ENGINEERING FLOW DIAGRAM OF THE PRODUCTION OF POLYAMIDE FROM ADIPIC ACID WITH HEXAMETHYLENEDIAMINE

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Delft
1. Introduction

In October, 1938, announcement was made of a group of new synthetic materials resembling silk and wool both in appearance and in chemical composition. This group, a member of the polyamide family, was given the generic name Nylon.

Carothers has shown that the material with bifunctional group has the possibility to form a linear polymer. In the case of the polyamides, the functional groups are amino and carboxyl groups, which may be distributed so that the molecule containing one amino and one carboxyl group, or that, of two molecules, one would contain two amino groups and the other two carboxyl groups.

In 1939, the Du Pont company set up a plant for the manufacture of Nylon product. Nylon was first appeared on the market as bristles on "Dr. West's Miracle Tuft Toothbrushes" and during the first year, 64,000,000 pairs of woman's nylon stockings were sold.

In 1941, the Nylon moulding powder appeared on the world market. At moment Nylon is produced at several different countries and sold under qwn trade name.

The following table shows the trade name and its producer.

<table>
<thead>
<tr>
<th>Trade Name</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AKULON</td>
<td>Polycaprolactam polymer of Algemene Kunstzijde Unie in Holland</td>
</tr>
<tr>
<td>Zytel</td>
<td>A series of Du Pont Nylon moulding powders from reaction of diamines and dibasic acids.</td>
</tr>
<tr>
<td>Rilsan</td>
<td>Polyamide-1,1 from 1,1-aminoundecanoic acide made by Organico in France</td>
</tr>
<tr>
<td>Tynex</td>
<td>Filaments of Du Pont Nylon from dibasic acids and diamines. (U.S.A.)</td>
</tr>
<tr>
<td>Versamid</td>
<td>A series of polymers made by General Mills from dimerized linoleic acid and polyamides. (U.S.A.)</td>
</tr>
<tr>
<td>Perlon-L</td>
<td>German version of nylon-6 from ( \varepsilon )-caprolactam</td>
</tr>
<tr>
<td>Nylenka</td>
<td>Polycaprolactam polyamides of American Enka Corporation. (U.S.A.)</td>
</tr>
<tr>
<td>&quot;Plaskon&quot;Nylon</td>
<td>Nylon-6 made by Barrett Division of Allied Chemical and Dye</td>
</tr>
<tr>
<td>Grilon</td>
<td>A type of Nylon-6 made in Switzerland</td>
</tr>
</tbody>
</table>
There are several types of polyamides and their properties are dependent on the starting raw materials, reaction condition and the modification with other materials.

After 1939, although the price of the polyamide higher than most of other synthetic polymers, the production of the polyamides increased remarkably, because of their superiority in the properties. In the Netherlands, the A.K.U. produced 430 tons of polyamide plastics and 2000 tons of polyamide synthetic fibers in the year of 1954. Meanwhile the total import of the plastics in this country was 1,8300 tons with 32.1 million guilders and the total export was 11800 tons with 32.1 million guilders in the same year. In United State of America the total production of the polyamide(textile, bristles, other fibre forms, gears, other molded products, adhesives and coatings) was about 300,000,000 pounds in 1955.

2. Chemistry of Nylon-6,6

Raw materials
a) Adipic acid

This was produced by the normal method of nitric acid oxidation of cyclo-hexanol obtained by hydrogenation of phenol. However, we can obtain this compound in the following way from petroleum.
b) Hexamethylenediamine

We can obtain this compound from adipic acid. (see the above scheme)

Polyamide formation

The formation of the polyamide from adipic acid with hexamethylenediamine is done in the following steps:

1) Nylon salt formation

Adipic acid and the hexamethylenediamine form hexamethylenediammoniumadipate (usually in aqueous solution), so called Nylon salt. This neutralization is exothermic reaction and the equivalent point is \( P_H = 7.63 \pm 0.3 \).

The control of the \( P_H \) of the formed nylon salt solution is very important, because this dominates the properties of the final polyamide.

2) Dehydration of the nylon salt

Nylon salt is dehydrated by heating to 225°C in a closed vessel in the presence of nitrogen gas and forms half polymer.

