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THE DIRECT PRODUCTION OF ANILINE

BY

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Submitted in partial fulfillment of the
requirements for the degree of Master
of Science in the College of Arts and
Sciences in the University of Alabama

University, Alabama

1929

ACKNOWLEDGMENT

The writer wishes to take this opportunity to thank Dr. Stewart J. Lloyd and Mr. A. M. Kennedy for suggesting this problem and for constant aid in its carrying out.

The writer wishes also to express his gratitude to the Federal Phosphorus Company, of Anniston, Alabama, at whose expense the work was performed.

Acknowledgment is made to the authors of textbooks and periodicals in the footnotes and bibliography.

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Chapter I

Introduction¹

The coal tar industry holds a unique position in the industrial world, as it is entirely the outcome of scientific research. The first seed was planted in 1825 when Faraday discovered benzene, which he obtained from the liquid products condensed on compressing the gas obtained from coal oil. A year later, 1826, Unverdorben obtained aniline by the mere distillation of indigo and called it "crystalline". Runge afterwards obtained it from coal tar oil, and having observed that it produced a violet blue coloration with chloride of lime, called it "kyanol". It was subsequently obtained from indigo by Fritsche by distilling this coloring matter with caustic alkali. Mitscherlich later obtained benzene from benzoic acid and from this produced nitrobenzene, this discovery paving the way for Zinin, who showed that benzidam (aniline) could be produced by the action of sulphuretted hydrogen in the presence of ammonia on an alcoholic solution of nitrobenzene.

Hoffman, in his first published paper, showed that Unverdorben's "crystalline", Runge's kyanol, Fritsche's aniline and Zinin's benzidam were all the same compound, and for which he selected Fritsche's name Aniline. His work on the separation of aniline from coal tar started

¹ Groggins, P. H., Aniline and Its Derivatives, pp. 1-5; Perkin and Armstrong, Hoffman Memorial Lecture, Trans. of Chemical Society, (1896).

in 1843, and continued after his arrival in England in 1845, and it is remarkable that practically all of the aniline used for his numerous researches was obtained by the laborious and costly process of distilling indigo with potash.

At this time, 1843, organic chemistry was still in its infancy as coal tar naphtha had not yet been investigated. Runge had isolated phenol, aniline, and quinoline. Naphthalene was known to exist in the tar, having been separated by Garden as early as 1820 and finally Dumas had discovered anthracene. This was about all that was known of the composition of coal tar at that time. In 1845 Hoffman showed that benzene must exist in coal tar naphtha, as he found that aniline could be produced from it. Upon his suggestion Charles Mansfield undertook to investigate the liquid hydrocarbons of coal tar and after much patient and persevering experimenting finally produced benzene and toluene in a pure state. From the latter Hoffman produced toluidine.

Hoffman's memory, however, will be revered not so much for his personal contributions to the early chemical literature as for his marked influence and inspiration as a teacher upon a host of brilliant chemists who studied under him, and had the pleasure and benefit of his personal advice and encouragement and who later united in referring to him as the pioneer and leader of coal tar chem-

istry. There can be no doubt that his researches on coloring matters have had a determining effect on the course of the development of the coal tar industry. To Perkin (one of his students), however, belongs the credit for the introduction and development of the industry, for he quickly realized the commercial importance of the numerous discoveries in coal tar chemistry which now followed in a tumultuous succession.

During his Easter vacation, in 1856, while experimenting on the futile task of attempting the preparation of quinine from allyl-toluidine, he found that no promising results could be obtained by converting the latter to a salt and treating with potassium dichromate. His interest in the reaction persisted, and he decided to repeat the experiments with a simpler base. Aniline was selected, and its sulfate was treated with potassium dichromate; in this instance a black precipitate was obtained, and on examination was found to contain the coloring matter since so well known as aniline purple, or mauve. Very soon after this discovery (made in a rough laboratory at home) Perkin found that it had the properties of a dye and resisted the action of light very well. He then managed to have Messrs. Puller, of Perth, test out some specimens of dyed silk, and from them received the following reply, which shows the state of the dyeing trade at that time, June, 1856.

"If your discovery does not make the goods too expensive, it is decidedly one of the most

valuable that has come out for a long time. This color is one which has been very much wanted in all classes of goods and could not be obtained fast on silk, and only at great expense on cotton yarns. I enclose you a pattern of the best lilac we have on cotton. It is dyed only by the one house in the United Kingdom, but even this is not quite fast, and fades by exposure to air. On silk the color has always been fugitive. It is done with cudbear or orchid and then blued to fade."

Considerable difficulties were met; first, in dyeing cotton, as no suitable mordant had been discovered for this new coloring matter and only the pale shades produced by the natural affinity of the dye for the vegetable fibre were obtained. Then fears were entertained that it would be too costly and finally prejudice against a new material that did not behave as the old products did had to be overcome. Despite the dissuading advice of Hoffman, Perkin, at eighteen, left college to continue his investigations and to proceed with the production of this dyestuff. A general patent was taken to include the oxidation product of salts of aniline, toluidine, xylidine, and cumidine.

In June, 1857, with the assistance of his father and friends, construction of a plant at Greenford Green near Harrow to manufacture dyes was commenced. None of the backers of the proposition had ever seen the inside of a chemical works. There was no standardized production equipment to select from, as the character of the operations to be performed was so entirely different from anything then in vogue. Only impure benzene could be obtained, and this varied greatly in quality. No nitric acid strong enough for

the preparation of nitrobenzene could be obtained commercially, and as there was no desire to complicate the infant undertaking by manufacturing this substance, experiments were made using a mixture of sodium nitrate and sulphuric acid, using the latter in larger proportions than necessary to give an acid sodium sulfate. This method was troublesome at first, but was finally conquered, and very large quantities of nitrobenzene were made this way, this being the first time that nitrobenzene was prepared in iron vessels.

It was only three years before the above-mentioned works were started (1854) that Bechamp showed that finely divided iron borings and acetic acid were capable of converting nitrobenzene into aniline. Had it not been for this discovery the coal tar industry could not then have been started.

In a short time, however, aniline purple proved itself to be an important coloring matter which could be produced on a manufacturing scale. It attracted much attention, and, as a consequence, many others commenced its manufacture. Investigation followed investigation, patent followed patent, and new manufacturers with new shades and new dyes made their appearance. The little works at Greenford Green soon found that it could no longer keep pace with the constantly increasing demands and before long France and Germany were laying down the foundations upon

which to build the gigantic dye industry that now enriches the nations.

The following prophetic article appeared in the North American Review, for March, 1896, and subsequent events and today's march of progress both bear out the far-sighted vision of its author.

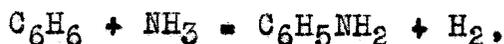
"It is fair to hold that the country that has the best chemists will in the long run be the most prosperous and the most powerful. It will have at the lowest cost the best food, the best manufactured materials, the fewest wastes and unutilized forms of matter, the best guns, and strongest explosives, the most resistant armour. Its inhabitants will make the best use of their countries' resources; they will be the most healthy, and the most free from disease; they will oppose the least resistance to favorable evolution; they will be the most thrifty and the least dependent on other nations. The education of its people in chemistry and the physical sciences is the most paying investment that a country can make. Competition today between nations is essentially a competition in the science and application of chemistry."

Chapter II

Purpose of Investigation

The purpose of the writer's investigation was to work out a method for the direct production of aniline from benzene and ammonia. The present method of production involves the nitrating of benzene by the use of nitric acid, a very expensive source of nitrogen; followed by the reduction of the nitrobenzene by hydrogen in the presence of iron and some hydrochloric acid. In addition an exact temperature must be maintained to insure safety and efficiency.

An inspection of the heats of formation of the substances involved in the reaction,



shows that the reaction is essentially endothermic going from left to right. The substances involved have the following heats of formation:¹

<u>On Left</u>	<u>On Right</u>
$\text{C}_6\text{H}_6 = -11,300$ calories	$\text{C}_6\text{H}_5\text{NH}_2 = -19,800$ calories
$\text{NH}_3 = 12,000$ calories	_____
Total = 700 calories	Total = -19,800 calories

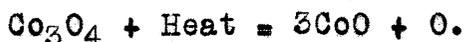
From these figures the desired reaction evidently absorbs considerable heat, and obviously its equilibrium will be shifted to the right with increased temperature.

On the other hand the ammonia decomposes rather readily

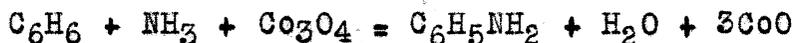
 1 Hodgman, C. D. and Lange, N. A., Handbook of Chemistry and Physics, (twelfth edition), p. 552.

into its elements at high temperature, so that there was a narrow range of temperature in which to work. The problem was to find a catalyst which would accelerate the desired reaction to a maximum extent without at the same time accelerating the decomposition of NH_3 . It is evident also that the equilibrium would be shifted strongly to the right by the instant removal of the hydrogen produced, hence the use of oxide catalysers and other hydrogen removers was strongly indicated.

