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Oxidation of phenanthrene.

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UNIVERSITY OF LOUISVILLE

OXIDATION OF PHENANTHRENE
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A Thesis

Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of
MASTER OF CHEMICAL ENGINEERING
Department of Chemical Engineering

By

Frank Hunt Miller, Jr.
///

1942

OXIDATION OF PHENANTHRENE

Frank Hunt Miller, Jr.

Approved by the Examining Committee

Director

May 15, 1942

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A B S T R A C T

This investigation was on the oxidation of phenanthrene. The oxidation was attempted by passing unheated atmospheric air through liquid phenanthrene, by passing preheated atmospheric air through liquid phenanthrene, and by passing unheated pure oxygen through liquid phenanthrene, varying the temperature of the phenanthrene and using no catalyst.

Only traces or small yields of the dibasic acids were obtained in any of the runs that were made.

INTRODUCTION

The purpose of this research is to investigate the oxidation of phenanthrene to diphenic acid.

Phenanthrene is one of the many by-products of the destructive distillation of coal. The usefulness of the by-products of coal carbonization determines, to some extent, the economic success of the carbonization process. This investigation was undertaken to increase the economic value of phenanthrene.

Much research has been and is being carried on to find profitable uses for phenanthrene. However phenanthrene in its original form is of little value and probably will be usable only as a starting material that may be changed chemically into more useful chemicals. The process that has received the most interest is that of the oxidation of the phenanthrene to diphenic, phthalic, and maleic acids. The dibasic acids can be used by varnish and synthetic resin producers for the manufacture of various resins.

HISTORICAL

The increasing use of by-product coke by the metallurgical industries has, in recent years, caused the utilization of the by-products to become more important. In the separation of the constituents of coal tar, phenanthrene is isolated fairly pure and may be considered to be, for practical purposes, pure phenanthrene.

Discussion will be limited to the processing of phenanthrene to form diphenic acid, since that reaction was investigated in this research. The mechanism of the oxidation of phenanthrene to carbon dioxide and water has been fairly well established by many investigators to be:

phenanthrene $\longrightarrow$ phenanthraquinone $\longrightarrow$ 6,6' diphenic acid $\longrightarrow$ O-phthalic acid $\longrightarrow$ phenol $\longrightarrow$ maleic acid $\longrightarrow$ $\text{CO}_2 + \text{H}_2\text{O}$.

The first investigators to work on phenanthrene carried out their reactions in a stepwise fashion, in order to discover the intermediate steps in the total oxidation to carbon dioxide and water. The German chemists of the second half of the last century performed the reactions in the first two steps of the total oxidation.

In 1873 phenanthrene was first oxidized to phenanthraquinone by Graebe (7), who oxidized purified phenanthrene with chromium trioxide in hot acetic acid solution. Later phenanthraquinone was prepared by Anschütz and Schultz (1) in 1879 similarly, using potassium dichromate and

sulfuric acid. These investigators mentioned the concomitant production of some diphenic acid as the reaction was carried out. Later, phenanthraquinone was prepared electrolytically from a suspension of phenanthrene in twenty per cent sulfuric acid using cerium sulfate as a catalyst by Meister, Incius, and Bruning in 1902, (10).

Diphenic acid was prepared from phenanthraquinone first by Fittig and Ostermayer (4) in 1873 according to the following procedure: a solution of phenanthraquinone in sulfuric acid is poured slowly into a solution of potassium dichromate in water. The heat of dilution of the sulfuric acid is sufficient to start the oxidation and the reaction is completed by refluxing for four hours. The acid is extracted from the precipitate with sodium carbonate solution. This was repeated by Schmitz (12) in 1878, by Graebe and Aubin (8) in 1888, and by Gotz (6) in 1902. Diphenic acid also was obtained by boiling phenanthraquinone with aqueous and alcoholic potash by Anschutz and Schultz (1) in 1879 and the experiment was repeated by Meyer and Spengler in 1905 (11).

