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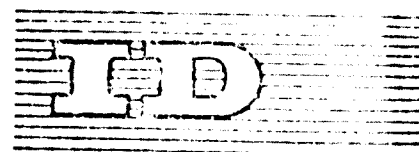
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Baku, USSR, 21 - 31 October 1969

THE IMPORTANCE OF THE PHOTONITROSATION PROCESS

FOR THE PRODUCTION OF NYLON-6 MONOMER^{1/}

by

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Tokyo Japan

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SUMMARY

THE IMPORTANCE OF THE PHOTONITROSYLATION PROCESS FOR THE PRODUCTION OF NYLON-6 MONOMER ^{1/}

by

Yoshiharu Ito

Toyo Rayon, Japan

Our PNC process converts cyclohexane to cyclohexanone in one step without using hydroxylamine reducing to half the ammonium sulphate produced as by-product in the conventional process.

Research work started in 1950 and the first commercial plant came on stream in 1952 and by 1968 we had a capacity of 200 million lbs./annum of caprolactam (nylon-6 monomer).

The paper details the reason for the long period of research necessary and then discusses the operation of the process. This consists of the treatment of cyclohexane with nitrosyl chloride (produced by the reaction of hydrogen chloride with a sulphuric acid solution of the gases produced by the oxidation of ammonia.) Cyclohexanone oxime hydrochloride is formed under conditions

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involving illumination with ultra violet light preferably between a wave length of 350 and 500 m μ . This product is submitted to the Beckmann rearrangement by treatment with sulphuric acid in the conventional manner.

The mechanism of the reaction is considered in some detail as are the reaction conditions necessary to avoid the production of undesirable by-products. Special high pressure mercury vapour lamps of up to 50 Kw capacity have been developed which reduce power consumption to about 2.5 KWH per kg of oxime produced. The removal of thermal energy and methods of dealing with the corrosive action of nitrosyl chloride are discussed.

We regret that some of the pages in the microfiche copy of this report may not be up to the proper legibility standards, even though the best possible copy was used for preparing the master fiche.

Summary

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Table 1

Development of PNC Process

	Total production MM Lbs/yr	Capacity . Kw	L a m p Oxime yield g oxime/Kwh
1950 Basic research started			
1952		1	50
1958 Bench scale plant		5	130
1960 Pilot plant		10	200
1962 Commercial plant	8	10	
1963 New plant	32	20	
1964 1st extension	48	20	300
1966 2nd extension	110	20,40	400
1968 3rd extension	200	40,60	400

The review of the PNC process development is shown in Table 1. Our research work started in 1950. The first commercial production has been on stream at about 25 million pounds per year since 1963. At present 200 million pounds of ϵ -caprolactam is produced by the PNC process in our Tokyo plant.

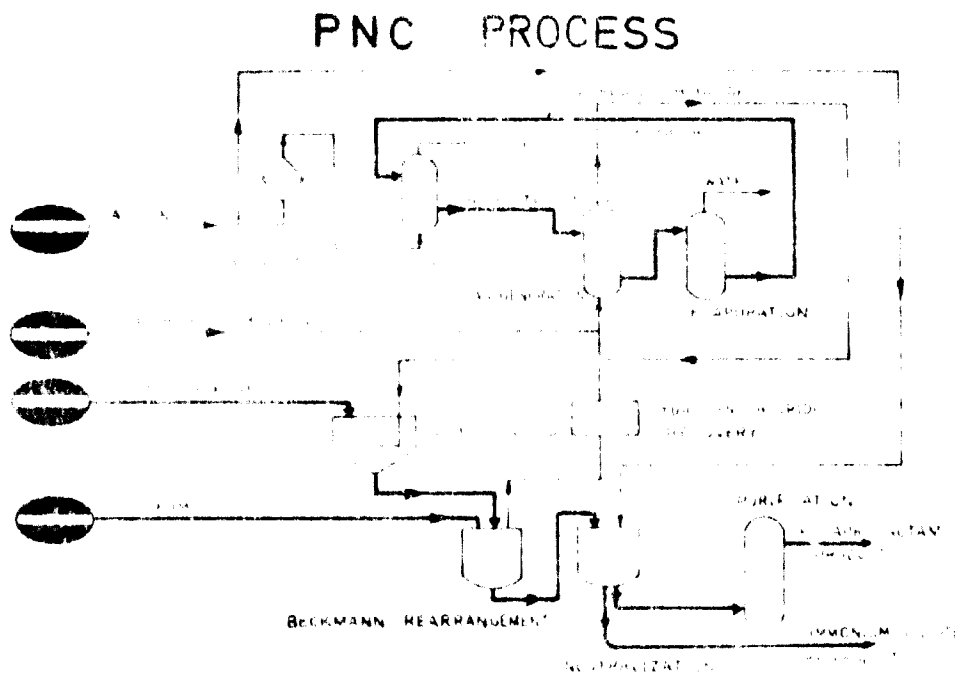
The reason why such a long time was required to commercially develop the PNC process was that the solution of the technical problems consumed a great deal of time:

- 1) Suppression of side reactions incidental to the photonitrosation and stabilization of the continuous reaction.
- 2) Development of lamps having both large capacity and high efficiency.
- 3) Design of photo-reactors and determination of economic capacity of the photo-reactor.
- 4) Selection of corrosion-resistant materials.
- 5) Development of a process for economical manufacture of nitrosyl chloride.

TOYO RAYON, BASF in Germany, Allied Chemicals in the United States, and the Soviet Union are proceeding with the research work. However, we have resolved all the aforesaid problems and established the process on an industrial basis.

The process is schematically outlined in Figure 2.

Figure 2



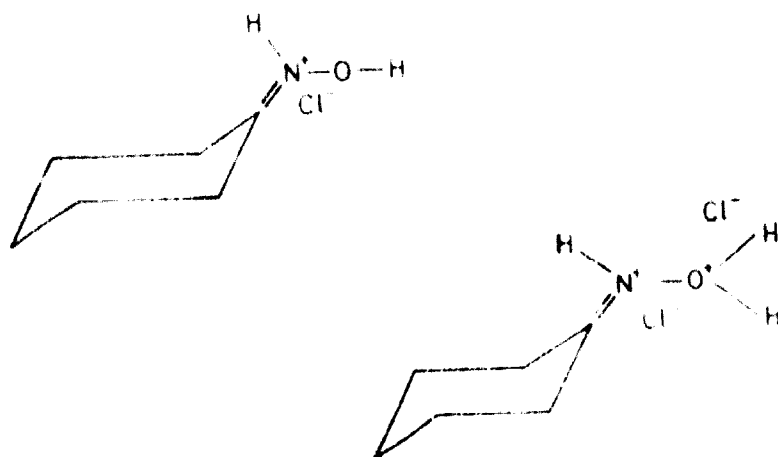
The industrial operation of the PNC process is broadly divided into the following three reaction steps:

- 1) Manufacture of nitrosyl chloride--The nitrogen trioxide gas obtained from the oxidation of ammonia is absorbed in sulfuric acid. The nitrosyl sulfate acid formed reacts with hydrogen chloride to generate nitrosyl chloride. A complete circuit to a system of sulfuric acid is established by removing the water that is formed from the acid solution.
- 2) Manufacture of cyclohexanone oxime hydrofluoride--The cyclohexanone oxime hydrofluoride formed by photo-irradiation of cyclohexanone is insoluble in cyclohexane so that it can be separated continuously from the bottom of the photo-reactor.
- 3) Manufacture of ϵ -caprolactam--The cyclohexanone oxime hydrofluoride can be subjected to Beckmann rearrangement reaction with sulfuric acid. The hydrogen chloride is recovered from Beckmann rearrangement reaction and recirculated for use in the manufacture of nitrosyl chloride.

350 μ to 600 μ independently of the wave length. This is often to be admitted as the mechanism of the photo-nitrosation.