An example of a possible substance that would cause a shift to the right would be cobalto-cobaltic oxide, Co_3O_4 , which, when heated, liberates free oxygen as shown below,



The oxygen is then free to unite with the hydrogen given off in the reaction, as follows,



In this reaction the heats of formation would be:

<u>On Left</u>	<u>On Right</u>
$\text{C}_6\text{H}_6 = -11,300$ cal.	$\text{C}_6\text{H}_5\text{NH}_2 = -19,800$ cal.
$\text{NH}_3 = 12,000$ cal.	$\text{H}_2\text{O} = 58,300$ cal.
$\text{Co}_3\text{O}_4 = \underline{193,400}$ cal.	$3\text{CoO} = \underline{173,500}$ cal.
Total = 194,100 cal.	Total = 222,000 cal.

From these figures it can be seen that the equation would be exothermic going from left to right.

To further this investigation the writer has carried out a number of experiments using various catalysers. These experiments are discussed individually in Chapter X.

Chapter III

Physical Constants of Pure Aniline

The importance of aniline to the dye industry has long been recognized, but no practical method of analysis has been available for general use in judging its quality.

A survey of chemical methods of analysis disclosed the fact that due to the rather large experimental errors, most of them fail when the purity of the aniline exceeds 99.5 percent. Attention was therefore turned to the question of the application of the physical constants for accurately judging the purity. It would naturally be expected that the physical constants of such a common intermediate would long since have been established beyond any reasonable doubt. As a matter of fact, a great number of investigators have made a study of aniline but, instead of establishing these points, widely divergent results have been published.

On consulting the literature¹, no less than sixteen different values for the freezing point of aniline were found. These vary between -8° and -5.96° Centigrade, where the values for the boiling point ranged from 182.5° to 184.8° Centigrade. The following freezing points have been considered as most reliable, and are those generally accepted:

1 Groggins, P. H., Aniline and Its Derivatives, pp.125-30.

<u>Authority</u>	<u>Year</u>	<u>Freezing Point</u>
Ampola and Rimatori	1897	-5.96 ^o C.
Timmermans	1911	-6.20 ^o C.
Jones and Sanderson	1920	-6.00 ^o C.

The most reliable boiling points are:

<u>Authority</u>	<u>Year</u>	<u>Boiling Point</u>
Timmermans	1911	184.40 ^o C.
Callender	1899	184.10 ^o C.
Bechmann	1914	184.30 ^o C.

As a result of these discordances, C. L. Knowles prepared a sample of pure aniline and determined accurately its physical constants. In the course of this work it was soon discovered why so different values had appeared for the physical constants of aniline, since to purify aniline and maintain it in a pure state was found to be a matter of considerable difficulty.

After many test Knowles arrived at the following physical constants:

Boiling Point..... 184.32--184.39^oC.
 Freezing Point.....-6.24^oC.
 Specific Gravity..... 1.0268 at 15^o/15^oC.
 Refractive Index.....-1.5850 at 20^oC.

Effect of Moisture:- One property of aniline which caused considerable trouble in Knowles' work, and which apparently has received but very little attention in the past, is its extreme hygroscopicity. It is believed that this alone accounts to a large extent for the conflicting results found in the literature. If aniline in the pure

state be exposed to air for but one hour, the freezing point and boiling point are materially affected; consequently extreme care must be taken in determining constants of the pure material. If undue time is required for these determinations, no accurate figures can be obtained. For this reason Knowles freshly distilled all samples in vacuo.

In order to demonstrate clearly the effect of moisture on the purity of aniline, Knowles determined freezing points hourly on a sample exposed to the air. The initial freezing point was -6.35 degrees Centigrade, after one hour it had fallen to -6.60 degrees Centigrade, after sixteen hours it was -7.30 degrees Centigrade, and after forty six hours a freezing point of -8.20 degrees Centigrade was obtained.

Chapter IV

Commercial Preparation of Aniline

Since 1864 aniline has been prepared on a manufacturing scale by the reduction of nitrobenzene. It is the accepted practice for the producer of aniline to have his own plant for nitrating benzene, this being considered the initial step in the production of aniline.

The nitration of benzene is carried out in closed cast iron vessels. The operating control is of necessity quite rigid, as slight deviations from standard practice may result in low yields and also lead to the introduction of the element of danger in the operation.

Nitration of Benzene

The nitration of benzene may be briefly described as follows:¹

The nitration is brought about by adding mixed acid to benzene, controlling the temperature at 75 degrees F. when paddle agitation is used; a considerably higher nitrating temperature, 140 degrees F., is permissible when a more perfect agitation is used. Cycle acid, that is, waste acid from a previous charge in which some nitrobenzene is still present, is blown into the nitrator in sufficient quantity to cover the bottom paddles. This acid is used for the purpose of hastening the reaction, and as it

¹ Groggins, P. H., Aniline and Its Derivatives, pp. 69-90.

afterwards dilutes the mixed acid added, it makes for a more uniform temperature and even reaction.

If cycle acid were not used it would take several hours longer to carry out the nitration owing to the increased difficulty in controlling the temperature. Brine is turned into the coils and about 2,000 pounds of cycle acid are blown into the nitrator. Then 2,600 pounds of benzene are pumped from the scale tank after the cycle acid reaches 75 degrees F.

After the benzene is in and the temperature fixed at 75 degrees F., mixed acid is started into the nitrator. The mixed acid can be fed into the top, or undersurface. When the undersurface feed is used, the acid runs into a lead funnel placed on the agitator just above the top paddle. A lead line leads from the funnel to one of the lowest paddles. Here the lead line makes a loop and goes back to an upper paddle where a distributor is attached to the end of the line. The loop in the lead line is always full and prevents spluttering, as the mixed acid here comes into contact with the benzene when surface feed is used.

During the nitration the temperature is held between 70 and 75 degrees F. by feeding acid slowly with a continuous flow of brine or cooling water through the coils. When all but the last 1,000 pounds of acid has been added, the flow is increased. The rate is governed so that at the close of the acid feed the temperature is 100 degrees F. After

the mixed acid is all in, the temperature is raised to 140 degrees F. by taking the brine flow off the coils. The whole charge is then run from the nitrator to the settling house.

During the first part of the run the acid must be added only slowly, but as the nitration progresses the mixed acid can be added more rapidly. The rate of feed, however, depends entirely on the temperature as controlled by the brine and efficiency of nitration.

An average analysis of the mixed acid used, and of the resultant waste acid, is:

<u>Mixed Acid</u>		<u>Waste Acid</u>
52.50%.....	H ₂ SO ₄	71.50%
39.50%.....	HNO ₃50%
.50%.....	HNO ₃ SO ₄75%
7.50%.....	H ₂ O.....	27.50%

The settling house is provided with a number of large conical-bottomed lead tanks, each capable of holding one charge. The charge from the nitrator is allowed to settle here for about twenty four hours when the waste acid is drawn off from the bottom of the lead tanks to a blowcase and delivered to the waste acid settling tanks for additional settling or for treatment with benzene next to be nitrated, which will extract the residual nitrobenzene. The nitrobenzene is then dropped into another blowcase and delivered to the neutralizing house. The neutralizing tub may be either a large lead, conical-shaped tub containing an air spider for agitating the charge of nitrobenzene during the

washing process, or a standard iron kettle similar to a nitrator with sleeve and propeller agitation.

The neutralizing tub is filled with a heel of warm water run in from a hot water tub, and the nitrobenzene is run into it. The charge is thoroughly agitated, and then allowed to settle. The supernatant acid water is then run off through side outlets into a labyrinth where practically all of the enmeshed nitrobenzene will settle out.

The charge is now given a neutralizing wash followed by a wash with aniline water from the reducer house if any has to be worked up and finally run off at the base of the tub into a blowcase from which it is delivered to the nitrobenzene storage house, where it is again settled and final traces of water removed. This crude nitrobenzene can now be distilled for other purposes.

In some plants the neutralizing wash is omitted. The nitrobenzene delivered to the reducer house is consequently slightly acid. Provided the acidity is kept below one half of one percent no harmful effects on the equipment are noticeable.

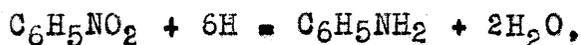
When the nitrobenzene in the waste acid is not extracted by counter-current washing with benzene next to be nitrated, it is recovered from the spent acid by allowing the acid to settle in large lead tubs from eight to twenty four hours, the length of time for settling depending upon production demands. The percentage of nitrobenzene soluble in

waste acid depends upon the temperature. In the hot summer months it has been found to be as high as one percent while in winter when the nitrobenzene freezes the percentage drops as low as 0.45 percent. The average amounts of nitrobenzene which were determined by making ether extracts on the waste acid, for the latter part of August and for September, proved to be 0.7 percent which is about 0.8 percent loss of the percentage yield.