The research of Gibbs and Conover (5), which in 1918 resulted in a process for the manufacture of phthalic anhydride, and in which vaporized naphthalene was mixed with air and passed over a heated catalyst, led to the later process

discovered by Lewis and Gibbs (9) for the manufacture of phenanthraquinone by vaporizing the phenanthrene, mixing it with air and passing the mixture over a heated catalyst. The patent they obtained on this latter process in 1918 was assigned to the public.

In 1922 Gibbs obtained another patent, U. S. Patent No. 1,444,068, on a process for the oxidation of mixtures of anthracene and phenanthrene, such as may be obtained by the removal of carbazol by caustic fusion from anthracene press cake. This patent claimed the production of phthalic anhydride and anthraquinone when the vapors of phenanthrene and anthracene were mixed with oxygen and passed over the oxides of vanadium, molybdenum, or chromium. Gibbs assigned it to E. I. duPont de Nemours and Company, Wilmington, Delaware.

In 1937 Yu. S. Zal'kind and V. V. Kesarev (13) published the results of an extensive research inquiring into the vapor phase oxidation of phenanthrene by air in the presence of solid catalysts. Their best results, 41 per cent mixed diphenic and phthalic acids, were obtained when the reaction chamber was held at 390° C., the catalyst contact time was four seconds and the phenanthrene supplied to the reaction chamber was at 220° C. The catalyst mass used in this instance was 70 per cent vanadium oxide and 30 per cent uranium oxide fixed on pumice.

At about the same time Chowdbury and Saboor (3) were carrying on similar researches on the vapor phase oxidation of naphthalene and phenanthrene with air in the presence of tin and vanadium catalysts. Their best yield was 22.35 per cent phthalic anhydride on oxidation of phenanthrene mixed with air over tin vanadate - asbestos catalyst at 420° C.

In 1939 and 1940 Bracken (2) attempted the oxidation of phenanthrene dissolved in benzene using soluble catalysts with air at room temperature. He found that benzene oxidized preferentially and obtained no oxidation of phenanthrene.

The most promising of these processes on a commercial scale is the catalytic vapor phase oxidation. The yields, however, are not entirely satisfactory, and this process entails some difficulties since high temperatures must be used on account of the high boiling points of phenanthrene and the end products.

THEORETICAL

The oxidation of phenanthrene has been accomplished by many investigators, as has been mentioned previously. The mechanism for the stepwise oxidation, as first proposed by Chowdbury and Saboor (3) is as follows:

It is seen from this reaction that there are two useful derivatives, diphenic acid and phthalic acid, both of which are used in the synthetic resin industry.

The addition of oxygen to a molecule to break it into oxidized parts or to make an oxidized molecule must be performed by an oxidizing agent. The number of possible oxidizing agents is greatly limited because the agent to be used must be relatively cheap, and it must be soluble, unless it is a gas, in liquid phenanthrene or in a solution of phenanthrene in one of its solvents. By far the cheapest oxidizing agent is air. It was decided to use, if possible, air for the oxidizing agent.

The advantage of agents other than molecular oxygen, such as is in air, is that the agents themselves are relieved of their oxygen, releasing it in the atomic state, which state is much more reactive than the molecular state. The use of a catalyst with molecular oxygen, however, decreases this advantage, since the catalyst is considered to convert molecular oxygen to the atomic or "nascent" state. It may be necessary, if the air is used for the oxidizing agent, to use a catalyst.

There are two factors to be considered in the problem, equilibrium and reaction rate. The oxidizing agent and reaction conditions must be such that a favorable equilibrium is reached, and that the reaction rate causes this equilibrium to be reached in a reasonable time. The use of the proper catalyst, while not affecting the final equilibrium, will increase the reaction rate.

The oxidation may be accomplished in the liquid state or the vapor state. Oxidation in the liquid state may be performed by bubbling air through liquid phenanthrene or through phenanthrene dissolved by a suitable solvent, if the solvent is stable with respect to the oxidizing effect of the air being bubbled through. Oxidation in the vapor state is done by blowing heated gas (either air or oxygen) through melted phenanthrene, to pick up phenanthrene vapor and passing the hot mixture of gas and vapor through a heated catalyst mass. The vapor state reaction is sometimes

carried out in a pressure chamber, using a batch process instead of the above described continuous process. In the latter process solid phenanthrene is put into the reaction vessel, the oxidizing gas is added under pressure, and the vessel is heated to a temperature that will melt the phenanthrene and vaporize a considerable portion of it. If a catalyst is to be used it is added with the phenanthrene, if a solid or liquid at room temperature, or added with the oxidizing gas if a gas at room temperature.

