THE PRODUCTION OF NYLON FROM FIBRE.

BY

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I. INTRODUCTION

The problem for study is the synthesis of nylon, and the study of the difficulties involved.

For years, American scientists have searched for a substitute for silk, of which fifty-one million pounds were imported in 1939. Seventy-five percent of this was consumed in the manufacture of hosiery, while considerable amounts went into essential military products such as parachutes and shroud lines, powder bags and flare cloths.

A yarn which combines high elasticity and tensile strength with light weight is required for such purposes. With the advent of nylon, a truly synthetic product was found for the place of silk which was listed as a strategic material, and was becoming increasingly scarce.

Late in 1939, the first spinning machine for nylon yarn was started in DuPont's new plant at Seaford, Delaware. This plant also produces the flake nylon, which is made into the monofilament used as brushes, fishing leaders, and surgical sutures. In 1943, production of nylon was sixteen million pounds per year and was increasing rapidly with the building of new plants.

Now, with the supply of silk cut off, and with increased demand for military uses of nylon, the product is restricted to military users. Many products are advertised for postwar applications of nylon. At present, the cost of production is greater than for competitors, rayons and silk.

The difficulties in production are the cause for the expense. The main bottleneck is the manufacture of cyclohexanone from phenol. Attempts have been made to put the production on a continuous basis instead of the batch
type production. This is the second outstanding problem. A continuous process has been patented but the results of the operations involved have not been publicized.

It is the object of this study to make nylon on a laboratory scale, with emphasis being placed on the problems mentioned: manufacture of cyclo- 
hexanol, and design of a pilot plant for continuous operation.
II. LITERATURE REVIEW

Theory: Sylon is a general name for all synthetic fiber-forming polyamides. Sylon No. 66, the product commercially produced as Sylon, is the subject of this thesis. It is the product of the condensation and polymerization of adipic acid and hexamethylenediamine. In structure, the polyamides resemble the natural proteins such as silk and wool:

![Structure of Natural Fiber Proteins](image)

In the case of silk, R is mostly methyl, but wool has a more complicated structure, including cystine, leucine, glutamic acid, arginine, and a number of other components.

![Structure of Sylon](image)

All of these differ from cellulose, from cotton and wood pulp, in that the protein substances contain amine linkages, whereas no nitrogen is found in cellulose:

![Structure of Cellulose](image)
Thus nylon is related to the natural protein fibers, rather than to the other artificial fibers on the market, not only in structural formula, but in properties.

This thesis does not deal with the uses and properties of the product, and the reader is directed to references (2), (3), (11), and (16) for such information.

History: Ever since the seventeenth century when the alchemists gave up the search for a method to produce gold from the baser metals, scientists have searched for an artificial silk.

In 1834, Robert Hooke, and in 1734, A. A. F. Monnier suggested methods for spinning artificial fibers, but not until the 1880's were any fibers produced, when a Manchester silk manufacturer, Schwabe, spun fibers from natural gum and resins. The fibers were weak and not nearly as attractive as those produced by Mercer, who introduced the "mercerization" (10) of cotton in 1844.

Probably the first rayon produced was nitrocellulose (10), exhibited by the Count de Chardonnet at the Paris Exposition in 1889, creating a furor in the textile world, despite the fragility and generally poor physical properties of the threads produced.

In 1890, a Frenchman, L. H. Despiau, patented the original cuprammonium process (10), although the fact that cellulose could be dissolved in cupric hydroxide and ammonia had been discovered in 1857 by Schweitzer.

Then in 1892, the viscose process (10), producing cellulose xanthate was patented by Cross and Nenan in England.

Cellulose acetate (10) appeared commercially in 1902 when the first successful process for a product of this type was patented in the United
States by Walker, Little, and Stark.

Despite much work and recent improvements in manufacture and processing, rayons are still far from being the ideal fiber.

In 1927 the work that led to nylon was begun by Dr. Wallace Hume Caruthers working in the DuPont Research Laboratories. During the course of his investigation he synthesized various ethers and esters of cellulose but found them no improvement over the existing rayons. Caruthers then discarded cellulose and turned to research in the field of polycondensation.

By 1928, he had produced polyesters with average molecular weight of 5,000 by combining dihydric alcohols and dibasic acids. With the use of the molecular still, it was found that the removal of water increased the molecular weight to from 10 to 25 thousand. With increase in molecular weight, the properties changed, the product going from a semi-opaque, waxy, brittle solid to one which was tough, elastic and rather transparent. The "superpolyester" fibers were superior to those of the polyester, and they could be "cold-drawn".

"Cold-drawing" orients the molecules into approximate parallelism with the axis of the fiber, resulting in improved properties in the fiber.

Along with its advantages, this superpolyester had one outstanding disadvantage - it had a very low softening point, prohibiting its practical use. In an attempt to obviate this difficulty, Caruthers made the superpolyamide of 5-nine hexanoic acid (caproic acid). This substance also had the required physical properties but its softening point was extremely high, prohibiting any ease of spinning. It was insoluble in
practically all organic solvents, phenols and formamide being notable exceptions. All of his attempts to find a middle ground between these two sets of compounds, to produce a readily spinable, practical fiber, met with failure, and in 1930, he actually gave up the synthetic fiber project.

Several months later he resumed his work, this time with 9-amino nona-noic acid, obtaining super polymers with properties very close to those he was seeking. He subsequently prepared super polymides from various amine acids and diamines and dibasic acids.

On February 28, 1935, a new historic date, he produced the super polyamide from hexamethylene diamine and adipic acid. This compound, referred to as "66" (the first numeral for the number of carbon in the diamine and the second for the number in the acid) could be spun into fibers that, upon cold drawing, were superior to any fibers then known, in tensile strength, elasticity, flexibility, and in many other ways. This was nylon.