Reduction of Nitrobenzene.¹

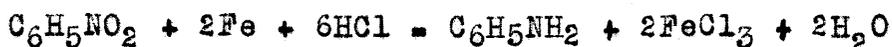
The reduction of the nitrobenzene into aniline is brought about progressively by the addition of iron and ferrous chloride. If hydrochloric acid is used, there is a temporary, more or less, violent evolution of hydrogen gas and steam until the acid has combined with free iron to form ferrous chloride and with any aniline present to form its salt. The aniline hydrochloride in the presence of an excess of finely divided iron becomes quickly hydrolyzed and the free acid liberated combines at once to regenerate ferrous chloride.

Considerable discussion has taken place regarding this reaction, particularly in an effort to explain the consumption of less acid or chloride than the amount called for by the formula. If we represent the reduction as taking place as follows,



 1 Groggins, P. H., Aniline and Its Derivatives, pp.150-53.

then the above formula implies the presence of hydrogen in sufficient quantities to completely reduce the nitrobenzene, and calls for sufficient hydrochloric acid for its generation. But in practice only about one-sixtieth to one-fortieth of the acid required by the reaction



is actually used. This is probably due to the fact that water and metallic iron, in the presence of ferrous chloride, can act as reducing agents.

The reduction is carried on in cast iron kettles of all sizes, the larger ones finding greater favor owing to their more economical operating cost. These reducers are equipped with removable side and bottom lining plates, made of either cast iron or acid proof brick. The brick lining very effectually resists the grinding action of the borings, and gives general satisfaction. A specially designed reducer blade for agitation carries plows that can be removed and replaced through the side door of the reducer.

The reducer is equipped with a suitable feeding device which will deliver the iron borings to the machine as required. An iron borings supply bin is placed up and high and delivers the finely ground iron to the funnel on the reducer. The borings bin is attached to a scale so that the charge going into the reducer is continuously and accurately being weighed. The bin is usually filled by small

industrial cars that dump about a charge each time.

Suitable flanged or screwed openings are left for the introduction of the nitrobenzene and acid. Steam openings are made either into the top or sides or into a hollow core through the shaft that drives the agitator plows. A sight box is placed directly over the reducer, to enable the operator to watch the progress of the reduction as all the condensed vapors are led back through this mechanism into the reducer.

The vapors from the reducer are led up to a condensing tank equipped with cooling coils designed to expose the maximum cooling surface. The condensed liquids are led back to the reducer until reduction is complete. The condensed liquids are then led to the distilling tanks.

As soon as the connections to the distilling tanks are opened steam pressure on the tanks is increased to 15-20 pounds, and the live steam line opened so as to maintain a constant volume in the reducer. A full flow of water is now maintained on the condenser which governs the rate of distillation, as care must be taken to avoid the uncondensed gases going to the distilling tanks. The steam distillation is carried on until samples from the condenser show that practically all the aniline has been distilled over, and that only a trace remains in the reducer sludge. About six hours is required to steam distill about 860 pounds of oil from an 800 gallon reducer.

The charges of aniline from the reducer house are pumped to settling tanks in the aniline distillation house. The charge is permitted to settle for several hours, when the aniline is drawn off from a connection at the bottom to an aniline blowcase. When aniline water makes its appearance the feed to the aniline blowcase is stopped, and the water is drawn off from an upper valve about 18 inches from the bottom of the tank and delivered to the feed tanks for the water stills. The aniline in this water is recovered in the stills.

The importance of cooling the charges of aniline cannot be overestimated, since above 98 degrees the solubility of aniline in water increases with remarkable rapidity. If proper cooling is not done a large percentage of aniline is delivered to the water stills.

The crude aniline delivered from the reducer house and drawn off from the bottom of the receiving tanks into a blowcase is now blown to settling tanks over the rectifier. The oil is permitted to stand for some time until the emulsified water rises to the top. This is decanted off and the aniline is drawn into the rectifier by means of a vacuum line. In the rectifier, which is usually a large, horizontal tank, the crude aniline is again distilled and condensed. When the condensation products are shown to be pure, water-white aniline, they are led to the large aniline storage tanks.

Although the method just described is the one most extensively used for manufacturing aniline, it has a number of undesirable features. The process is very indirect, starting with benzene, converting it to nitrobenzene, and finally converting the nitrobenzene to impure aniline. This feature is in itself a very objectionable one because of the waste incident to such an indirect procedure.

Nitric acid is a very expensive source of nitrogen, but it is the only one that can be satisfactorily used for the nitration of the benzene. Besides being an expensive process, the nitration of benzene has a serious element of danger due to the fact that very exact temperature must be maintained in order to insure safety and efficiency.

Considerable research has been done in an effort to perfect a more satisfactory method of producing aniline. A number of methods have been found and some of them patented, but none have been found that warrant scrapping the plants already in operation in favor of the newer process. A few of these newer methods will be briefly described in the next chapter.

Chapter V

Other Methods of Producing Aniline

from Benzene Derivatives.

Groggins¹ has assembled and briefly described a number of patented processes. In addition to them the following ones are worthy of note:

French Patent 397,485²-Feb. 25, 1908. This patent covers a method of preparing aniline oil, its homologues and substitution products by the action of ammonium hydroxide on chlorobenzene in the presence of salts of copper. The copper salts play the role of catalysts.

United States Patent I, 124,776²-Jan. 12, 1915. This patent covers a method of producing aniline oil from nitrobenzene in the presence of a catalyst. Nitrobenzene vapor is mixed with an excess of hydrogen and led in a continuous stream over hot, finely divided ferrous oxide mixed with asbestos. The catalyst is kept at a temperature between the boiling point of nitrobenzene and the lowest temperature at which the ferrous oxide could be reduced. In like manner, toluene can be produced.

Method of Sabatier and Senderens³-- As early as 1902 P. B. Sabatier and J. B. Senderens had done some work along the line covered by the above patent. They found that

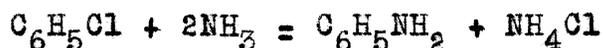
1 Groggins, P. H., Aniline and Its Derivatives, pp.147-53.

2 Slaughter, J. R., Direct Production of Aniline, p. 17.

3 Sabatier, P. and Senderens, J. B., New Method of Preparing Aniline, Journal Physical Chemistry, Vol. VI, p.356.

nitrobenzene could be almost completely converted into aniline by the following process. The vaporized nitrobenzene was mixed with an excess of hydrogen and passed over freshly reduced copper at a temperature between 300 and 400 degrees Centigrade. When there is not enough hydrogen, some azobenzene is produced. With freshly reduced nickel heated to 200 degrees Centigrade, a very pure grade of aniline can be produced. If the nickel is heated much higher than the above temperature the chief products obtained are benzene and ammonia. It is interesting to note that a similar reduction can be brought about by the use of water gas.

Quick's Method:¹- At the University of Wisconsin, Quick, in 1920, produced aniline according to the following reaction,



using salts as catalysers. He found that cuprous salts were more effective than cupric salts and his best results were obtained by the use of cuprous iodide. The addition of finely divided iron to the catalyst improved the appearance of the aniline produced but retarded the action. The use of activated charcoal also improves the appearance of the product and does not have the retarding effect of iron. Best results were obtained by using concentrated ammonia.

Brown and Henke's Method:²- In 1922 O. W. Brown and C. O. Henke did extensive research in the study of the catalyt-

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- 1 Quick, A. J., Aniline from Chlorobenzene, Journal American Chemical Society, Vol. 42, pp. 1033-1043, (1920).
 2 Slaughter, J. R., Direct Production of Aniline, p. 17.

ic reduction of nitrobenzene with hydrogen. Their first work was with finely divided nickel and copper. A suitable apparatus for the study of catalysis in the vapor phase was employed. They found that the nickel is best prepared by igniting the nitrate at 450 degrees Centigrade and reducing the oxide in hydrogen at 380 degrees Centigrade. The best method of preparing the copper is to ignite at 415 degrees Centigrade and reduce below 475 degrees Centigrade. It was shown that the compounds formed by the catalytic reduction depend upon the temperature to which the catalyst is previously heated, a low temperature leaving the catalyst too active, and a high temperature leaving the speed of reduction greatly reduced. The best temperature for reduction of nickel was found to be 192 degrees Centigrade and for copper, 280 degrees Centigrade. The yield of aniline is increased as the rate of flow of the nitrobenzene is decreased. Brown and Henke are of the opinion that nickel would be better as a catalyst because it can be used at a greater rate although the yield from copper is slightly higher.

In subsequent work done the same year and published in the same volume of the various journals, these two men tried a great number of catalysts under a wide range of conditions. Correlating their results from these various experiments they found that the catalytic activity of a substance is a function of the atomic weight.