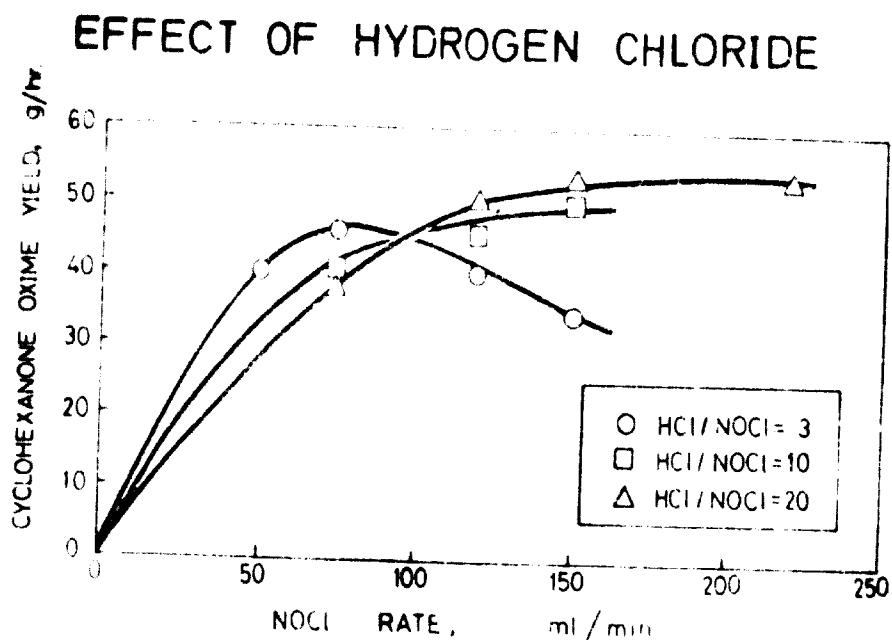
Figure 4

STRUCTURE OF CYCLOHEXANONE OXIME HYDROCHLO- RIDE



The product of the photo-nitrosation comprises mainly cyclohexanone oxime dihydrochloride. The nitrosocyclohexanone intermediate is unimerized in the presence of hydrogen chloride, and cyclohexanone oxime dihydrochloride, an oily substance, insoluble in cyclohexane. If hydrogen chloride is not added to the reaction system the nitrosocyclohexanone is rearranged to an oxime monohydrochloride, and part of the nitrosocyclohexanone is converted into bisnitrosocyclohexane. The structures of none of the chlorides of cyclohexanone oxime were investigated by means of infrared, ultraviolet, and NMR spectra. As a result, it has been decided that the monohydrochloride in presence of hydrogen chloride attaches to the nitrogen atom and another proton to that of an oxygen atom in dihydrochloride (Figure 4). How I show you how to suppress side reactions.