The product had been discovered, but a lot remained to be done before it could be produced commercially. The raw materials, hexamethylene diamine, and adipic acid, were merely laboratory curiosities, and must be produced commercially. By 1936, Roger Williams, also of DuPont had developed a process for the production of adipic acid from phenol. The diamine was then produced from the acid.

By the middle of 1938 a pilot plant was in full operation, making nylon products. Unfortunately Carothers died on April 29, 1937.

**General Steps in Process:** The raw material used commercially for nylon production is phenol. Phenol is reduced to cyclohexanol, which is then oxidized to adipic acid. Hexamethylene diamine is made from this, by first making the ammonium salt and heating this to form the amide, which is
reduced to the amine.

The adipic acid and hexamethylenediamine are reacted to form the salt, which is then polymerized to form the nylon product.

Formation of cyclohexanone: A number of methods have been described for this reaction. Most experimenters agree on a catalyst containing porous nickel, formed by treating an alloy of aluminum and nickel with caustic. Ungrade and McLaren (16) used Raney nickel, which is formed from an alloy of equal parts of nickel and aluminum treated with caustic. Agapov, Bag, and Volokitin (6) used an alloy of 27% nickel and 73% aluminum activated by caustic treatment.

There is a difference of opinion concerning the pressure and temperature to be used, although most experimenters have worked with liquid phenol. Pressures range from 1 to 117 atmospheres, while temperatures range from 60 to 270 degrees Centigrade. Houghton (12) recommends a large excess of hydrogen while Šišago (1) recommends a 1 to 5 mole ratio of phenol to hydrogen. No description of apparatus is given.

By-products are to be expected from this reaction: Cyclohexanone, cyclohexane, cyclohexane, and possibly cyclohexadiene and benzene may be produced under some conditions. Agapov (12) claims a yield of 95% cyclohexanone at 60 degrees Centigrade and atmospheric pressure, although the basis for this yield is not given.

Formation of adipic acid: Adipic acid may be obtained by oxidation of cyclohexanone with 50% nitric acid at 50-60 degrees Centigrade in the presence of ammonium vanadate. Foster (7) claims a 72% yield, basis not given.
The acid may be obtained by oxidation of cyclohexanone with 50-55% nitric acid at 80-85 degrees, according to Hill and Kelly (10), and at 60 degrees Centigrade according to Oda, Hikuda, Isihara, and Morisita (14).

Cyclohexanone may be oxidized by concentrated nitric acid to give adipic acid in low yields, but cyclohexanone prepared from it may be oxidized with a mixture of sulfuric acid and sodium dichromate to give 45-50% adipic acid. (17)

Dressbach (4) describes a method of oxidizing cyclohexanone in which a mixture of not more than 10% oxygen in some inactive gas is passed through cyclohexanone containing a small amount of cyclohexanone as catalyst, at a pressure of at least 10 atmospheres. The adipic acid and cyclohexanone are recovered from the resulting mass, method of recovery not given.

A British patent (5) describes the oxidation of cyclohexanone in an organic acid solvent in the presence of a cobalt, copper, or manganese salt at 60-180 degrees Centigrade under 2 to 1000 atmospheres pressure in the presence of air, using cyclohexanone as an initiator.

Formation of ammonium adipate: Several Japanese experimentors (14) recommend treating fused adipic acid with dry ammonia at 200 degrees Centigrade in silica gel to form adipamide directly.

Walter Coopay proposes an apparatus for vaporizing adipic acid in the presence of ammonia to form the salt (5). The apparatus is heated and contains rotating disks. Greenwald and Worthington (9) suggest bringing the acid into contact with the wall of a heated metallic transfer medium such as a conical jacketed tube maintained at a temperature high enough to effect immediate vaporization but not decomposition of the acid.
Formation of Hexamethylenediamine: The Japanese experimenters (14) mentioned suggest dehydration of the amide with phosphorus pentachloride to form the nitrile, which is reduced with sodium and alcohol to give 70-80% hexamethylenediamine.

Hill and Kelly (10) give a general method for synthesis of amides from ammonium salts. The salt is boiled with a dehydration agent, removing the water and shifting the reaction equilibrium to form the amide from the salt. In order to obtain the amine with the same length of carbon chain, it is necessary to convert the amide to the nitrile by heating with a dehydrating agent as mentioned. Hill and Kelly (10) state that thionyl chloride is superior to phosphorus chloride.

The nitrile may be reduced by hydrogen and nickel at about 200 degrees Centigrade. It is possible to reduce the amide directly to an amine of the same length carbon chain by using metallic sodium in amyl alcohol. (10)

Formation of Hexamethylenediammonium Adipate: Though the polyamide can be formed directly from the amine and the acid, it has been found advantageous to first form the salt and later polymerize it. Formation of the salt avoids the difficulty of preserving isolated amines in a state of purity and tends to eliminate impurities in the starting materials, an important factor in the synthesis. Proper ratio of amine to acid is also important in the reaction. The proper ratio was found by using sodium electrodes to determine the inflection point in the pH curve, which indicated the concentration at which the two components were present in amounts equivalent to each other in a water solution. (13)

A mixture of 144 parts of hexamethylenediamine, 174 parts adipic acid, 1500 parts 95% ethanol, and 410 parts of water are warmed until complete solution is obtained. The mixture is then cooled, which causes sepa-
ration of the less soluble salt in the form of white crystals. The salt is separated by filtration and recrystallized from 1500 parts of 95% ethanol and 200 parts of water, yielding 247 parts of the pure salt with a melting point of 123-126 degrees Centigrade. (13)