Chapter VI

Cost Factors in Present Method of Production¹

At the outbreak of the World War there came to the consumers of dyestuffs a panicky realization that foreign dyestuffs might not get through the barrier of blockades. The infant industry here was besought to extend itself to supply a portion of the immediate requirements. A period of hasty experimenting set in. Dyestuffs, poor and otherwise, found eager purchasers. The industry then began to develop to gigantic proportions. Costs--yields--economies were ruthlessly disregarded until the retrenchment move at the close of the war, already in operating evidence in other industries, bumped heavily into the chemical consuming market. Then came a period of idleness and reflection, followed by an appalling deflation of every phase of the industry.

A realization had come about that hereafter products had to be produced economically. These products had also not only to compare favorably with foreign materials but had to, in many cases, be far superior in order to overcome inherited prejudice and alien propaganda.

Factors Affecting Costs

Successful manufacturers need no reminder that present competition demands highest efficiencies in every phase of -----
1 Groggins, P. H., Aniline and Its Derivatives, pp.91-97.

operation. An attempt will be made, however, to set down several broad divisions, wherein, if the highest efficiencies are reached, sound economical operation must follow:

- I. Determination of best method of production
- II. Selection of best type of equipment
- III. High operating efficiencies
- IV. Large productivity for equipment used
- V. Purchase of materials at favorable prices
- VI. Low overhead and fixed charges

The numerical arrangement of the above cost factors represents their relative importance.

Discussion

I. It is unquestionably true that the choice of the most efficient method of operation is of the utmost importance. Even the largest organization possessing every facility for economical operation, and in a position to install the most expensive machinery, cannot compete favorably unless the system adopted contains certain inherent characteristics making for low cost production. The foremost item in the economical production of aniline oil is the selection of the right process. The subject justifies continual investigation, particularly along new lines, for with the march of progress in the manufacture of equipment, processes once impossible are now feasible.

II. The selection of equipment is one which is receiving considerable attention at present. This, in a large measure, is due to the beneficial influence of the chemical expositions, at which the manufacturers of chemical equip-

ment have taken the opportunity for aggressive sales campaigning. Large size equipment within reasonable power loads is conducive to increased production at lower operating costs. Smaller vessels multiply the sources of loss and require more operating labor. For equal capacity, large-sized units require less capital outlay, less floor space and less supervision.

III. Probably the most interesting document to the operating chemist is the periodical operating report. This report shows the yield of finished product from raw material used, based on actual physical inventories. The magnetism of these reports giving information as to the successful conversion of raw ingredients into soluble products is the attraction that keeps many men in a field, which is often deleterious to health, and comparatively unremunerative as to value received for services rendered.

IV. Continuous operation at maximum capacity makes for lower costs and smoother operation.

V. Firmly established companies, with extensive credits, are unquestionably in a position to obtain better contracts for raw materials. The greater the volume of business, the greater will be the concession for their trade. Of course an alliance of organizations whereby "favored nation" clauses are incorporated so that one concern can obtain benzene at a very low price, while the rest of the market is begging for that material at competitive prices,

makes for an inequitable but actual basis of competition.

VI. A number of comparatively small plants are producing aniline today despite several serious handicaps. They do not consume a large percentage of their product, nor do they obtain the best costs on raw material. In order to offset these handicaps, the benefits of a more personal supervision in a smaller plant enter. The large organization, with a considerable overhead burden and oftentimes subjected to financial manipulation, taps the business for what may amount to a disastrous drain, whereas the smaller producer limits this cost item to the lowest possible figure.

Each system of operation requires a different set of cost figures for operating expense, power, and fixed charges. Even the same unit will require modifications each month based on production and other factors. It is thus only possible to indicate in a general but quite accurate way the factors in determining the cost of producing aniline.

Stage I.

Nitration of Benzene to Nitrobenzene

Molecular Weight Benzene, C_6H_6	78
Molecular Weight Nitrobenzene, $C_6H_5NO_2$	123
Theoretical Yield.....	157.7
Standard Yield for Determining Cost.....	153.5

To Produce 100 Pounds Nitrobenzene

65.15 lbs. Benzene @ 3.0 cents.....	\$1.95
71.00 lbs. H_2SO_4 @ .75 cents.....	.54
55.00 lbs. HNO_3 @ 6.00cents.....	3.30
1.00 lb. Na_2CO_3 @ 2.00 cents.....	.02
Total Material Cost.....	<u>\$5.81</u>

Credits

69.0 lbs. H_2SO_4 , in waste acid, @ 0.5 cents..\$0.345
 .9 lbs. HNO_3 , in waste acid, @ 5.0 cents... 0.045
\$0.390

Therefore, Net Material Cost per 100 lbs.....\$5.42

Operating Costs.....\$0.15

1. Operating Labor and Direct Supervision
2. Repairs Labor
3. Repairs Material
4. Supplies

Power Costs.....\$0.20

1. Electric
2. Steam
3. Air
4. Water
5. Brine

Overhead.....\$0.52

\$0.87

Net Cost per 100 lbs. Nitrobenzene.....\$6.29

Nitrobenzene--Percentage Cost Analysis

Operating Cost..... $\frac{.15}{6.29} = 2.4\%$ of total

Power Cost..... $\frac{.20}{6.29} = 3.2\%$ of total

Overhead..... $\frac{.52}{6.29} = 8.3\%$ of total

Raw Materials..... $\frac{5.42}{6.29} = 86.1\%$ of total

Stage II.

Reduction of Nitrobenzene to Aniline

Molecular Weight Benzene..... 78
 Molecular Weight Nitrobenzene..... 123

Molecular Weight Aniline.....	93
Theoretical Yield C_6H_6 to $C_6H_5NH_2$	119.2
Standard Yield C_6H_6 to $C_6H_5NH_2$	109.7
Theoretical Yield $C_6H_5NO_2$ to $C_6H_5NH_2$	75.6
Standard Yield $C_6H_5NO_2$ to $C_6H_5NH_2$	71.5

To Produce 100 Pounds Aniline from Nitrobenzene

140 lbs. Nitrobenzene, @ 6.29 cents.....	\$8.80
160 lbs. Iron Borings, @ .75 cents.....	1.20
15 lbs. HCl or equivalent $FeCl_2$, @ 1 cent.	<u>.15</u>

Total Material Costs.....\$10.15

Operating Costs..... \$1.00

1. Labor Operating
2. Repairs
3. Supplies
4. Direct Supervision

Power Costs..... \$0.80

1. Electricity
2. Steam
3. Air
4. Water

Overhead..... \$0.50

1. Administration
2. Depreciation
3. Insurance
4. Fixed Charges

Total Materials Cost per 100 lbs. Aniline.\$10.15

Total Net Cost per 100 lbs. Aniline.....\$12.45

Aniline--Percentage Cost Analysis

Operating Costs.....	$\frac{1.00}{12.45} =$	8.0% of total
Power Costs.....	$\frac{.80}{12.45} =$	6.4% of total
Overhead.....	$\frac{.50}{12.45} =$	4.0% of total
Raw Materials.....	$\frac{10.15}{12.45} =$	81.6% of total

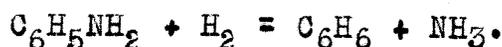
To the experienced operator it is very apparent that the above figures call for excellent operating control, and the introduction of raw materials at very favorable prices. The cost figures also presuppose some regularity of operation as they do not provide for long periods of non-production. However it must be remembered that these figures are set forth merely to convey the importance of obtaining factors. When these are known they make for more efficient operation due to the fact that each charge can be scrutinized.

Chapter VII

Direct Production of Aniline from Benzene

by Other Investigators.

Sabatier¹ has shown that a mixture of aniline and hydrogen can be converted into benzene and ammonia when heated to a temperature of 350 degrees Centigrade in the presence of a suitable catalyst. He found that the best results were obtained by the use of finely divided nickel. The aniline is decomposed according to the following equation,



That the above reaction is reversible has been demonstrated by Meyer and Tanzen². In their experiments dry ammonia gas was led into benzene at a temperature of 75 degrees Centigrade and the mixed vapors led through a porcelain tube which was kept at a temperature of 550 degrees Centigrade in an electric furnace. The product condensed was a brown liquid. This liquid was distilled and at first only benzene came over. That part of the liquid that distilled over between 160 and 190 degrees Centigrade was examined for aniline by treating with hydrochloric acid. A white salt was formed which gave a test for aniline. Their

1 Sabatier, P., Catalysts in Organic Chemistry, p. 684.

2 Meyer, R. and Tanzen, A., Pyrogene Acetylen-Kondensationen, Berichte der Deutschen Chemischen Gesellschaft, Vol. 46, pp. 3183--3199, (1913); Slaughter, J. R., Direct Production of Aniline, p. 17.

yield was very small in comparison with theoretical yields.