Of the above methods of oxidation of phenanthrene only the continuous vapor state process using air has been successfully accomplished. This was done by Zal'kind and Kesarev (13) and Chewdury and Saboor (3), the former obtaining a yield of 41 per cent mixed diphenic and phthalic acids, and the latter obtaining 22.35 per cent phthalic anhydride (probably finding and not reporting some diphenic acid). No successful oxidations have been accomplished by passing air through melted phenanthrene or a phenanthrene solution.

Following a line of increasingly costly methods the progression is as follows:

1. Bubbling unheated air through melted phenanthrene.
2. Passing preheated air through melted phenanthrene.
3. Continuous vapor phase processes.

4. Passing unheated air through phenanthrene in solution with a non-oxidizable solvent.
5. Passing heated air through phenanthrene in solution with a non-oxidizable solvent.
- 6., 7., 8., 9., 10. These same processes, in which pure oxygen is substituted for air.
11. Bubbling oxidizing agents other than air or oxygen through melted phenanthrene.
12. Continuous vapor phase processes in which volatile oxidizing agents other than air or oxygen are used.

This progression may not hold true, however, in a case where a high yield in a relatively costly process would make the unit cost on the material produced lower than a less costly process in which the yield is low.

Since it had been already established by both Zal'kind and Kesarev, and Chowdury and Saboor that phenanthrene can be oxidized by air, it was decided to attempt to oxidize phenanthrene by melting it and passing air through it; then, if the yield on this procedure was not high enough to make the unit cost on the material produced lower than the unit cost using the continuous vapor phase process, to proceed to the next more costly process, and so on.

EXPERIMENTAL

APPARATUS

The apparatus used for the experimental work consisted of a large glass test tube (one inch in diameter and eight inches in length), which was the reaction chamber; a Wood's metal bath around the test tube; and a stopper for the tube which contained three holes, one for the entrance of the oxidizing gas, one for a 360° C. thermometer, and one for the exit of reacted gas. The reacted gas was conducted from the reaction tube to a large air condenser which was a piece of glass tubing three quarters of an inch in diameter and eighteen inches in length.

For the various kinds of experimental runs there were various kinds of auxiliary equipment attached to the above reaction tube and condenser. When the oxidizing gas was atmospheric air, unpreheated, there was a vacuum aspirator connected to the exit end of the air condenser. During the run in which preheated atmospheric gas was used as the oxidizing agent, there was a small coil of copper tubing (outside diameter three sixteenths of an inch) attached to the oxidizing gas entrance of the reaction tube. On this run also a vacuum aspirator was connected to the exit side of the air condenser.

When unpreheated oxygen was used as the oxidizing gas the oxygen was blown through the reaction tube from a high pressure oxygen storage tank and the vacuum

aspirator was not used.

A sketch of the above described apparatus appears on the following page.

EXPERIMENTAL APPARATUS

FIG. I

PROCEDURE

The experimental reactions to produce diphenic acid from phenanthrene were preceded by some preliminary tests to set up a method of analysis of reacted mixtures.

The method used by Bracken (2) was adopted with changes necessitated by a difference in the material to be analysed. The procedure was as follows: The reacted material was in two parts, the material which remained in the reaction tube at the end of the run, and the material which had been carried from the reaction tube to the air condenser, either by being vaporized in the reaction tube and condensed in the condenser or by being entrained in the gas that was being bubbled through the phenanthrene in the reaction tube.