*Polymerization of the salt:* Several methods of polymerizing the salt have been proposed. Commercially no solvent or diluent is used. The reactors used are constructed of, or lined with, silver, tantalum, chromium plate, or chromium-containing ferrous salts, and are used under oxygen-free conditions. The process is somewhat as follows:

Two moles of hexamethylene-diamine adipamide and 0.02 mole of adipic acid (viscosity stabilizer) are placed in a 2 liter silver-lined autoclave, equipped with a stainless steel stirrer and reflux condenser. The air is removed by evacuation, filled with nitrogen, and again evacuated. Then 80 lb. per sq. in. nitrogen pressure is put on the autoclave, the stirrer started and the temperature raised to 260 degrees Centigrade over a period of 1.5 hours. Pressure is decreased during 30 minutes to atmospheric pressure and heating and stirring continued for 2.5 hours longer. Then the pressure is decreased to 500 mm. for several minutes. After cooling, the polymer is removed from the autoclave as a white solid. (13)

Polymerization is also possible in an inert solvent for the polymer, such as cresol, phenol, xyleneol, or diphenyl-propene.

The use of inert non-solvent represents the third method. High-boiling hydrocarbons may be used. Exclusion of air is important for the reaction in all cases because oxidation may occur and discolor the product. (13)

Horton Shor (15) states that the salt is delivered to the top of a tower down which it flows to emerge as the polymer, after which it is autoclaved to complete the polymerization while a constant stream of nitrogen is bubbled through the mass removing the water formed by condensation.

*Finished Product:* In the commercial process, the molten polymer is delivered from the autoclave to chilled rolls which solidify the product in ribbons which are chipped and ready for treatment in the product factories.
III. EXPERIMENTAL

A. Purpose of Investigation

The purpose of the investigation is the study of the synthesis of nylon from penol as a raw material, the laboratory synthesis of nylon, and the design of a plant for continuous production of nylon.

B. Plan of Procedure

Hydrogenation of Phenol: The catalyst will be made by alloying 27 parts of nickel with 73 parts of aluminum and treating the alloy, in the form of turnings, with acetic solution to give active nickel.

The apparatus will be set up as shown in drawing 1. The temperature will be held between 60 and 75 degrees Centigrade. The rate of hydrogen will be determined and the phenol rate adjusted so that 1.5 moles are fed in the same time that 3 moles of hydrogen are fed. The time will depend on the time for the phenol to pass through the reactor, which is determined by the hydrogen rate.

The product will be distilled, using a water condenser up to 100 degrees Centigrade and an air condenser will be used above this distilling temperature. The fraction up to 100 degrees Centigrade will be cyclohexane and cyclohexene. This will be condensed in the water condenser. The fraction up to 180 degrees Centigrade will be cyclohexanol and cyclohexene, which will be condensed in the air condenser (m.p. of cyclohexanol: 25 degrees Centigrade).

The residue will be phenol which will be returned to the hydrogen-
<table>
<thead>
<tr>
<th>Compound</th>
<th>Melting Point (deg. C.)</th>
<th>Boiling Point (deg. C.)</th>
<th>General Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
<td>48</td>
<td>192</td>
<td>colorless, needle-like crystals when pure, pink color due to impurities</td>
</tr>
<tr>
<td>Cyclohexanol</td>
<td>24</td>
<td>161</td>
<td>hygroscopic, sol. in most org. solvents, mod. sol. in water</td>
</tr>
<tr>
<td>Cyclohexanone</td>
<td>-43</td>
<td>155</td>
<td>water white to yellow, sol. in water</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6.5</td>
<td>61</td>
<td>colorless, mobile, misc. with most lacquer solvents</td>
</tr>
</tbody>
</table>
Apparatus - Hydrogenation of Phenol

1. Separatory funnel used for phenol feed.
2. Water condenser used for reactor
3. Side arm Erlenmeyer flask for collecting product.
4. Gas collecting bottle - excess H₂ bubbled through phenol (pre-feed)
5. Heat exchanger - metal
6. Catalyst - bead or flake shapes.

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VIRGINIA POLYTECHNIC INSTITUTE
Blacksburg, Va.

PROPOSED APPARATUS FOR
HYDROGENATION OF PHENOL

Drawn by MA
Checked by
App'd by

Case No. 46
File No.
Dwng No. 1
Formation of Adipic Acid: The cyclohexanol and cyclohexanone fraction from above will be oxidized in a Florence flask with reflux condenser, from which the waste gases will be led outdoors.

About 5 parts of nitric acid will be used per part of the hydrocarbon mixture, with a small amount of ammonium vanadate. The temperature will be maintained at 25 degrees Centigrade until gases (oxides of nitrogen) are no longer evolved. The temperature will then be raised to 50 degrees Centigrade, and maintained till no more gases are evolved, when the reaction will be assumed finished.

Treatment of the resulting mass will depend on the character of the mass. If crystals are obtained, filtration and recrystallization will be carried out. If a solution is obtained, it will be distilled to remove water and remaining cyclohexanol and cyclohexanone.

Formation of Adipic Anhydride: The adipic acid will be fused (m.p. 133 degrees Centigrade) and gaseous ammonia will be bubbled slowly through it in a Florence flask, using a small amount of phosphoric acid as catalyst.

Formation of Hexamethylene Diamine: The amide will be treated with metallic sodium in alcohol, and the resulting product will be distilled.

Formation of Salt: The amine and the acid will be dissolved in equimolecular proportions in ethanol and water, warming to obtain solution. The salt formed will be crystallized from the solution by cooling.

Polymerization: The salt will be heated and fused, bubbling nitrogen through the mass. A reflux condenser will be used on a Florence flask, the nitrogen being led outdoors from the condenser.
C. Materials

**Phenol**: Obtained from Chemical Engineering Department stock room. No label. Deep pink crystals. Quantity used - 550 grams.