3) Formation of the final polyamide

The half polymer is heated to the melting point of the final polyamide to proceed the polymerization by removing the water in the system and the condensation water. The removing of the water controls the quality of the final product, because the trace of the water in the system avoid the further progress of the polymerization (by the reversible reaction).

\[
(n+1) \text{NH}_2\text{(CH}_2\text{)}_6\text{NH}_2 + (n+1) \text{HCOO(CH}_2\text{)}_6\text{COOH} \rightarrow \text{Diammonium adipate} \\
\rightarrow \text{NH}_2\text{(CH}_2\text{)}_6\text{NH(}\text{CO \(n\) (CH}_2\text{)}_6\text{CO} \text{(CH}_2\text{)}_6\text{COOHNH(}n\text{)}}_n \text{CO(O(CH}_2\text{)}_6\text{COOH + (2}n+1\text{)} \text{H}_2\text{O}
\]

An inert atmosphere of nitrogen is usually provided in order to avoid the oxidation and decomposition of the polymer.
The polymerization reaction must be so arranged that the terminal groups cannot condense from each end of the molecule to form a cyclic substance thus:

\[ \text{HNH}-(\text{CH}_2)_m-\text{CO-NH}-(\text{CH}_2)_n-\text{COHN} \rightarrow (\text{CH}_2)_m + \text{H}_2\text{O} \]

Carothers had found that if a diamine and a dicarboxylic acid of formula \( \text{NH}_2-(\text{CH}_2)_m-\text{NH}_2 \) and \( \text{HOOC}-(\text{CH}_2)_n-\text{COOH} \) respectively were induced to condense, then cyclization would not take place if \( n \) were equal to or greater than 4 and if \( m \) were not less than 3. The radical length of the polymer is the sum of \( n + m \) and for successful superpolymerization this length should not be less than 8 and preferably 9.

3. Properties of Nylon-6,6

The adipic and the hexamethylenediamine was the given raw material in my case and the Nylon-6,6 is the polyamide from the above compounds which is produced by Du Pont company in U.S.A. The number 6,6 in the Nylon-6,6 means this polyamide is produced by the condensation of the diamine with 6 carbon atoms and the dibasic acid with 6 carbon atoms.

According to the literature, The Nylon-6,6 has the following properties:

- Molecular weight
- Melting point
- Density
- Tensile strength, at 73°F
  - at 170°F
- Elongation
- at 73°F
  - at 170°F
- Modulus of elasticity
  - at 73°F
- Rockwell hardness
- Flow temperature
- Coefficient of linear thermal expansion
- Thermal conductivity
- Specific heat
- Diellectric constant, at 10³ cycles
- Water absorption
- Flammability

The Nylon-6,6 can resist against:

- Weak acids, weak alkalis, strong alkalis, alcohols, esters, aliphatic hydrocarbons, aromatic hydrocarbons
- Strong acids

The Nylon-6,6 is attacked by:

- 16,000-32,000
- 265°C
- 1.14
- 10,500 lb/in²
- 7,600
- 90%
- 320
- 400,000 lb/in²
- R118
- >480°F
- 5.5 \( 10^{-5} \)
- 1.7 BTU/hr/ft²/°F/in
- 0.4
- 4.0
- 1.5%
- Self extinguishing
- Weak acids, weak alkalis, strong alkalis, alcohols, esters, aliphatic hydrocarbons, aromatic hydrocarbons
- Strong acids
4. Use

As I described previously, the nylon-6,6 possesses some excellent properties. The polyamide from adipic acid with hexamethylenediamine (so called Nylon-6,6) applied as synthetic fibre or molding powder. However, I prepared the polyamide which is more suitable for the application other than the synthetic fibre. This is done to keep the molecular weight of the final product as low as possible, that is to say to give a low intrinsic viscosity to the final product, without losing its excellent mechanical and other properties, because the nylon with very high molecular weight is very difficult to mold.

I admire the following articles as the major uses of my product.

a.) Filament

Nylon filament has exceptionally good resistance to abrasion. This toughness is one of the outstanding characteristics which is illustrated in the leading applications in the form of monofilament for bristles. These are not only used for personal use as tooth-brushes and hair brushes, but also for industrial brushes, because it is inflammable and has good solvent resistancy. The leading industrial uses of the Nylon bristles are bottle washing, textile printing, dry cleaning and salvage disposal.

b.) Coating

The nylon has excellent electrical characteristics and used for coating wires used in electrical equipment.

c.) Molding powder

The molded articles have the valuable combination of properties, namely, high temperature resistance together with great toughness. The leading molded articles are bobbines, combs, beakers, flexible spools and coil formers.