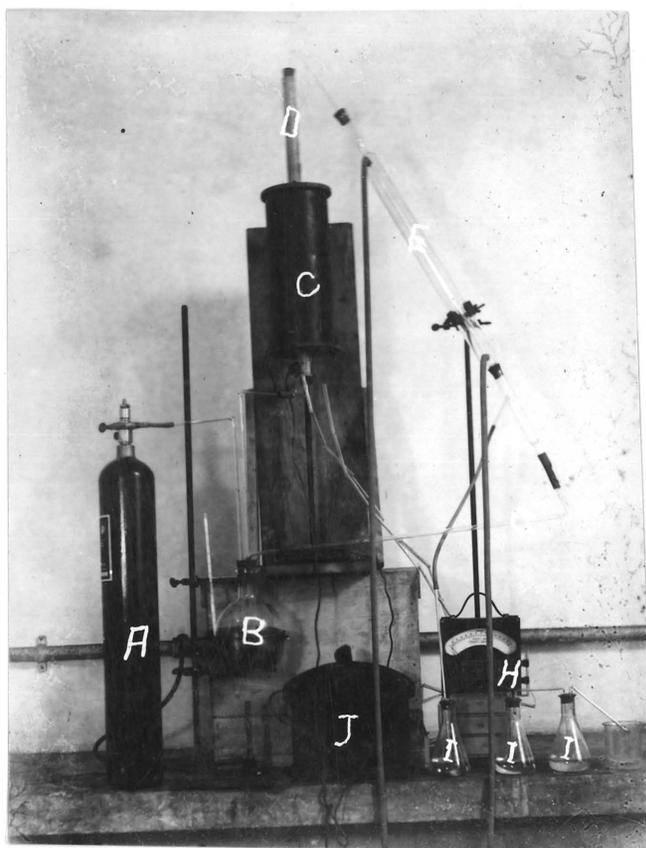
Contrary to Meyer and Tanzen, Wibaut¹ found that no appreciable amount of aniline is formed in a porcelain tube below 700 degrees Centigrade without a catalytic agent. He secured best results with reduced iron, nickel, and copper. In his work the dry ammonia gas was led into benzene at a temperature of 75 degrees Centigrade and the mixed vapors led into an iron tube sixty centimeters long and whose temperature was about 700 degrees Centigrade. The catalysts were mixed with asbestos in the iron tube. Like Meyer and Tanzen, Wibaut obtained very small yields.

These experiments demonstrate the possibility of preparing aniline directly, by the reaction between benzene and ammonia. In order to make the reaction one of practical importance some catalyst will have to be found that will bring about a much higher yield from a given amount of material. With this object in view the experiments now to be described were carried out. They differ from the above experiments in that a silica tube was used instead of either porcelain or iron.

1 Wibaut, J. P., Zur Bildung von Anilin aus Ammoniak und Benzol, Berichte der Deutschen Chemischen Gesellschaft, Vol. 50, pp. 541--546, (1917).

Chapter VIII

Description of Apparatus Used



A--Ammonia Tank
 B--Benzene Flask
 C--Electric Furnace
 D--Silica Tube
 E--Water-cooled Condenser

F--Gas Outlet Valve
 G--Delivery Tube
 H--Pyrometer
 I--Recovery Flasks
 J--Rheostat

The dry ammonia gas from tank, A, passes over the surface of the benzene in flask, B, which is heated to approximately 75 degrees Centigrade. The combined vapors of ammonia and benzene pass into the electric furnace, C, through

a silica tube, D, which contains the catalyser.

The vapors then pass into the water condenser, E. Excess gases pass out through the arm of the T-piece and into the recovery flasks, I, the first two being partially filled with water and the third containing sulfuric acid.

The liquid from the condenser passes through the delivery tube, G, and back into the benzene flask, B, to be recirculated, leaving any aniline in the bottom of the flask.

The pyrometer, H, measures the temperature of the electric furnace. The rheostat, J, regulates the temperature of the furnace by adjusting the resistance through the circuit.

At the end of each run the end-product in the benzene flask was concentrated down to one-half its volume. This solution, which contains the aniline produced, was titrated, as shown in the following chapter, to determine the percentage of aniline present.

Chapter IX

Estimation of Small Quantities of Aniline

Qualitative Tests.Calcium Hypochlorite Test:-

One drop of $C_6H_5NH_2$ put into a filtered solution of bleaching powder, $Ca(ClO)Cl$, or of sodium hypochlorite, $NaOCl$, gives an intense violet coloration which slowly turns brown and fades. In the experiments performed by the writer calcium hypochlorite was used.

Aniline Black Reaction:-

A few drops of strong H_2SO_4 are added to a drop of $C_6H_5NH_2$ in a basin. The pasty mass is stirred with a glass rod. On adding a few drops of potassium dichromate solution, an intense blue color is produced. This is called aniline black. The intensity of the blue varies inversely with the amounts of concentrated H_2SO_4 and potassium dichromate added--the more H_2SO_4 and $K_2Cr_2O_7$ added, the more greenish blue the solution.

Since H_2SO_4 and $K_2Cr_2O_7$ added to a few drops of pure benzene give a deep green product, this test was not used.

Runge's Violet Test:-

Five cubic centimeters of the dilute liquid are treated with one drop of dilute sodium hydroxide solution, three drops of saturated aqueous solution of phenol, and four cubic centimeters of freshly saturated, filtered solution of bleaching powder. Allow to stand for one-half. The

liquid is distilled with fifty cubic centimeters of water and its color is compared with those produced under similar conditions containing respectively 0.10, 0.15, and 0.20 percent of aniline.

This test gives a reliable qualitative estimation of aniline, but it is not used as a quantitative determination since the average colormetric determinations are not dependable.

Three New Reactions for Aniline, by Juan B. Peset.¹

Add to a drop of aniline 0.5 cubic centimeters of concentrated HNO_3 (d. 1.4) and 1--2 drops of a concentrated KMnO_4 solution: a series of color changes are produced, ending finally in intense blue which becomes somewhat yellowish on adding ammonia.

If one cubic centimeter of an aqueous AcOH solution and 0.2--0.3 grams of Na_2O_2 be added to a drop of aniline, no coloration is at first produced, but on heating a canary yellow color appears.

If BaO_2 be added instead of Na_2O_2 , the color is dark red.

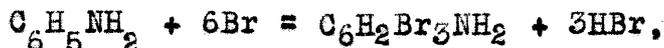
In each of the tests the colored substance can be extracted by amyl alcohol which affords a means of making the test more sensitive. The last two reactions are quite sensitive, it being possible to detect the equivalent of 1/1600 drop of aniline.

1 Peset, Juan P., Three New Reactions for Aniline, Chemical Abstracts, Vol. VI, p. 982, (1912).

Quantitative Tests.

Volumetric Method of Estimating Aniline, by M. Francois.¹

This method is based on the conversion of aniline into tribromaniline according to the equation,



indigotin disulfuric acid, which is not attacked until the aniline has been acted upon, being used to indicate the completion of the reaction.

A solution of about five grams of bromine per litre is employed, and is conveniently standardized by means of aniline hydrochloride. On account of the loss of the element, which occurs on exposing a solution of bromine to air, the burette used should be large enough to hold the volume necessary for several determinations, and should be closed with a plug of pressed cotton-wool. The operation of standardizing the solution is as follows:- A rough test is made by putting ten cubic centimeters of the aniline hydrochloride solution (1.392 grams/litre), along with two drops of indigo carmine solution, into a narrow-necked flask, and gradually adding the bromine solution until the blue color is destroyed. A more exact test is then made with the same volume of aniline hydrochloride solution, almost the whole quantity of reagent found by the preliminary test to be necessary being rapidly introduced, with as little exposure to

 1 Francois, M., Volumetric Method of Estimating Aniline,
 Journal of The Society of Chemical Industry, Vol. 18,
 p. 866, (1899).

air as possible, then two drops of the indigo carmine solution, and, finally, the remaining quantity of the solution requisite for the decolorization of the mixture being added.

The amount of aniline in the volume of solution taken for an estimation should be about 0.01 grams. If ammonia be present along with the aniline, the mixture must be neutralized or acidified with HCl before titration.

The following result indicates the accuracy of the method:- Quantity of aniline taken equals 0.01 grams; bromine required (11.6 cc. of a solution containing 0.00435 grams/cc.) equals 0.05046 grams; bromine theoretically required equals 0.0516 grams.

Volumetric Estimation of Aniline. by G. Deniges.¹ The author points out that the method of estimating aniline, which was recently published by Francois, has been described by him in a thesis presented to the Faculte des Sciences of Paris in 1891, and again in his work, "Precis de Chimie Analytique", published in 1897.

The method given therein is as follows:- A solution containing per litre 15.5 (93/6) grams of aniline and 50 cubic centimeters of HCl solution, is used to standardize the bromine solution. Ten cubic centimeters of it are placed in a flask along with one cubic centimeter of HCl solution, and to this the bromine solution is added until

¹ Deniges, G., Volumetric Estimation of Aniline, Journal The Society of Chemical Industry, Vol. 18, p.866, (1899).

a permanent pale yellow coloration is produced.