These two reacted masses were, either separately or together, macerated with a standard water solution of sodium hydroxide at the boiling temperature of the solution. The water soluble acids, diphenic, phthalic, and maleic, were thereby extracted from the water insoluble materials, phenanthrene and phenanthraquinone by forming the ionized sodium salt and water with the sodium hydroxide. The reactions are:

The water solution of sodium hydroxide contained an amount of sodium hydroxide in excess of the amount necessary to react with the amount of acids present. The excess sodium hydroxide was titrated with standardized sulfuric acid after the extraction was made. The percentage conversion of the phenanthrene was calculated from the amounts of sodium hydroxide and sulfuric acid used. The testing of the analytical procedure, blank runs, and various oxidation trials were so detailed and varied that they will be discussed separately under "Data and Results."

DATA AND RESULTS

The Test Analyses

Run 1. (Blank) Twenty-five g. phenanthrene was boiled with H_2O for 15 minutes. Supernatant water was titrated with 1.037 normal NaOH while still in contact with the liquid phenanthrene. The phenolphthalein end point was less than .01 ml.

Run 2. Two grams phthalic anhydride and 25 g. phenanthrene were melted together and then boiled for 15 minutes with 250 ml. H_2O . The supernatant water was titrated with 1.037 normal NaOH while still in contact with the liquid phenanthrene using phenolphthalein indicator. Pink color appeared permanently at 26.5 ml.

$$\text{Equivalent wt. phthalic anhydride} = \frac{148.11}{2} = 74.06 \text{ g.}$$

$$\text{Equivalents phthalic anhydride used} = \frac{2}{74.06} = .0270$$

$$\text{Equivalents shown to be present by test} = \frac{1.037 \times 26.5}{1000} = .0275$$

Result: The amount of phthalic anhydride present was discovered with an accuracy within the limit of experimental error.

Run 3. The manufacture of phenanthraquinone from phenanthrene as done by Graebe (7).

Two hundred twenty-five g. H_2SO_4 (sp. gr. 1.84) was placed in a 1000 ml. florence flask with 300 ml. H_2O .

Seventy-five g. KCr_2O_7 was added to the flask and dissolved. Twenty-five g. crude phenanthrene (90% phenanthrene, 10% anthracene, trace carbazole) was placed in the flask and the mixture was heated gently with a reflux condenser attached to the top of the flask. Seventy-five grams $\text{K}_2\text{Cr}_2\text{O}_7$ was added to the mixture and boiled for one hour. The mixture was cooled and placed in two 1500 ml. beakers, half in each beaker. The beakers were filled with water and the aqueous mixture was filtered in an attempt to retain the crystallized phenanthraquinone on the filter paper. Several large lumps of what appeared to be unreacted phenanthrene remained in the bottoms of the beakers. The residue was crushed while still wet and placed in a 400 ml. beaker. H_2SO_4 (sp. gr. 1.84) was poured into the beaker until it covered the wet solid and the mixture was allowed to stand for 48 hours.

The acid was diluted by adding water to the beaker in the ratio of (water to acid) 10 to 1. Then the acid was poured off and the residue washed with 1 normal NaOH and with water. The residue from this wash was digested with sodium bisulfite solution in which phenanthraquinone is soluble and anthraquinone insoluble. The digestion was filtered into a filter flask containing a solution of dil. H_2SO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$. A precipitate appeared inside the

filter flask. The residue was rejected. The precipitate contained in the contents of the filter flask was coagulated by the addition of a small amount of conc. H_2SO_4 and filtered again. The residue was dried (filtrate rejected), dissolved in ether, filtered (residue rejected), and the filtrate evaporated on a watch glass. The melting point of the crystallized solid was determined to be $160 - 165^\circ\text{C}$. with a heated stage melting point apparatus.

A small part of the phenanthraquinone was placed in a test tube with .2 g. powdered zinc and 5 ml. of .1 normal NaOH. This mixture was boiled for 30 seconds and filtered while hot. If anthraquinone had been present the filtrate would have been deep red. The filtrate was pale yellow. This was a negative qualitative test. A small amount of the phenanthraquinone was placed in a test tube and 5 ml. H_2SO_4 (sp. gr. 1.84) added. A deep green color indicated the positive presence of phenanthraquinone.