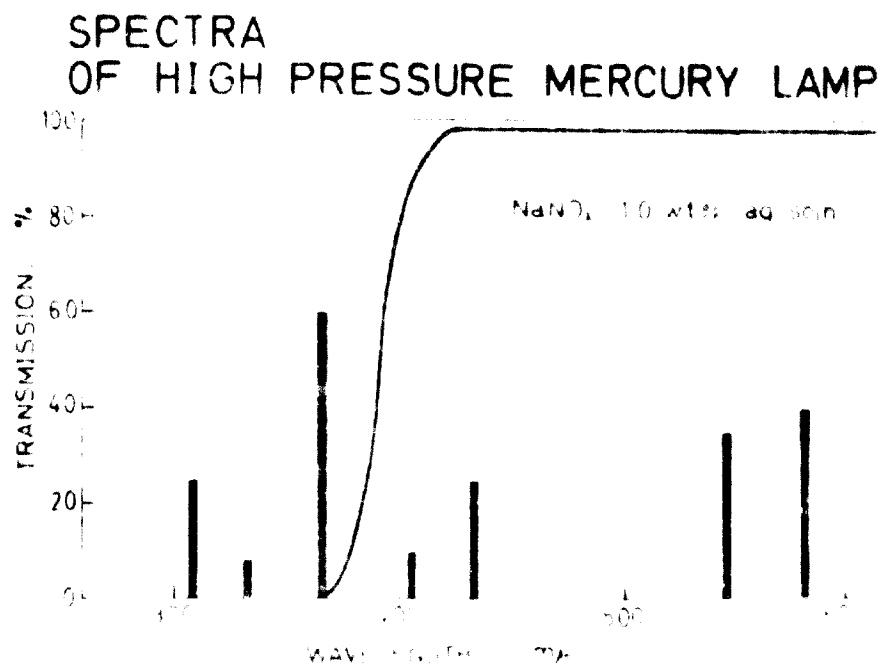
Figure 5



It is known that the cyclohexanone oxime, bisnitrosocyclohexane, and cyclohexanone oxime monohydrochloride formed by the photo-nitrosation further react with nitrosyl chloride to form 1-chloro-1-nitrosocyclohexane etc. The gem-chloronitrosocyclohexane absorbs light and decomposes into a brown tarry substance. It attaches itself to the surface of the light source tube, thus reducing the light flux. However, from Figure 5 it can be seen that these side reactions can be suppressed effectively by introducing large quantities of hydrogen chloride into the nitrosyl chloride gas. Cyclohexanone oxime, bisnitrosocyclohexane, and cyclohexanone oxime monohydrochloride are unstable to nitrosyl chloride. They are converted by hydrogen chloride into the cyclohexanone oxime dihydrochloride which is practically stable to the nitrosyl chloride. From the fact that the use of nitrogen in place of hydrogen chloride does not achieve the same result, it is concluded that the aforementioned addition of hydrogen chloride does not act as a diluent only. Another advantage of introducing the hydrogen chloride is that it prevents the oily hydrochloride deposited on the wall of the light source tube from turning into a brown tarry film. Formation of tarry films on the surface of the light source tube results in the absorption of actinic light and retardation of the reaction rate.

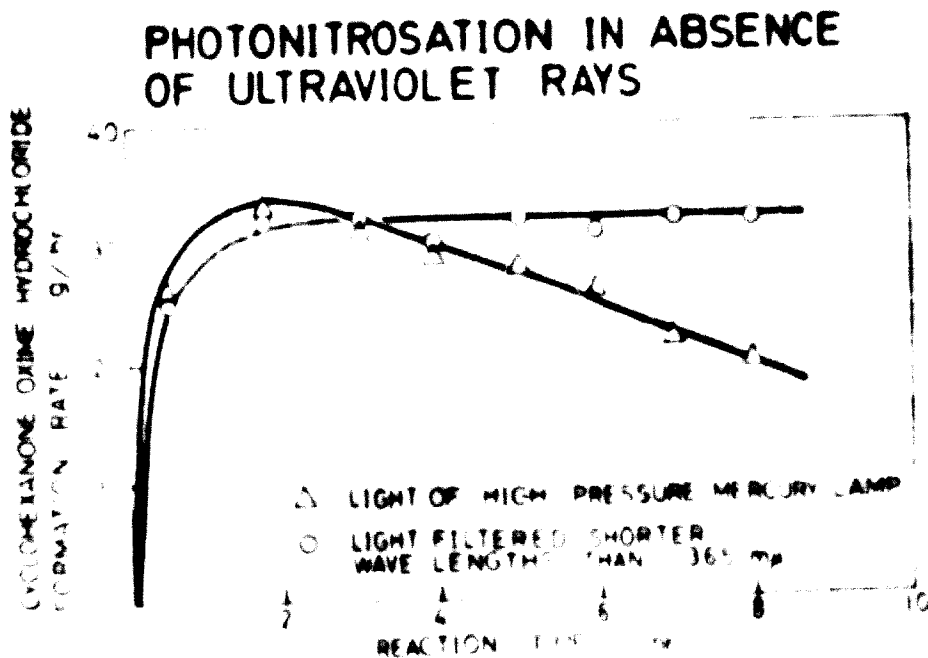
To suppress the growth of such tarry films, various improvements have been proposed, including, for example, addition of aliphatic acids to cyclized oil and recycling of chlorinated by-products obtained during the photo-nitration. However, none of these improvements have proved satisfactory.

Figure 6



We have discovered that the film formation is caused mainly by ultraviolet rays. The spectra of high pressure mercury lamp is shown in Figure 6. The photo-nitrosation was carried out in the presence of hydrogen cyanide in the actinic light which was filtered to remove wave lengths shorter than 350 mμ given by a high pressure mercury lamp.