If a cubic centimeters of the latter solution be required, the amount of bromine in a litre of it is 800/a grams. The aniline to be tested is dissolved in water, and the solution is acidified with hydrochloric acid. A small quantity of this is taken and titrated with the bromine solution, the end of the reaction being shown by the formation of a permanent yellow coloration, due to the presence of bromine in excess. No indicator is required.

Estimation of Aniline, by M. N. Schapchnikoff.¹

Reinhardt has described a method of estimating aniline quantitatively, by brominating with a solution of potassium bromate, the aniline being dissolved in excess of hydrobromic acid solution.

The author, M. N. Schapchnikoff, has improved this method by employing commercial potassium bromate, which can be obtained very pure, instead of making it in each experiment as Reinhardt did.

A solution of eight grams of KBrO_3 per litre is used, and to dissolve the aniline one gram of base is taken for 60 grams of hydrobromic acid of 25 percent HBr. This solution is diluted so that one litre contains ten grams of base.

Control experiments are made with pure aniline distilling at 182 degrees Centigrade and with pure p-tolui-

1 Schapchnikoff, M. N., Estimation of Aniline, Journal The Society of Chemical Industry, Vol.17, p.803, (1898).

dine of melting point 45 degrees Centigrade. The bromate solution is run into the amine solution until, after allowing the precipitate to settle, the color is just yellow. If much toluidine is present, the end point is rather difficult to see, owing to the precipitate and the solution being slightly red.

Results are calculated from the formula,

$$\frac{x}{t} - \frac{p-x}{t'} = n,$$

where p is the total weight of bases employed, x equals the weight of aniline, t equals the number of cubic centimeters of KBrO_3 solution when pure toluidine is used, n equals the number of cubic centimeters of KBrO_3 solution used in the experiment. t and t' are determined in a separate experiment. The KBrO_3 solution does not change during a month.

Determination of Aniline in Aqueous Solution, by C. M.

Carson.¹

Since aniline does not give a sharp end-point with any indicator, it is necessary to use as a color standard a solution of pure aniline, enough 0.1 N H_2SO_4 to neutralize it exactly, and the same amount of indicator as used in the samples to be titrated.

In using bromophenol blue (tetrabromophenolsulfonphthalein) the color standard is prepared by adding three drops of a 2.5 percent alcoholic solution of the indicator to 10 cubic centimeters of a solution containing 2.05 grams of

 1 Carson, C. M., Estimation of Aniline in Aqueous Solution,
 Ind. and Eng. Chem., Vol. 17, pp. 62-63, (1925).

aniline per 100 cubic centimeters. The volume is made up to 100 cubic centimeters and the calculated amount (22.05 cc.) of 0.1 N H_2SO_4 to neutralize the aniline is then added.

Ten cubic centimeters of the solution under examination are pipetted out into 100 cubic centimeters of water, three drops of the indicator added, and 0.1 N H_2SO_4 run in until the color of the standard is matched. The color change is from red to yellow, and it should be noted that with ordinary speed of titration the red color persists in returning after the end-point is apparently reached. Hence add H_2SO_4 a few drops at a time till the red color does not return.

More uniform results, although having a larger divergence from the known amounts, were obtained with p-dimethyl-amidoazobenzene. Eight drops of a one percent alcoholic solution are used. The color change is from yellow to rose-red, and approximate results may be obtained, as with the bromophenol blue, with the use of a standard aniline solution. Such a standard is advisable for accurate determinations. In using this indicator the end-point is marked by the entire absence of any yellow color. The rose-red color when obtained may fade out; hence additional 0.1 N H_2SO_4 should be added, one or two drops at a time until the red color becomes permanent.

Quantitative Determination of Aniline in Benzene Solution.

Since the experiments were carried out with the anil-

ine in benzene instead of aqueous solution, the writer has devised a quantitative scheme of estimating small percentages of aniline in benzene solution. The test is based primarily on C. M. Carson's test¹ using bromophenol blue as an indicator.

Standard tests were estimated in preliminary runs. A two percent solution of aniline in benzene was prepared, and from this 1.5 percent, 1 percent, 0.5 percent, 0.2 percent, and 0.1 percent solutions were made up.

Twenty cubic centimeters of the two percent solution were placed in a flask and 3 drops of a 2.5 percent alcoholic solution of the indicator added. The solution was diluted with 100 cubic centimeters of distilled water. The color was an intense violet, and enough 0.1 N H_2SO_4 was added to change the color to a bright yellow.

To determine the end-point a blank test using 20 cubic centimeters of pure benzene, 3 drops of the indicator, 100 cubic centimeters of distilled water, and enough 0.1 N H_2SO_4 to give a permanent yellow color was prepared. It was found that 1.6 cubic centimeters of 0.1 N H_2SO_4 would give the color for matching the standard tests.

Each of the other known solutions of aniline in benzene was carried through the same procedure as that of the two percent solution.

The following results were obtained:

1 Carson, C. M., Estimation of Aniline in Aqueous Solution, Ind. and Eng. Chem., Vol. 17, pp. 62-63, (1925).

Percent $C_6H_5NH_2$	0.1N H_2SO_4	Minus 1.6cc. for Blank
2.0%	51.1cc.	49.5cc. for 2.0%
1.5%	38.8cc.	37.2cc. for 1.5%
1.0%	26.4cc.	24.8cc. for 1.0%
0.5%	14.1cc.	12.5cc. for 0.5%
0.2%	7.9cc.	6.3cc. for 0.2%
0.1%	4.8cc.	3.2cc. for 0.1%

The table shows that a 0.1 percent solution of aniline in benzene would require 4.8 cubic centimeters of 0.1N H_2SO_4 , but 1.6 cubic centimeters of the acid would be needed to bring pure benzene to the standard color; so that for calculations 1.6 cubic centimeters would be subtracted from the total number of cubic centimeters used in the titration.

After each experiment the final product was concentrated to one-half its volume to insure the liberation of all ammonia present. This is very essential as ammonia will act on the indicator in the same manner that aniline does. Then twenty cubic centimeters of this concentrated solution were put in a flask, 3 drops of the indicator and 100 cubic centimeters of distilled water added, and the solution titrated with the standardized acid. The color is compared with that obtained in the blank test.

The correction was made for the blank test, and the result compared to the above table to determine the concentration of the aniline present. It can be seen that if just 1.6 cubic centimeters of 0.1N H_2SO_4 were required to match the standard color, there would be no aniline present.

Chapter X

Description and Results of Experiments

The writer has carried out a number of experiments using various substances as catalysers. It is the purpose in this chapter to point out the important factors of each test.

Two series of runs were made, one with the furnace temperature at 450-480 degrees Centigrade, and the other with the furnace temperature maintained at 600 degrees Centigrade. In both series the temperature of the benzene bath was held between 60 and 75 degrees Centigrade.

Red Iron Oxide Ore:- (1). The first catalyser used was a red iron oxide ore (Fe_2O_3 --hematite) from Holt, Alabama. The ore was broken into small cubes to fit in the silica tube. During the run some needle-like crystals settled out in the condenser. They proved to be diphenyl. Dense white fumes passed over into the recovery flasks throughout the operation. The tests showed a small yield of aniline. The Fe_2O_3 was apparently reduced to Fe_3O_4 . The silica tube contained a little carbon, showing that some benzene had been decomposed.

(2). A second test was carried out with some more of the same ore. Practically the same results were obtained; a positive test for aniline, needle-like crystals of diphenyl in the condenser, dense white fumes passing off,

the hematite converted to magnetite, and a little benzene decomposed, leaving carbon in the silica tube.

(3). A third test was made using the reduced ore from the second run mixed with some fresh ore. The white fumes were not dense, but there was a greater yield of diphenyl than previously. The entire condenser, with a spiral tube, was covered with the diphenyl crystals. A positive test for aniline was also obtained, showing 0.35 grams of aniline per 100 cubic centimeters of solution.

The tests show that a greater yield of diphenyl is obtained when the ore is in the reduced condition.

(4). A fourth test was made using some more of the red iron oxide ore from Holt, Alabama. A colorless distillate passed over through the condenser. The accompanying fumes were not very dense.

A few crystals appeared in the condenser. It was not determined what they were, but they were neither diphenyl nor ammonium carbonate.

The qualitative test was negative, but the quantitative test showed the presence of 0.073 grams of aniline per 100 cubic centimeters of solution.

The catalyser was not reduced.

(5). A fifth test was made with a different sample of the red iron oxide ore. The white fumes passing into the recovery flasks were not very dense.

The qualitative test was negative. The quantitative

test showed the presence of 0.05 grams of aniline per 100 cubic centimeters of solution.

The ore was not reduced.