**Absolute Ethanol**: Obtained from Chemistry Department stock room. No label. Quantity used - 100 ml.

**80% Ethanol**: Obtained from Chemistry Department stock room. No label. Quantity used - 300 cc.

**Sodium Hydroxide**: Quantity used - 700 grams. Label:

Sodium Hydroxide, U.S.P. Pellets
5 lb. (2-268K)
Lot No. 83940

Made in U.S.A.
J.T. Baker Chemical Co.
Phillipsburg, N.J.

**Aluminum**: Obtained from Chemistry Department stock room. Quantity used - 200 g. Label:

Aluminum
Metal Turnings
Gal. St. 27.9
The Coleman & Bell Co., Norwood O., U.S.A.

**Sulfoxylol**: Obtained from Dr. Lucas of the Chemistry Department. No label. Liquid at 25 degrees Centigrade.

**Calcium Chloride**: Quantity used - 500 grams. Label:

Calcium Chloride, Purif. Anhyd. Granular
5 mesh for drying tubes
CaCl₂ MW 110.99
Differs from in water content
Lot No. 11342
J.T. Baker Chemical Co.
Phillipsburg, N.J.
Asbestos: Obtained from Chemistry Department stock room, acid treated and burned, no label. Quantity used - 50 g.

Aluminum-Nickel Alloy: Raney Nickel Alloy obtained from Gilman Paint and Varnish, Nashville, Tenn. 70% Al, 30% Ni. Quantity used - 350 g.

II. Equipment

1. Two 500 ml gas bottles
2. Round-bottom flask - one 500-ml.
3. Gas bottle - one 300 ml.
4. Beakers - four 1-liter pyrex
5. Erlenmeyer flasks - Two 500-ml.
6. Bunsen burner - one
7. Galvanized basket - one 3-gallon
8. Gas-drying bottle - one
9. Stopcocks - two glass
10. Ring stands - three
11. Flask clamp - one steel
12. Funnel - one glass
13. Burette - one with open end
14. Miscellaneous glass and rubber tubing
15. Centrifuge - International Chemical Centrifuge, 110 volts, Basket diam. 5 inches, depth 2 inches
17. Sidearm Erlenmeyer flask - one 500-ml. pyrex
18. Water trough - one galvanized 8x2x4 inches
19. Distilling flask - one 200-ml. pyrex
20. Condenser — one pyrex water-jacketed. Jacket length 12 inches
21. Erlenmeyer flasks — two 50 ml. pyrex
22. Erlenmeyer flasks — two 250 ml. pyrex
23. Balance — Chemical Rubber Co., Cleveland 0. Cap. 710 g.
24. Thermometer — One, range 0-220 C.
   3 HP motor
26. Buchner funnel — diam. 3 inches
27. Drying oven — Sargent Electric Drying Oven 110 v. 600 w.
E. Methods of Procedure

The procedure followed in this investigation consisted of three preparations of the activated nickel catalyst and three attempts to hydrogenate phenol in the presence of the prepared catalyst.

Catalyst Preparation - Run No. 1: The two and one half pound bars of nickel-aluminum alloy were broken into pieces of 3/8 to 1 inch diameter, using a hammer and chisel. A portion of the material was treated as follows: 127 grams of sodium hydroxide were dissolved in 500 ml. of distilled water in a one liter beaker, and then 107 grams of the alloy were added one lump at a time. The reaction was allowed to subside after each addition so that the liquid did not bubble over the rim of the beaker. The beaker was left in a cold water bath (30 deg. C.) overnight, and the reaction was found to be still in progress with slow evolution of hydrogen the following day.

The beaker was heated on a hot plate and the contents stirred with a stirring rod until the rate of hydrogen evolution became rapid, but not violent enough to cause bubbling over the beaker rim. Heating was carried on slowly and the temperature raised gradually to 90 deg. C., as the evolution became slower. Distilled water was added when needed to keep the volume of solution constant at the original volume. It was necessary to place the beaker in a cooling bath (water at 16 deg. C.) when the bubbling became too violent, in order to prevent bubbling over.

The evolution of hydrogen ceased; the nickel was allowed to settle completely, and the solution was decanted. The nickel was washed with 250 ml. portions of distilled water and the water was decanted after allowing the nickel to settle out completely. The material was washed until
the washings were neutral to litmus. The nickel was left in distilled water (25 deg. C.) for ten hours to allow any occluded caustic to diffuse into solution. The water was then decanted and the nickel washed with 80 cc. of 95% ethanol; the ethanol was decanted and the nickel dried for two hours at 105 deg. C. in an oven.

**Catalyst preparation - Gun No. 2**: Since the time required for the reaction was so great, twelve days in all - most of which time was required for the reaction to occur - it was decided to use smaller pieces of alloy. The lumps (3/8 to 1 inch diameter) were fed to the laboratory jaw crusher (jaw setting at 1/8 inch). The product obtained ranged from 1/8 to 3/8 inch diameter. This was used in the preparation of the second batch of catalyst.

The procedure followed in this preparation of the catalyst was exactly the same as for the first batch, with the following exceptions. (1) When hydrogen was no longer evolved (7 days), though lumps of alloy were still present, the caustic was decanted and the nickel was washed twice with 250 ml. portions of distilled water at 25 deg. C., the wash water being decanted after each wash. (2) A solution of 60 grams of sodium hydroxide in 250 ml. of distilled water was added to the nickel and it was observed that a gas was again evolved. After two hours, the reaction ceased and the batch was washed and treated as was the first batch.