A .2 g. sample of the product was placed in ether solution and was titrated with .1 normal NaOH. The end point was at 1 ml. This indicated an incomplete removal of sulfuric acid.

Run 4. A mixture of phenanthrene, phenanthraquinone (prepared in the laboratory), and diphenic acid was made up in the following proportions:

Phenanthrene	6.00 g.
Phenanthraquinone	4.09 g.
Diphenic Acid	2.00 g.

This mixture was placed in a casserole, melted, and the reacted mixture analysis performed on it. The acid extraction with sodium hydroxide solution and back titration of the solution showed the presence of 2.83 g. of diphenic acid. Extraction of the phenanthraquinone from the phenanthrene with sodium bisulfite solution as in the preceding run yielded 1.14 g. phenanthraquinone. The remaining phenanthrene weighed 6.77 g.

The diphenic acid result was high because of insufficient removal of the acid from the phenanthraquinone. The phenanthraquinone contained enough sulfuric acid to show a test for .0481 g. of diphenic acid. The error in the diphenic acid determination above .0481 g. may be accounted for in the experimental work. The phenanthrene value was probably high and the phenanthraquinone was low because of incomplete extraction of phenanthraquinone from the phenanthrene by sodium bisulfite solution.

Experimental Runs

Approximately 20 g. phenanthrene was placed in each of six large pyrex test tubes. An oil bath was made of 1000 ml. beaker and cottonseed oil, with a thermometer suspended in the oil. Each of the tubes was placed in the

oil bath and heated at an elevated temperature for a short time, while air was passed through the liquid phenanthrene. At the end of the heating period the phenanthrene was dumped into a casserole covered with 100 ml. distilled H_2O , and titrated with .107 normal NaOH and phenolphthalein at $100^{\circ} C.$ to determine acid content of the phenanthrene. All the data are on the following tables. The amounts of acids were so small that a direct titration with NaOH was satisfactory.

Data:

<u>Run</u>	<u>Wt. Phenanthrene</u>	<u>Reaction Time</u>	<u>Reaction Temp.</u>	<u>ccNaOH</u>
5	21.11 g.	35 min.	$200^{\circ} C.$	0.35
6	22.00 g.	45	$225^{\circ} C.$	0.35
7	25.89 g.	40	$250^{\circ} C.$	0.35
8	21.50 g.	45	$275^{\circ} C.$	0.55
9	23.01 g.	45	$300^{\circ} C.$	0.50
10	34.75 g.	45	$325^{\circ} C.$	0.35

Twenty g. of phenanthrene was titrated as a blank and 0.35 cc. of NaOH was used.

Result: Only traces of the mixed acids were formed.

The apparatus shown in the sketch on page 16 was assembled and liquid phenanthrene was treated by passing preheated atmospheric air through it. The sodium hydroxide

extraction method was used to analyze the reacted mixtures. Bromthymol blue was used from this point on as an indicator.

Data:

<u>Run</u>	<u>Reaction Time</u>	<u>Reaction Temp.</u>	<u>% yield mixed acids</u>
11	1 hr. 0 min.	280 - 325° C.	0.054
12	2 hr. 30 min.	280 - 320° C.	0.0258
13	1 hr. 0 min.	280 - 320° C.	0.059
14	1 hr. 50 min.	305 - 315° C.	0.062
15	1 hr. 0 min.	310 - 320° C.	0.080

The temperature of the preheated air was not determined. The length of the preheated tube was 3.5 feet, and it was heated to a bright red color in each of the above runs.

The apparatus shown in the sketch on page 16 was changed in that the preheater was removed and a line to a compressed oxygen tank was substituted in its place. The suction aspirator was disconnected. The gases coming from the air condenser were bubbled through a small beaker of distilled water before being exhausted to the atmosphere. Both the water in this beaker and the reacted mass in the reaction tube were analyzed for mixed acids in reporting the percent yield. The oxygen was not preheated.