Synthetic Red Iron Oxide:- The catalyser was prepared in the following manner: $\text{Fe}(\text{NO}_3)_3 \cdot 2\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ was dissolved in water. Small pieces of pumice were added and the solution was heated almost to boiling. This was allowed to cool and stand overnight. Then the pumice was removed, dried, and heated nearly to boiling in an ammonium hydroxide solution and left overnight. The pumice was then removed, put in distilled water, left overnight, and then dried before being put in the electric furnace. The catalyser was heated at 450 degrees Centigrade for one-half hour before starting. Brown NO_2 fumes came over into the recovery flasks.

The ammonia and benzene vapors were then passed over the catalyser in the furnace. A green liquid came over at first, but it became colorless as the operation proceeded.

The qualitative test was negative. The quantitative test showed the presence of 0.04 grams of aniline per 100 cubic centimeters of benzene solution.

The pumice was blackened, but there was very little carbon in it.

Brown Iron Oxide Ore:- The brown iron oxide ore was divided into small cubes to fit the silica tube. Dense white fumes accompanied the procedure, and a few crystals of diphenyl were deposited in the condenser. The tests

showed the presence of 0.12 grams of aniline per 100 cubic centimeters of solution.

The brown ore was slightly carbonized at the end of the run, giving it a darker color.

Gray Iron Oxide Ore:- The gray iron oxide ore was obtained from the district around Talledega, Alabama. It was heated at the operating temperature for one-half hour before starting, but no results were noted. After the operation began, a green liquid passed through the condenser. The color gradually faded until a colorless liquid was evident. A white precipitate, which had a strong ammonia odor, settled out in the condenser and also in the bottom of the second recovery flask. Sodium hydroxide was added to a few of its crystals and ammonia gas was evolved. Upon adding hydrochloric acid to a few crystals, they effervesced, indicating the formation of carbon dioxide gas. The conclusion was drawn that the crystals were ammonium carbonate. The residue was dissolved in water, but it was found that a small portion settled out in the flask, and these crystals proved to be diphenyl. The test showed the presence of 0.105 grams of aniline per 100 cubic centimeters of solution.

Manganese Dioxide:- The manganese dioxide, in lump form, was obtained from the Geology Department of the University of Alabama.

Dense white fumes passed over into the recovery flasks

during most of the operation. A small amount of diphenyl crystallized in the upper part of the condenser. The qualitative test for aniline was negative, but a yield of 0.034 grams of aniline per 100 cubic centimeters of solution was detected quantitatively.

Charcoal:- The blocks of charcoal were sawed up into small cubes and placed in the silica tube. A few crystals of ammonium carbonate settled out in the condenser. The condensate was green at first, but after the first half hour it was colorless. White fumes passed off during the run. There was no qualitative test for aniline, but the titration showed a yield of 0.023 grams of aniline per 100 cubic centimeters of solution.

Soot:- Ordinary soot from a stove chimney was next used. Nothing of importance was observed during the run. The qualitative test was negative, and the quantitative test showed the presence of only 0.005 grams of aniline per 100 cubic centimeters of benzene solution.

Chromite:- The chromite ($\text{Cr}_2\text{O}_3 \cdot \text{FeO}$) was obtained from Louise, Georgia. Dense white fumes came over, and in the laboratory could be detected the odor of hydrogen sulfide. The condensate was pale green at first and then colorless.

The first recovery flask containing 200 cubic centimeters of water turned a greenish-yellow color and soon filled up. The second flask turned the same color, and the third flask, containing concentrated H_2SO_4 , turned a deep

brown-yellow color. No aniline was detected qualitatively, but by the titration 0.036 grams of aniline per 100 cubic centimeters were obtained.

Calcium Carbide:- The ammonia gas was passed over the CaC_2 alone for about thirty minutes. Dense white fumes came over into the recovery flasks. A green oily liquid settled out on the surface of flask number one. This liquid showed no aniline when tested.

Then the benzene was passed over with the NH_3 in the usual manner. The dense fumes continued, and at first, the condensate was pale green.

The qualitative test of the end-product was negative, but the titration showed the presence of 0.042 grams of aniline per 100 cubic centimeters of solution.

Uranium Oxide:- The catalyser was prepared in the following manner: Some uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was dissolved in water to give a saturated solution. This solution was heated to the boiling point (118 degrees C.) and small pieces of pumice were put in the beaker and stirred for some time--to give the air and water content of the pumice time to be replaced by a layer of the solution. The pumice was held under the surface of the solution and allowed to stand overnight. Then it was placed in the silica tube of the electric furnace and heated to 480 degrees Centigrade for one-half hour until all the volatile matter had a chance to escape. Dense brown fumes of NO_2 passed over

through the condenser, leaving uranium oxide as the catalyser.

White fumes accompanied the run throughout. The green condensate later turned colorless.

The qualitative test was negative; while the quantitative test showed the presence of 0.021 grams of aniline per 100 cubic centimeters of solution.

Cobaltic Oxide:- The catalyser was prepared in the following manner: A saturated solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was prepared. Small pieces of pumice were put in the solution whose temperature was raised almost to boiling; so that the air and water content of the pumice would be replaced by the cobaltous nitrate solution. This was allowed to stand overnight. The pumice, impregnated with cobaltous nitrate, was then removed, rinsed in cold water, and put into a solution of dilute caustic soda, and heated slightly. Cobalt hydroxide precipitated on the surface of the pumice, and this was allowed to stand overnight. The next morning the pumice was washed with hot water, put in the electric furnace, and heated for one-half hour at the operating temperature.

Nitrous oxide fumes came over in the condenser. After the experiment started, white fumes came over during the entire four hours. The qualitative test was negative, but the quantitative test showed the presence of 0.015 grams of aniline per 100 cubic centimeters of benzene solution.

Sodium Vanadate:- The catalyser was prepared in the following way: Vanadium Pentoxide was dissolved in strong caustic soda solution. Pumice was put in the flask and the solution was heated nearly to boiling. This was allowed to stand overnight. The pumice was then put in the electric furnace and heated for one-half hour at the operating temperature before starting. A colorless liquid came over into the condenser. There were no fumes.

Then the ammonia and benzene vapors were passed into the furnace. Dense white fumes and a light green liquid came over during the biggest part of the run.

The qualitative test was negative. The quantitative test showed the presence of 0.031 grams of aniline per 100 cubic centimeters.

The pumice was only slightly carbonized.

Vanadium Oxide:- The catalyser was prepared as follows: Vanadium Pentoxide was dissolved in strong caustic soda, pumice was added to the solution which was brought nearly to boiling. This was allowed to cool. The pumice was removed and put in a flask of hydrochloric acid and again heated nearly to boiling. This was allowed to soak overnight. The pumice was then washed with water and heated in the furnace for one-half hour before starting. A red liquid came over at first.

The ammonia and benzene vapors were then passed into the furnace. The liquid was green at first and later color-

less. There were no dense white fumes.

The qualitative test was negative. The quantitative test indicated the presence of 0.043 grams of aniline per 100 cubic centimeters of solution.

Cuprous Iodide:- The catalyser was prepared in the following manner: Glass wool was soaked in a solution of boiling cupric sulfate. The glass wool was then removed and allowed to dry. It was then put in a cold saturated solution of potassium iodide. Again the glass wool was dried and allowed to stand overnight. The catalyser was heated at the operating temperature one-half hour before starting. A little free iodine came over at first.

No unusual results were observed in this run. The qualitative test was negative. The quantitative titration showed the presence of 0.02 grams of aniline per 100 cubic centimeters of solution.

Magnesium:- Magnesium ribbon was put in the electric furnace. Dense white fumes came over during the run. The liquid was colorless.

The qualitative test was negative. The quantitative test showed 0.047 grams of aniline per 100 cubic centimeters of solution.

The catalyser was examined after the run. There was very little magnesium left. The literature was surveyed for any possible compounds of magnesium with the aromatic hydrocarbons, and it was found that magnesium diphenyl,

$\text{Mg}(\text{C}_6\text{H}_5)_2$, exists.¹ It is possible that some of this compound was formed.

Carnotite Ore:- The carnotite ore, which contained fifty two percent uranium oxide and eighteen percent vanadium oxide, was broken up into pieces and placed in the electric furnace. White fumes accompanied the reaction throughout. After four hours, the ore was highly carbonized, having been changed from a yellow to a black color.

The qualitative test was negative. The quantitative test indicated the presence of 0.016 grams of aniline per 100 cubic centimeters of benzene solution.