**Phenol Preparation**: The phenol to be used was deep red in color, the color denoting impurities characteristic of phenol. It was observed that the coloring was in the liquid on the phenol crystals. A laboratory basket centrifuge (description on page 12) was used to remove this liquid.
A lightweight muslin strip was used as a filter cloth. The crystals were dropped into the revolving basket from a spatula, and the free liquid centrifuged off was caught in a beaker. Distilled water at 25 deg. C. was added from a wash bottle, in a jet moved from top to bottom as the color disappeared from the wall of crystals. The resulting crystals were almost colorless, having only a slight pink tint. The crystals obtained were placed in an evaporating dish in a desiccator in which calcium chloride was used as the absorbent.

Preparation of apparatus for hydrogenation: The apparatus for hydrogenation of phenol was set up as shown in drawing 2, page 19.

Hydrogenation of Phenol - Run No. 1: One liter of 3 N sodium hydroxide was prepared for use in the hydrogen generator.

The reactor was charged with the following materials:

- phenol - 277.2 g. (crystals from desiccator)
- asbestos fibers - 41.6 g.
- catalyst - 31.1 g.

The method of charging was as follows. The three components were mixed in a 1-liter beaker by means of a stirring rod until the mixture appeared to be uniform. The mass was poured carefully into the reactor. Aluminum shavings were put in the generator to form a layer about 3/8 inches thick.

The water bath for the reactor was heated by live steam led in through a rubber hose until the thermometer in the reactor registered 20 deg. C., at which time the steam was turned off. Three ml. of caustic solution at 25 deg. C. were then admitted to the generator. Since no gas bubbled through the reactor, three minutes later three more milliliters of caustic were admitted to the generator. Gas bubbles began to bubble through the reactor. The rate of gas evolution became so rapid, and the heat generated so great that the Varme-seal used for joints was melted, and the gas
Run No. 1

Key
1. Burette (50 ml)
2. Erlenmeyer flask (500 ml)
3. Gas drying bottle (Ca C2)
4. Gas collecting bottle (500 ml)
5. Galvanized bucket

Scale: None

APPARATUS FOR HYDROGENATION OF PHENOL

DEPARTMENT OF CHEMICAL ENGINEERING
VIRGINIA POLYTECHNIC INSTITUTE
Blacksburg, Va.

Drawn by: mds
Checked by: App'd by
Case No. 46
File No. 0
Dwrg No. 2
drier was cracked. The hydrogen collecting bottle was filled, and excess hydrogen bubbled up through the water in the trough. No evidence of reaction was observed in the reactor.

Varno-seal joints were replaced by rubber tubing and an Erlenmeyer flask was substituted for the gas drying bottle. A glass nozzle (0.005 inch opening) was installed on the end of the hydrogen inlet in the reactor, to give better dispersion and contact of the hydrogen and the liquid phenol. The generator was then put into operation as before, after heating the reactor as described above. The top was blown off the generator due to excessive pressure developed inside. Investigation showed that this excessive pressure was due to the fact that the asbestos fibers, now thoroughly soaked with phenol, had settled to the bottom in a heavy mass. An attempt to agitate the mass by means of a stirring rod was unsuccessful due to its closely packed nature. Since observations showed that the apparatus was inadequate in that it did not provide dispersal of the hydrogen through the liquid, or keep the catalyst in suspension, and that excessive pressure was built up due to the settling of the asbestos, the run was discontinued.

Catalyst Preparation - Run No. 5: Additional information concerning preparation of Raney Nickel was found and the procedure used in the third catalyst preparation is a modification of that given by Drake*. The charge used was the same as in previous runs, i.e. 500 ml. distilled water, 127 g. sodium hydroxide, 107 g. alloy (1/2 to 1 inch diameter).

The alloy was added to the caustic solution and the reaction allowed

* Drake, N. L. "Organic Syntheses" Vol. 31 pp. 15-17
John Wiley & Sons, Inc. N. Y.
to proceed until the evolution of hydrogen ceased. The liquid became viscous and milky. The liquor was well agitated with a stirring rod, and decanted into a one liter beaker, the liquor carrying the finely divided nickel with it. This liquid was set aside for further treatment. The lungs of unreacted alloy remaining in the first beaker were washed twice with 250 ml. portions of distilled water at 25 deg. C. A solution of 100 g. of sodium hydroxide in 500 milliliters of distilled water was cautiously added, care being taken to prevent excessive foaming. The reaction was allowed to proceed until the evolution of hydrogen almost ceased. The reaction was then heated on a hot plate and kept at a temperature sufficient to keep the gas evolution rapid but not likely to cause the liquid to bubble over the beaker rim. The final temperature attained was 90 deg. C., at which temperature the mixture was kept until no more bubbles formed.

The resulting mixture and the other portion of the batch previously set aside were treated in the same manner, though kept separate. The treatment was as follows. The suspension was diluted with an equal volume of distilled water and allowed to settle until the nickel had completely settled out, but the precipitate was still in suspension. The liquid was decanted, carrying the milky suspension with it. The remaining nickel was washed with 250 ml. portions of distilled water at 25 deg. C. until no sign of the precipitate remained. A solution of 50 g. of sodium hydroxide in 250 ml. of distilled water at 25 deg. C. was then added. Slight evolution of hydrogen was observed. The reaction was heated on an electric hot plate to 90 deg. C., care being taken not to heat too rapidly and cause foaming. When no further evolution of
hydrogen was observed, the liquid was decanted and the nickel washed with
250 ml. portions of distilled water at 25 deg. C until the washings were
neutral to litmus paper. The nickel was then washed with 100 ml. of 95% 
ethanol, then with 100 ml. of absolute ethanol, the liquid being decanted
in each case. The product was washed into a 250 ml. Erlenmeyer flask
with absolute alcohol, and stored there under the absolute ethanol, the
flask being tightly corked.

Hydrogenation of Phenol - Run No. 3 : The phenol for this run was
prepared exactly as before.