Data:

<u>Run</u>	<u>Reaction Time</u>	<u>Reaction Temp.</u>	<u>%Yield Mixed Acids</u>
16	1 hour	245° C.	0.146

Run	Reaction Time	Reaction Temp.	% Yield Mixed Acids
17	1 hour	265° C.	0.276
18	1 hour	300 - 310° C.	0.302

CONCLUSIONS AND RECOMMENDATIONS

The oxidation of phenanthrene to mixed diphenic, phthalic and maleic acids by passing atmospheric air, both unpreheated and preheated, and pure oxygen, unpreheated, through melted phenanthrene at various temperatures produced only traces of the mixed acids.

It is recommended that subsequent investigations continue as follows:

1. Use of preheated oxygen.
2. Use of air and oxygen heated and under pressure.
3. Use of a non-oxidizable carrier for liquid phase oxidization.
4. Use of catalysts for most promising of previous experiments.

APPENDIX

In addition to the project reported in the preceding sections of this thesis the author spent considerable laboratory time in working on three other projects of the Division of Industrial Research. The following are short reports of the nature of his work on the projects.

1. The Refining of Cadmium from Waste Ore.

The problem involved the reclaiming of cadmium from an industrial waste material of unknown source. The analysis of this waste ore showed the following:

Cadmium	80%
Arsenic	16%
Lead	4%

The initial separation was a digestion with dilute sulfuric acid. The sulfate of lead is quite insoluble. It was hoped that the cadmium would go into solution alone, but on analysis it was found that arsenic was dissolved by the dil. H_2SO_4 also. The amount of the original material that went into solution was found by using a gooch crucible.

The investigation was continued, using the dilute H_2SO_4 to dissolve the arsenic and cadmium. Then the removal of the arsenic was attempted by adding ferrous sulfate crystals, allowing them to go into solution, and adding hot milk-of-lime suspension to the acid solution until the solution became basic, in an effort to cause

coprecipitation of the arsenic. This method was successful in removing the arsenic from solution but also removed all but traces of the cadmium.

The method of attack was then changed. The solid material was treated with a mixture of concentrated nitric and hydrochloric acids. The chloride of lead is insoluble, for practical purposes. The resulting solution of arsenic and cadmium chlorides was then evaporated to dryness and heated at 150° C. for several minutes. The chloride of trivalent arsenic is a liquid at room temperature and boils at about 130° C. It was hoped that the arsenic would be converted to the trichloride and be vaporized at 130° C. This would leave only a residue of cadmium chloride. This approach failed, probably because there was pentavalent arsenic present in the original material.

The investigation here was discontinued, because the raw material was taken off the market.

2. The Utilization of Wood Waste for a Plastic.

This project was an investigation of the possibility of using a wood waste in the form of sawdust and sander dust as a plastic forming material or as an extender or diluent in a standard moulding compound.

The equipment used to manufacture test pellets that were made for experimental purposes was a standard laboratory hydraulic press of 5000 pounds per square inch

capacity when used with a 1 inch (inside diameter) molding-die. The die was a standard 1 inch inside diameter 1.5 inch outside diameter, metallurgical specimen mounting die.

The molding procedure was as follows: The mixture was placed in the die and the heating element placed around the die with the current on. The two were placed in a laboratory press, a thermometer being put into the top of the die, in a well, through the press frame, a hole having been made in the press frame for this purpose. The pressure on the die was adjusted to 2000 p.s.i. (pounds per square inch) and held there. When the thermometer, which rose slowly from room temperature, reached 100° C. the current was turned off in the heating element, and the element was allowed to stay around the die for 5 minutes while the pressure was 2000 p.s.i. At this time the pressure was released and the heating element was quickly replaced by a water cooled cooling element. When the temperature reached 55° C. (the press was held at 2000 p.s.i. during the cooling period) the pressure was released, the die taken apart and the pellet removed.