Molybdic Oxide:- The catalyser was prepared as follows: Ten grams of molybdic acid were dissolved in 14.4 cubic centimeters of concentrated NH_4OH and 27.1 cubic centimeters of water: slowly and with constant stirring the solution thus obtained was poured into 48.9 cubic centimeters of concentrated HNO_3 and 114.8 cubic centimeters of water. The mixture was kept in a warm place for several days until a portion heated to 40 degrees Centigrade deposited no yellow precipitate of ammonium phosphomolybdate. The solution was decanted from any sediment and preserved in a glass-stoppered bottle.²

A portion of the ammonium molybdate was heated nearly to boiling; pumice was put in it and stirred for half an

1 Meyer, V. and Jacobson, P., Lehrbuch der Organischen Chemie, Zweiter Band, p. 357, (1902).

2 Griffin, R. C., Technical Methods of Analysis, p. 772.

hour to eliminate all water and air content from its surface. This was allowed to stand overnight. The pumice was then heated in the furnace for one-half hour before starting. Brown fumes, followed by white ones, passed over into the recovery flasks. A colorless liquid came over also, leaving molybdic oxide as the catalyser.

After starting, white fumes and a pale green liquid passed over, but the liquid later became colorless.

A black oil settled in the bottom of the benzene flask. It was evaporated to a small volume and allowed to stand. It crystallized out in black, straw-like needles, which were water-soluble. A qualitative test showed the oil to be a molybdenum compound, but its formula was not determined.

The general qualitative test was negative, but the quantitative test showed the presence of 0.01 grams of aniline per 100 cubic centimeters of benzene solution.

This completes the list of catalysers used when the temperature of the electric furnace was held between 450 and 480 degrees Centigrade.

In the following tests the furnace temperature was raised to 600 degrees Centigrade. Other conditions were kept the same.

Red Iron Oxide Ore:- The red iron oxide ore was divided into small pieces and placed in the furnace. The liquid coming over was green at first, but later became col-

orless. The fumes passing into the recovery flasks were not very dense. There was no crystalline material in the condenser.

The qualitative test was negative. The quantitative test showed the presence of 0.077 grams of aniline per 100 cubic centimeters of solution.

The iron oxide ore was only slightly reduced after the four hour run.

Silver Oxide:- The catalyser was prepared in the following manner: A saturated solution of silver nitrate was heated and pumice was put in it, and allowed to cool after heating for one-half hour. The pumice was then removed and placed in a hot solution of caustic soda and let stand overnight. It was then washed with cold water and heated in the furnace for one-half hour.

After starting the liquid was pale green and later it became colorless. The white fumes had a perceptible odor of diphenyl.

The qualitative test was negative; the quantitative test showed the presence of 0.05 grams of aniline per 100 cubic centimeters of solution.

Lead Sulfide:- The lead sulfide was broken into pieces suitable for the silica tube. The liquid was pale green throughout the run. A few crystals of ammonium carbonate settled out in the condenser.

The qualitative test was negative. The quantitative

test showed the presence of 0.023 grams of aniline per 100 cubic centimeters of solution.

The galena was only slightly carbonized.

Cupric Oxide:- The catalyser was in lump form. It was broken up in convenient sized pieces to fit the silica tube. The condensate was colorless and there were no fumes.

The qualitative test was positive. The quantitative test indicated a yield of 0.11 grams of aniline per 100 cubic centimeters of solution.

The dark gray cupric oxide was a bright copper color when taken out of the furnace. The oxide had been completely reduced to metallic copper.

Nichrome Wire:- Nichrome wire was coiled and placed in the silica tube. The liquid coming over was pale yellow in color. Dense white fumes of diphenyl came over into the recovery flasks. The diphenyl odor was distinguishable in the laboratory. A few diphenyl crystals appeared in the condenser.

The qualitative test was negative, but the quantitative titration showed the presence of 0.06 grams of aniline per 100 cubic centimeters of benzene solution.

Aluminum:- The metallic sheet aluminum was cut into small pieces and placed in the electric furnace. The condensate was pale green at first and later colorless. Dense white fumes came over throughout the run.

The qualitative test was negative, but the quantitative

titration showed the presence of 0.059 grams of aniline per 100 cubic centimeters of benzene solution.

There was no apparent change in the catalyser after the four hour run.

Active Silica:- The catalyser was in small lumps that were suitable for the silica tube of the electric furnace. The condensate was green at first and later colorless. Dense white fumes came over throughout the process.

The qualitative test was negative, but the titration indicated the presence of 0.03 grams of aniline per 100 cubic centimeters of benzene solution.

Ammonia Catalyst:- The catalyst was already in small cubes. The liquid coming over was green at first. It became colorless after a short time. The white fumes had the odor of diphenyl.

The qualitative test was negative, but the quantitative test showed the presence of 0.11 grams of aniline per 100 cubic centimeters of solution.

The catalyser was left in the furnace for the next run.

The end-product, after being analyzed for aniline, was concentrated down to a very small volume and allowed to evaporate slowly. A deposit of two grams of diphenyl was obtained from it.

Reduced Ammonia Catalyst:- The catalyst was prepared in the following manner: The ammonia catalyst from the previous

run was left in the electric furnace. A flask containing some metallic zinc, copper sulfate, and water was attached in place of the benzene flask. The furnace was heated to 480 degrees Centigrade. Some hydrochloric acid was poured in the flask through a separatory funnel. The hydrogen produced in the reaction passed up through the furnace and reduced the magnetite ore to metallic iron. The reduction was carried on for four hours, making sure that most of the catalyst was reduced.

The experiment was then started. The liquid was green at first and later colorless. The white fumes had the odor of diphenyl. There was a slight deposit of diphenyl in the condenser.

The qualitative test was negative, but the quantitative titration showed the presence of 0.02 grams of aniline per 100 cubic centimeters of benzene solution.

The catalyser was only slightly carbonized.

Bauxite:- The catalyser was broken up into pieces to fit the electric furnace. It was heated at the operating temperature for one-half hour to drive off excess water. Throughout the run the liquid was colorless. The dense white fumes did not have a diphenyl odor.

The qualitative test was negative, but the titration showed the presence of 0.093 grams of aniline per 100 cubic centimeters of benzene solution.

The catalyser was highly carbonized after the run.

Nickel Oxide:- The catalyser was prepared as follows: A saturated solution of nickel sulfate was heated nearly to boiling. Some porous active silica was put into the solution and heated for several minutes. The solution was allowed to cool and stand overnight. The active silica was then removed and heated nearly to boiling in a strong caustic soda solution. This was allowed to stand overnight also. The silica was then dried and heated in the furnace at the operating temperature for one-half hour, to drive off the water and leave only nickel oxide as the catalyser.

The liquid coming over through the condenser during the four hour run was colorless. The fumes were not very dense.

The qualitative test was negative. The quantitative titration showed the presence of 0.078 grams of aniline per 100 cubic centimeters of benzene solution.

This completes the list of catalysers used up to the present time in the direct production of aniline from benzene and ammonia.

Chapter XI

Summary of Results

It is the purpose of the writer in this chapter to give a brief summary of the work done thus far on the direct production of aniline from benzene and ammonia.

Following is a table of the catalysers used and the yield obtained from each test.

At 450--480°C.

<u>Catalyser</u>	<u>Production</u> (<u>In Grs./100cc. C₆H₆</u>)
Red Iron Oxide Ore	
Test No. 1.....	Undetermined
Test No. 2.....	Undetermined
Test No. 3.....	0.350
Test No. 4.....	0.073
Test No. 5.....	0.050
Red Iron Oxide (Artificial).....	0.040
Brown Iron Oxide Ore.....	0.120
Gray Iron Oxide Ore.....	0.105
Manganese Dioxide.....	0.034
Charcoal.....	0.023
Soot.....	0.006
Chromite.....	0.036
Calcium Carbide.....	0.042
Uranium Oxide.....	0.021
Cobaltic Oxide.....	0.015
Sodium Vanadate.....	0.031
Vanadium Oxide.....	0.043
Cuprous Iodide.....	0.020
Magnesium.....	0.047
Carnotite Ore.....	0.016
Molybdic Oxide.....	0.010

After these tests were made, the furnace temperature was raised to 600 degrees Centigrade. A list of the catalysers used in this second series of runs follows:

At 600°C.

<u>Catalyser</u>	<u>Production</u> (<u>In Grs./100cc.</u> <u>C₆H₆</u>)
Red Iron Oxide Ore.....	0.077
Silver Oxide.....	0.051
Lead Sulfide.....	0.023
Cupric Oxide.....	0.110
Nichrome Wire.....	0.060
Aluminum.....	0.059
Active Silica.....	0.030
Ammonia Catalyst.....	0.110
Reduced Ammonia Catalyst.....	0.020
Bauxite.....	0.093
Nickel Oxide.....	0.078

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Chapter XII.

Conclusion

The general conclusions drawn from the summary of the results in Chapter XI include the following:

- (1). No method of commercial importance has been discovered for the direct production of aniline.
- (2). Oxide catalysers have given the best results to date, the various forms of oxide iron ore and copper oxide heading the list.
- (3). Work on this direct production of aniline is being continued, using iron oxide containing promoters of various kinds.

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