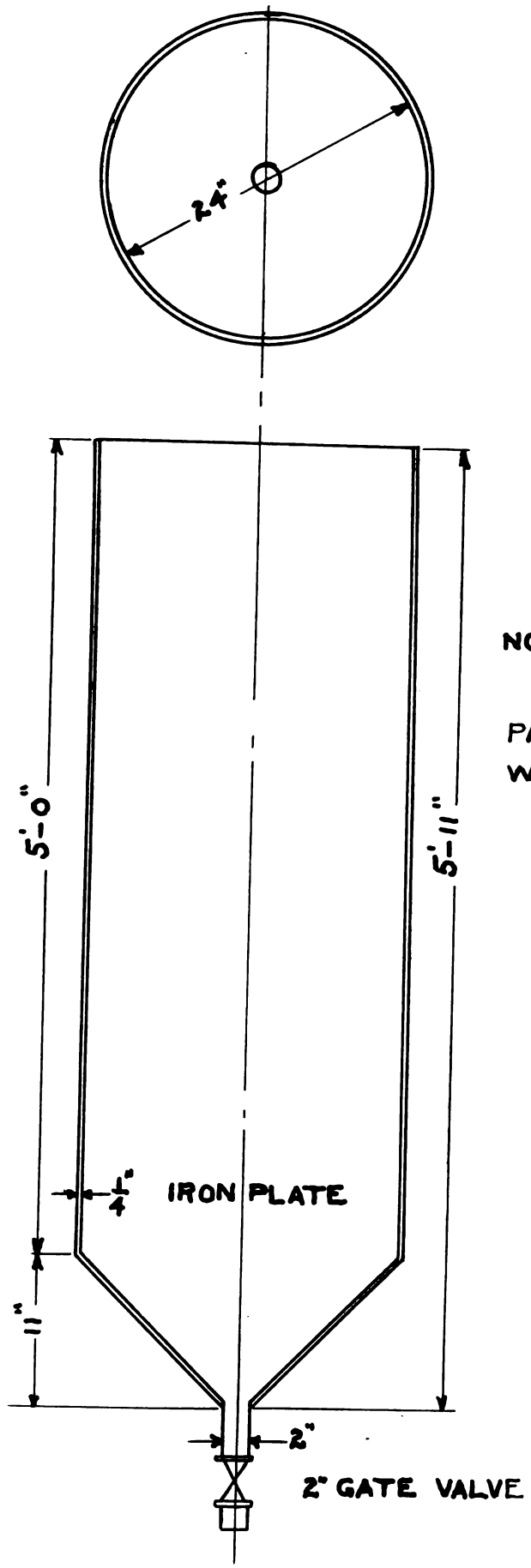


PLATE VII

SEPARATING TANK
1- REQUIRED



SPONGE FILTER

PLATE VIII