The apparatus was altered in view of the observations from the first
run. A 300 ml. round-bottom flask was used for the reaction vessel, as
shown in drawing 3, page 53. A gas distributor, consisting of a glass
bulb (diam. 0.6 in.) perforated with openings of 0.08 inch diameter
spaced 1/2 inch apart over the lower half of the bulb (bulb opening from
a glass tube of 0.3 inch inside diameter), was used on the hydrogen inlet
in the reactor. Glass beads of 0.2 inch diameter were put in the reactor
up to the level of the phenol liquid. This was done in an attempt to
obtain greater contact area between gas and liquid by forming smaller
bubbles of hydrogen than in the previous run (Run No. 1, p. 18) and to
obtain greater time of contact by delaying the rise of the bubbles
through the liquid. Since the activated nickel must be kept under liquid
at all times*, it was decided to keep it under cyclohexanol and charge
it into the reactor in that condition. Cyclohexanol was chosen as the
storage medium because it was the liquid expected to be formed in the
reaction, and thus would not be an impurity to be separated from the

* Drake, E. L. loc. cit
Run No. 2

Legend:
1. Gas collecting bottle - 300 ml.
2. Liter beaker
3. Erlenmeyer flask
4. Side-arm Erlenmeyer flask

Run No. 3

Legend:
1. Gas collecting bottle - 300 ml.
2. Liter beaker
3. Erlenmeyer flask
4. Side-arm Erlenmeyer flask

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REACTORS FOR HYDROGENATION OF PHENOL

Drawn by McJ
Checked by App'd by
Cas No. 146
File No. 1740
Dw No. 3
reaction mixture. The alcohol in which the catalyst was submerged was
decanted, and the nickel filtered in a Buchner funnel, washing with
cyclohexanol (50 cc.). The remaining nickel was washed from the funnel
with, and stored under, cyclohexanol.

The charge for the second run consisted of phenol, 94.0 grams;
glass beads, 149.2 grams; and 2 teaspoons of catalyst in cyclohexanol,
a settled and thick suspension as prepared in Run 3 of catalyst prepara-
tion (p. 20). The water bath for the reactor was heated by means of the
electric hot plate until the thermometer in the reactor registered 60 deg. C.
The generator was prepared as before, and caustic admitted at the rate
of 1 ml. per minute. Total time of operation was 10 hours with temperature
at 55-65 deg. C. Excess hydrogen was collected at the rate of 200 ml. per
half-hour. The operation was intermittent, requiring an over-all time of
30 hours. Operation was stopped by closing the pinchclamp that admitted
cauitic to the generator and disconnecting the electrical connection of
the hot plate.

Separation of Products: The reaction mass was poured into a
Buchner funnel and a vacuum of five pounds per square inch was applied
by means of an aspirator. The product obtained after such filtrations
was 53 cc. of a clear pink liquid at 25 deg. C.

The liquid was distilled in the conventional laboratory distilla-
tion apparatus, using a 200 ml. distilling flask. Two drops of condens-
ate were collected between 94 and 110 deg. C. Three drops distilled
in the temperature range of 110 to 176 deg. C. The remainder of the
liquid distilled at 175-178 deg. C. This fraction was a yellowish liquid
having a phenolic odor mixed with some unrecognizable odor. White,
needle-like crystals formed in this liquid. The remaining liquid was
decanted into another flask and similar crystals formed in it. The
liquid from these crystals was distilled. Thirty-three milliliters
were collected for distillation. The liquid distilled at 180 deg. C.
Solubility tests were conducted and found to conform to those known for
phenol, i.e. soluble in ether, alcohol, sulfuric acid, phosphoric acid,
sodium hydroxide, and insoluble in water and sodium bicarbonate.

Hydrogenation of Phenol — Run No. 3: It had been observed in the
previous run that water was condensing in the tube leaving the gas dryer.
(Refer to drawing 3, page 23) Since the hydrogen leaving the generator
and going through the dryer was hot (temperature not measured), evidently
the vapor pressure of the water prevented its complete absorption by the
calcium chloride. Thus, the apparatus was again altered to prevent
water vapor being carried into the reactor. A condenser was put in the
system, in the form of a rubber tube, a four foot length of which was
led through a water bath at 35 deg. C. (Refer to drawing 3, page 23)
The tube was connected to a side-arm Wlisnmayr flask which served as a
trap for the condensate. The reactor was also replaced; a 300-ml. gas
bottle was substituted for the round-bottom flask of the previous run.
Operation was conducted just as in run 2, i.e. the temperature was kept
between 55- and 65 deg. C, for ten hours, intermittent in operation.
After the above mentioned 10 hour operation an oil bath was substituted
for the water bath, and the temperature was raised to 130-140 deg. C for
seven hours, intermittently operated.

At this higher temperature, it was observed that fumes were emitted
from the reactor and condensed. Thus a laboratory glass condenser with
water at 10 deg. C. was attached to the outlet tube from the reactor, as shown in drawing 3, page 25. A condensate was collected, and by previously mentioned (page 25) solubility tests was found to be phenol, probably mixed with water.

**Separation of Products**: The glass and catalyst were removed from the liquid as before, using the Buchner funnel. On distillation, it was found that the liquid started boiling between 90 and 95 deg. C., and the remained between 95 and 99 deg. C. for a short period (estimated at two seconds) though no distillate came over. The temperature then rose rapidly to 150 deg. C., at which temperature the boiling took place for a short time (estimated at 3 seconds). The temperature then rose rapidly to 170 deg. C., where the remainder of the liquid boiled. The distillation was stopped without collecting this high-boiling fraction, because it was concluded that this, too, was phenol (B.P. 160-162 deg. C. at 760 mm.).
IV. DISCUSSION

A. Observations and Interpretations

While no quantitative results were obtained during the work, a great deal of information was obtained from observations of operation. It is easy to understand why the hydrogenation of phenol represents an outstanding bottleneck in the production of nylon. This discussion is concerned with the difficulties involved in the hydrogenation of phenol at temperatures of 60 and 140 deg. C. and at 1 atmosphere pressure.