Pellets were made of the following mixtures:

<u>Number</u>	<u>Parts Material</u>	<u>Parts Material</u>
A-1	5 (g.) dry sander dust	1½ (g.) urea
A-10	5 " " "	2 "

<u>Number</u>	<u>Parts</u>	<u>Material</u>	<u>Parts</u>	<u>Material</u>
A-3	5 (g.)	dry sander dust	3 (g.)	urea
A-2	5	" " "	2½	"
A-11	5	" " "	4	"
A-4	10 (g.)	wet sawdust green	1	"
A-5	10	" " "	3	"
A-6	10	" " "	4	"
A-7	10	" " "	5	"
A-8	5	dry sander dust	5 urea + 0.2	NH ₄ Cl
A-9	5	" " "	1	urea
A-12	10	wet sawdust green	2	"
A-13	10	" " "	6	"
AD-1	10 (g.)	dry sander dust	1 (g.)	"
AD-2	10	" " "	2	"
AD-3	10	" " "	3	"
AD-4	10	" " "	4	"

In the mixtures, number A-1, A-2, etc., on the preceding chart the mixtures were made and enough water added to make a paste. This paste was well mixed and then dried for three to four hours in an oven at 95 - 100° C. The pellets were then made from the dried material.

In the mixtures numbered AD-1, AD-2, etc., the sander dust was mixed in the dry state with the urea and the pellets made from this dry material.

A group of samples of wet sawdust, Chestnut or Rock Oak, Hickory, Red Oak, Beech, Chestnut, Yellow Poplar, Hard Maple, Soft Maple, Birch, and Red Oak (urea treated), were analyzed for moisture content and pellets were made of the group, one pellet of each specie. The proportions were enough wet sawdust to make five grams dry and two and a half grams of urea. Enough water was added to this mixture to make a paste, and the mixture was dried in a 100° C. oven, after thorough mixing. The same procedure was used in making these pellets as was used before.

There were next prepared saturated solutions of the following salts: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, NaCl , and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. These solutions are in equilibrium with air of the following relative humidities, respectively: 32.3%, 52.4%, 76.1%, 89.9%, when the air over them is allowed to come into equilibrium with the solution.

The solutions were placed in the bottoms of empty reagent jars and two-hole number 10 stoppers, with one glass tube extending through the top to below the surface of the solution and one glass tube extending to the space above the solution, were placed in series so that air might be drawn through each jar in series bubbling through each solution in succession. A jar containing pure water was added to the series. A small wire cage was fixed to the

under side of the stopper in each jar and two pellets, one coated with paraffin and one not coated were placed in the cage in each jar. The pellets were of the same composition as number A-2. The dimensions, diameter and thickness, of each pellet were measured with a micrometer and recorded. The object of this experiment was to find out whether the pellets undergo any change in dimensions after exposure to air of varying moisture content.

At this point the author stopped work on this project.

3. The Design of the Heating Element for a High Pressure Bomb.

A high pressure reaction unit had been constructed for use in the research on the oxidation of phenanthrene. The completion of the unit required the design of some method of heating the high pressure reaction chamber.

It was decided to wrap the bomb casing (see sketch on page 37), which holds the bomb while it is in use, with a sheet of mica for insulation and then wrap a length of electric heating element ribbon around the mica sheeting. The ribbon shall be standard chromel wire ribbon. After preliminary calculations it was decided, with the help of the catalogue of the Hoskins Manufacturing Company of Detroit, Michigan, to use two lengths of ribbon each 12

feet in length. The two lengths are to be connected in parallel.

The ribbon is to hold the mica in place and another layer of mica is to be wrapped around the ribbon to hold the ribbon in place. The outside layer of mica may be held on by wrapping ordinary baling wire around it and twisting the ends together or by using automobile radiator hose connectors. After the second layer of mica is firmly in place the remaining space in the bomb casing is to be filled with asbestos fibers to insulate the heating unit from the outside surface of the bomb casing.

FIGURE II
BOMB CASING

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Abbreviations of the titles of journals:

Annalen: Annalen der Chemie
Ber.: Berichte der Deutschen Chemischen Gesellschaft
Montash: Monatshefte fur Chemie und Verwandte Theile
 anderer Wissenschaften.

V I T A

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The author, son of Frank Hunt Miller and Ida Mae Miller, was born on October 4, 1918, at Rutherford, New Jersey. A few years later the family moved to Louisville, Kentucky, where he attended the Louisville public schools. He was graduated from the Louisville Male High School in 1936.

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