I have shown here the consumption of the nylon molding powder by industry in America during last few years for reference.
<table>
<thead>
<tr>
<th>Year</th>
<th>Automotive</th>
<th>Electrical</th>
<th>Gears, bearings and bushings</th>
<th>Medical</th>
<th>Textile</th>
<th>Other</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1950</td>
<td>350</td>
<td>90</td>
<td>1,050</td>
<td>430</td>
<td>90</td>
<td>90</td>
<td>2,100</td>
</tr>
<tr>
<td>1951</td>
<td>940</td>
<td>220</td>
<td>1,800</td>
<td>400</td>
<td>220</td>
<td>220</td>
<td>3,800</td>
</tr>
<tr>
<td>1952</td>
<td>1,672</td>
<td>350</td>
<td>3,380</td>
<td>700</td>
<td>350</td>
<td>350</td>
<td>6,800</td>
</tr>
<tr>
<td>1953</td>
<td>253</td>
<td>550</td>
<td>4,950</td>
<td>970</td>
<td>550</td>
<td>550</td>
<td>10,100</td>
</tr>
<tr>
<td>1954</td>
<td>3,380</td>
<td>750</td>
<td>6,300</td>
<td>1,000</td>
<td>620</td>
<td>750</td>
<td>12,800</td>
</tr>
<tr>
<td>1955</td>
<td>3,940</td>
<td>730</td>
<td>6,600</td>
<td>1,500</td>
<td>2,100</td>
<td>730</td>
<td>15,600</td>
</tr>
</tbody>
</table>

(All figures in $1000$ pounds)

5. Manufacturing process

I designed a engineering flow diagram for the production of the polyamide from adipic acid with hexamethylenediamine with 90 tons of annual production capacity.

There are number of patents which are concerned with the production of the polyamide from the above mentioned compounds. However, I have chosen the following method: there are no liquid (except water) in the system and we can process the last polymerization under the atmospheric pressure. Therefore we can simplify the equipment for the production.

Unfortunately I could not find any publication on the factory scale manufacturing method of the polyamide and I dont know even the production of the above product is done contineously or not in practice. However, I have seen some polyester resin makers in the Netherlands and the Bayer factory in Krefeld in W.-Germany and all of them are using batch process. Moreover, it is very difficult to produce polyamide contineously because of the long polymerization time (6 hours) in the polymerization kettle.

From these reasons, I have designed semicontinuous flow diagram with 100kg/6hours of production capacity.

\( V_1 \): In this tank the adipic acid water solution is made discontinuously.

Tank capacity = 4500 litre

Material balance:

In:
- Adipic acid = 66.4 kg
- Water = 3,330 kg

Out:
- Adipic acid = 66.5 kg
- Water = 3,330 kg

Solution
In this tank the adipic acid water solution is neutralized by the gradual addition of the Hexamethylenediamine (in solid form) and obtain so called Nylon salt (hexamethylenediammoniumadipate). According to the literature, the equivalent point of the neutralization is P_{H} 7.63±0.3. The tank V_2 has a cooling spiral (cooling with water), because the neutralization evolves the heat.

Tank capacity same as the tank (V_1)

Material balance:

In:
- Adipic acid 66.4 kg/hour
- Hexamethylenediamine 3,330 kg/hour
- Water 3,330 kg/hour

Out:
- Nylon salt with impurity 120 kg/hour
- Water 3,330 kg/hour

Temperature:
- In 20°C
- Out 20°C

Amount of heat (removed) 16,000 kcal/hour

Size of the cooling spiral:
- Pipe diameter 5/4"/1
- Coil diameter 0.6 m
- Number of coil 14

(Filter):
This is the horizontal plate filter (Maker: Sparkler Co.)

Capacity 5,000 l/hour

Size:
- Height 53"
- Diameter 29"

Material balance:

In:
- Nylon salt water solution with impurity 3,450 kg/hour

Out:
- Nylon salt 108 kg/hour
- Water 3,320 kg/hour
- Impurity and loss 22 kg/hour
Storage tank:
I placed two storage tanks between the filter and the heat exchanger, to proceed the further process continuously.