Activated Nickel Catalyst: The preparation and use of this type of catalyst presents difficult problems.

While it is necessary to heat the reaction mixture in preparation of the catalyst, great care must be taken not to heat rapidly enough to cause foaming and sputtering over the reactor. This difficulty could have been minimized considerably if a larger reactor than the 1-liter beaker had been available. The problem of temperature control and heat transfer would be increased if the production were put on commercial scale.

The extreme activity of the catalyst is probably due to the presence of capillary openings formed when the aluminum was dissolved from the alloy. Such openings would provide large surface of contact. Possibly the action is the adsorption of hydrogen gas, and vapor from the liquid, thus providing intimate contact of the two reactants. Then, if the action is due to the porous openings, care should be taken not to clog them. Therefore, water free of salts should be used in washing the catalyst. The washing of the catalyst on commercial scale could be done as a countercurrent liquid-solid extraction process.
Observations of the third catalyst batch (page 20) showed that the catalyst could be a dangerous fire hazard if not carefully stored and handled. During the operation, a small amount of the catalyst in alcohol was dropped on the work bench. In less than a minute, it began to glow, pop, and spatter over the bench. Some flying particles landed on the cloth covering the steam pipe insulation and started it smoldering. It was found accidentally that a minute quantity on the skin caused burning when it dried. This behavior of the third catalyst batch was convincing evidence that it was active, and by contrast, that the products of the first two preparations (pages 16 and 17) were not active because these had been dried in an oven.

Another problem is introduced by the fine particle (minus 100 plus 200) form of the catalyst. It is difficult to keep the particles in suspension in the liquid phenol. Efforts were made to keep the nickel from settling to the bottom of the reactor by providing surfaces throughout the reactor, on which the particles might rest. Asbestos fibers and glass beads were put in the reactor to retain the catalyst. Neither attempt was entirely successful, though both methods did prevent some settling of catalyst, as evidenced by the catalyst seen resting on the asbestos and glass beads during operation. The agitation supplied by the circulating gas was not sufficient to keep the catalyst in suspension, either. It was necessary to disconnect the reactor and shake the mass to disperse the catalyst.

**Phenol Used**: It was desired to have the phenol free from moisture but this condition was not attained. The phenol was centrifuged and washed with water. It was put in a calcium chloride desiccator. A crust formed
on the surface of the dish of crystals. This, no doubt, prevented drying
of the crystals underneath.

The impurities which impart the pink color to the phenol may have
some deterrent effect on the reaction. However, it was observed that
during hydrogenation the original pink color disappeared after about
15 minutes of operation. Thus it is believed that some reaction did take
place; the impurities are supposed to be some unknown oxidation product
of phenol. Therefore, some effective contact took place between the gas
and liquid in order to bring about reduction to the original phenol.

Hydrogen Used: It was originally planned to measure the absorption
of hydrogen in the reactor by measuring the hydrogen put in and that
collected as excess. The inlet hydrogen was to be measured by using a
standardized (28) caustic solution in the generator and measuring the
volume used. The excess hydrogen from the reactor was to be collected
over water. Thus the amount of hydrogen absorbed could be calculated.

However, it was observed that when nearly all of the aluminum in the
generator had been dissolved, the rate of hydrogen evolution could not
be kept at the desired rate (500 ml. per half-hour). Therefore, it was
not practical to wait until no further hydrogen was generated before
renewing the generator charge, and this method of measurement was
abandoned.

The reaction of caustic with aluminum was chosen in preference to
the more popular zinc-hydrochloric acid hydrogen generator, because the
gas generated would be more pure, and because the aluminum method gives
more hydrogen per volume of reagents. With hydrochloric acid it is
necessary to remove the acid vapors from the generated gas, and also there
is likelihood of sulfides and arsenic compounds in the gas if the zinc
used is not pure. In the generation it was observed that water was
carried over with the hydrogen and condensed in the tubes leading to the
reactor. Some of the water was removed by the condenser, trap, and drier
used in the third hydrogenation run (drawing 3, page 23) However, it was
observed that vapors were emitted from the reactor. These were condensed
and found to be phenol. The vapors were probably due to moisture in the
hydrogen admitted, which caused, in effect, a steam distillation of the
phenol.

Hydrogenation: The greatest difficulty in the hydrogenation of
phenol was the contact of the three phases at once, i.e. solid catalyst,
liquid phenol, and gaseous hydrogen. The gas showed no tendency to
dissolve, that is, no change in temperature occurred on initiation of the
hydrogen into the phenol, and the gas bubbles were seen to rise to the
surface without being absorbed and with no noticeable change in volume of
the bubbles.

The ideal contact between liquid and gas would be attained with
bubbles of one molecule each, which would be a solution of the gas in the
liquid. Since the bubbles are very nearly spherical in shape, the
largest ratio of surface to volume is found when the radius is at its
smallest. Thus, the smaller the bubbles, the better.

Attempts were made to introduce bubbles of the smallest possible size.
No definite size was sought, but it was hoped to get bubbles of 1/16 inch
or smaller. A nozzle was tried as described in procedure (page 18) A gas
distributor was tried in Run 3 of hydrogenation (page 25). This proved to
give smaller bubbles than an open glass tube, but they were still not
1/16 inch diameter. It was observed that the bubbles, even though they
might leave the distributor at 1/8 inch diameter, would aggregate to form larger bubbles of 1/4 or 1/2 inch diameter. The glass beads used in conjunction with the distributor (page 22) tended to retain the gas by forming pockets and by slowing the progress toward the surface. The glass beads did not completely eliminate the direct rise of the bubbles to the surface, because of channeling, but some bubbles did follow an indirect path to the surface.

**Product Separation:** The separation of products was unsuccessful. A small amount of cyclohexanol (the 2 or 3 ml. added with the catalyst - page 22) was known to be present, but was not indicated in the separation process. The effect of the presence of cyclohexanol on the boiling point of phenol is not known, but probably a concentration of 5% or over could be separated by distillation. Therefore, it is believed that no cyclohexanol was formed. The fact that the hydrogenated solution began to boil at 80-85 deg. C. was probably due to the water introduced with the phenol and with the hydrogen.
3. Recommendations

A great deal of work could be done to determine conditions for hydrogenating phenol to form cyclohexanol. The following are recommendations for further study of the problem of hydrogenation of phenol and manufacture of the activated nickel catalyst used in the process.

1. A 2-liter beaker should be employed for catalyst preparation, using the same quantity of reagents, in place of the 1-liter beaker used in this work. This would minimize the problem of bubbling over the beaker rim.

2. Hydrogenation of phenol should be tried at temperatures higher than 180 degrees Centigrade.

3. Hydrogenation of phenol should be tried at pressures greater than one atmosphere.

4. Agitation should be used in the reactor for hydrogenation to keep the catalyst in suspension.

5. Vapor phase hydrogenation should be attempted. Better contact of hydrogen and phenol would be attained if both were in gaseous form. However, some difficulty may be entailed in providing contact between catalyst and vapors, since the catalyst must be kept under liquid.
3. Limitations

The investigation of the hydrogenation of phenol and preparation of the activated nickel catalyst for the process was limited by the following factors:

1. The beaker used in preparation of the activated nickel catalyst was the largest obtainable (1 liter), but was not large enough. Use of this size beaker necessitated slower reaction to prevent the reacting mass from bubbling over the top of the container.

2. The apparatus available for hydrogenation was glass; this prohibited the use of pressure in the hydrogenation process.

3. The hydrogen used was generated in the laboratory, and it was not possible to introduce it into the reactor under pressure, nor was it possible to keep the rate of flow constant.

4. Temperature of reaction was limited by the heating bath for the reactor. The oil used was decomposing when the reactor was carried on at 130 deg. C. The hydrogenation of liquid phenol could have been attempted at temperatures up to 130 deg. C., the boiling point of phenol.
V. CONCLUSIONS

No quantitative results were obtained from the work, but the following conclusions can be drawn:

1. Activated nickel can be made from an alloy of 70% aluminum and 30% nickel by reacting with caustic solution in a beaker. The concentrations are as follows: 127 g. caustic in 500 ml. distilled water, 107 g. alloy. The reaction is kept at a temperature low enough to prevent bubbling over the beaker rim, and is finally heated to 90 deg. C. until no further reaction occurs. The product is particles of min a 100 mesh plus 200 mesh size. This is washed in distilled water and then in alcohol, and stored under absolute alcohol.

2. The activated nickel must be kept under liquid at all times; when dried, it loses its activity.

3. Cyclohexanol cannot be made under the conditions employed, i.e., rate of hydrogen, 500 ml. per half hour; temperature, 60 deg. C. for ten hours, and 130 deg. C. for seven hours; reagents, 94.0 grams phenol, 2 teaspoons activated nickel in cyclohexanol. (see also apparatus used, drawings 2 and 3, pages 19 and 23)
VI. SUMMARY

The first reaction in the synthesis of nylon from phenol is the manufacture of cyclohexanol by hydrogenating phenol. This reaction represents one of the main difficulties of the process, and was the problem studied in this project. The catalyst used for hydrogenation of phenol to form cyclohexanol was activated nickel.

The activated nickel was prepared from an alloy composed of 70% aluminum and 30% nickel. The aluminum was dissolved from the alloy with sodium hydroxide solution. The caustic was washed from the product with distilled water, and a final washing with ethanol was administered. Three preparations were performed. The first two batches were dried in an oven. The third was kept under absolute alcohol. The product obtained was particles of minus 100 plus 200 mesh size. The third batch prepared was seen to be active by the sputtering and glowing exhibited when a small amount dried in the air. The first two, by contrast, were not active because they were allowed to dry before being used.

Three attempts were made to hydrogenate phenol, using the catalyst prepared, and hydrogen generated with caustic and aluminum. Although none of the attempts was successful, the changes made in the apparatus and procedure are worthy of mention.

The first trial employed a 500-ml gas collecting bottle as a reactor. Asbestos fibers were put in the reactor to suspend the catalyst (batch 1), and a glass nozzle was used to disperse the hydrogen through the liquid phenol. The apparatus (see drawing 3, page 19) proved to be faulty and the run was not carried out.
In the second attempt a 300-ml. round-bottom flask was used as a reactor. The reactor was filled with glass beads to suspend the catalyst and disperse the gas bubbles. A perforated glass bulb on the hydrogen inlet was also used to disperse the hydrogen. Hydrogen was bubbled through phenol at 60 deg. C. for ten hours. The liquid resulting was distilled and tested. It was found to be phenol.

The third run was made using a 300-ml. gas collecting bottle for the reactor. Glass beads and perforated glass bulb were again used to disperse the gas. In the previous run it had been noticed that water was carried over into the reactor with the hydrogen, so a condenser and trap were put into the system (drawing 8, page 23) to remove moisture from the hydrogen. Hydrogen was admitted for 10 hours at 60 deg. C., and then for seven hours at 120 deg. C. The resulting liquid was distilled and tested, and found to be phenol.
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