(Heat exchanger):
This heat exchanger increases the temperature of the nylon salt solution from 20°C to 150°C by heating with steam (180°C)

Size:
Pipe length = 2 m
Pipe diameter = 1/2" / 5/8"
Number of pipe = 12
Diameter of exchanger = 0.2 m
Length of exchanger = 2.2 m

Material balance:
In:
Nylon salt = 108 kg/6 hours
Water = 3,320 kg/6 hours
Solution
Out:
Same as the incoming

Temperature:
In = 20°C
Out = 150°C
Quantity of the introduced heat = 445900/6 kcal/hour

(Evaporator):
In this evaporator the dilute water solution of the nylon salt is concentrated to 60% solution by heating to 150°C with steam (180°C).

Size:
Pipe diameter = 1"
Length of pipe = 1 m
Number of pipe = 40
Diameter of evaporator = 0.3 m
Length of evaporator = 1.2 m
Material balance:

In:
Nylon salt = 18 kg/hr solution
water = 554 kg/hr

Out:
Nylon salt = 18 kg/hr solution
water = 12 kg/hr
water = 542 kg/hr (removed as steam to outdoor)

Temperature:
In = 150°C
Out = 150°C

(Autoclave):
The concentrated nylon salt solution (60%) flows into the autoclave continuously with the mass flow of 30 kg/hr at 150°C. During this period (6 hours), the autoclave was operated to keep the temperature of the contents to 150°C. Meanwhile calculated amount of hexamethylenediammoniumacetate and adipic acid are added to the autoclave to control the molecular weight of the final product.

According to the literature²,³), we can control the molecular weight of the final polymer by addition of the diamine-monobasic acid salt, monoaminodibasic salt, or monoaminemonobasic acid salt. The required amount of the above salts to give a certain viscosity to the final product, is calculated with the following relation,

\[
\text{Moles of stabilizer required} = \frac{\text{Mol. Wt. of salt}}{(16,000)(\eta)} \cdot \text{moles of salt}
\]

where
\[
\eta : \text{intrinsic viscosity} = \frac{\ln \eta_r}{C}
\]
\[
\eta_r : \text{viscosity of a dilute solution of the polymer divided by the viscosity of the solvent in the same unit and at the same temperature.}
\]
\[
C : \text{Concentration in grams of polymer/100cc solu.}
\]

The relation between the intrinsic viscosity and the molecular weight is, ⁴)

\[
[\eta] = K M^a
\]

where K and a are constant determined, respectively by the intercept and the slope of the \(\eta\) - mol. wt. curve.
The K and a value for the poly-ε-caproamine at 25°C with sulfuric acid as the solvent are $2.9 \times 10^{-4}$ and 0.78, respectively.

When 30 kg of 60% nylon salt solution was collected in the autoclave (during 6 hours), the polymerisation was done in the following way:

whole mass was heated 2 hours at 225°C (the maximum pressure 225 lb/in²) under N₂ gas atomosphere, then increase the temperature to 264°C and keep at this temperature for 4 hours under 1 atmosphere N₂ gas and removed water (include the condensation water).

Material balance:

In:

Nylon salt = 108 kg/6 hours
Water = 72 kg/6 hours
Adipic acid = 0.36 kg
Hexamethylenediammonium acetate = 0.4 kg

this is the amount required to give 18,000 of mol.wt. to the final product

Out:

Nylon = 100 kg/6 hours
Water = 80 kg/4 hours (include 8 kg condensation water) removed as waste

Temperature:

In = 150°C
Out = 264°C

Heat balance:

Heat given by the Dutherm heating system
= 14,400 kcal/hr = heat required to increase the temperature of the mass from 150°C to 264°C

(Cooling wheel):

In practice the wheel is external cooling aluminium wheel. I have cooled the wheel internally with 15°C water spray and the used water is sucked away. The nylon is cooled on the wheel in the form of 10 cm wide ribbon with 1 mm thick.

The wheel is moving with 5 cm/sec of the speed to decrease the initial temperature (260°C) to 30°C

Size of the wheel:

Diameter = 1.25 m
(Crusher):
The cooled nylon ribbon is crushed into the nylon flakes.

Literatures
1) Carothers: U.S.P.2,130,947(September,20,1938)
    " U.S.P.2,130,948( " " " )
    Flory : U.S.P.2,172,374(Spt.,12,1939)
    Carothers: U.S.P.2,130,523(Spt.,20,1938)
    Carothers : U.S.P.2,163,584(June,27,1939)
    Spanagel : U.S.P.2,163,636(June,27,1939)
2) Flory : U.S.P.2,172,374(Spt.,12,1939)