Figure 7



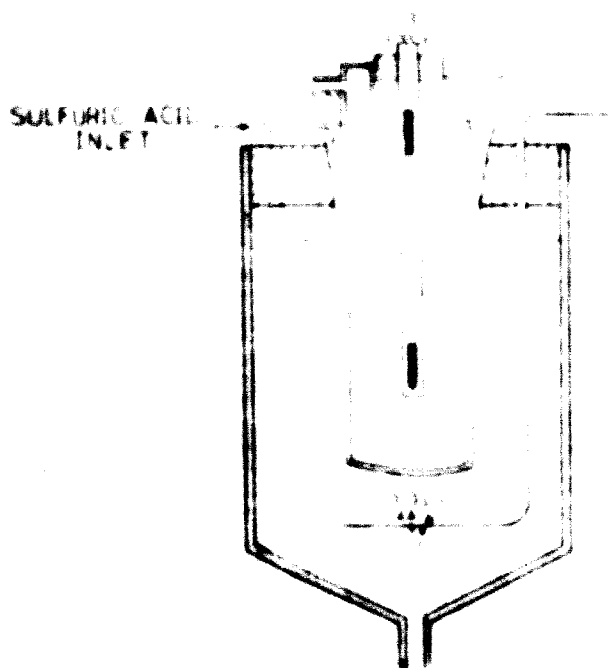
It resulted in a stable continuous reaction without formation of tarry films (Figure 7).

Nitrosyl chloride has a powerful absorption in the ultraviolet region. Most of the ultraviolet rays emitted are absorbed by nitrosyl chloride close to the surface of the light source tube, and the oily reaction product formed in this area readily deposits on the surface of the light source tube. Therefore, although the ultraviolet rays are effective in dissociating the nitrosyl chloride, elimination of these rays is necessary to establish the stable continuous reaction.

Despite careful selection and control of the operation conditions of the photo-nitrosation reaction, small quantities of tarry matter accumulated on the outer surface of the lamp. After several days this tarry matter reduced the light admitted to the reaction zone, causing a reduction in oxime yield.

Figure 3

SCHEMATIC DIAGRAM OF PHOTO REACTOR



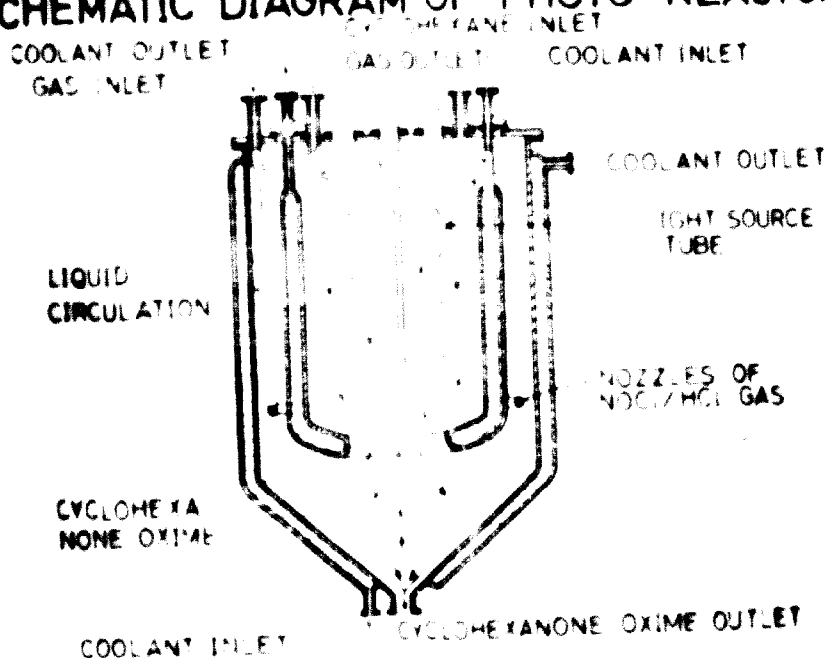
To quickly remove tarry color bodies from the outer surface of the film, we have developed a process of continuously or intermittently supplying the tarry colored films by passing over them a dilute acid in the form of a spray. The surface of the film is wetted from an inlet pipe. This process has been found experimentally effective. A concentrated sulfuric acid solution for this purpose can be utilized in series to speed Beckmann rearrangement.

Light Source

In the initial stage of our research work, experiments were carried out using small size low light source. To establish the photo-oxidation process on an industrial basis, it was the foremost requirement to develop a source which has a large capacity and high efficiency. It was necessary to evaluate various factors such as the limiting efficiency of the light source, operating life, spectra, and distribution of specific energy. In the first commercial plant high pressure mercury lamps of 15 KW capacity were used. We have developed special high pressure mercury lamps of 40 KW and 60 KW capacity which reduce the power consumption to about 100 per Kg of oxime produced.

Figure 9

SCHEMATIC DIAGRAM OF PHOTO REACTOR



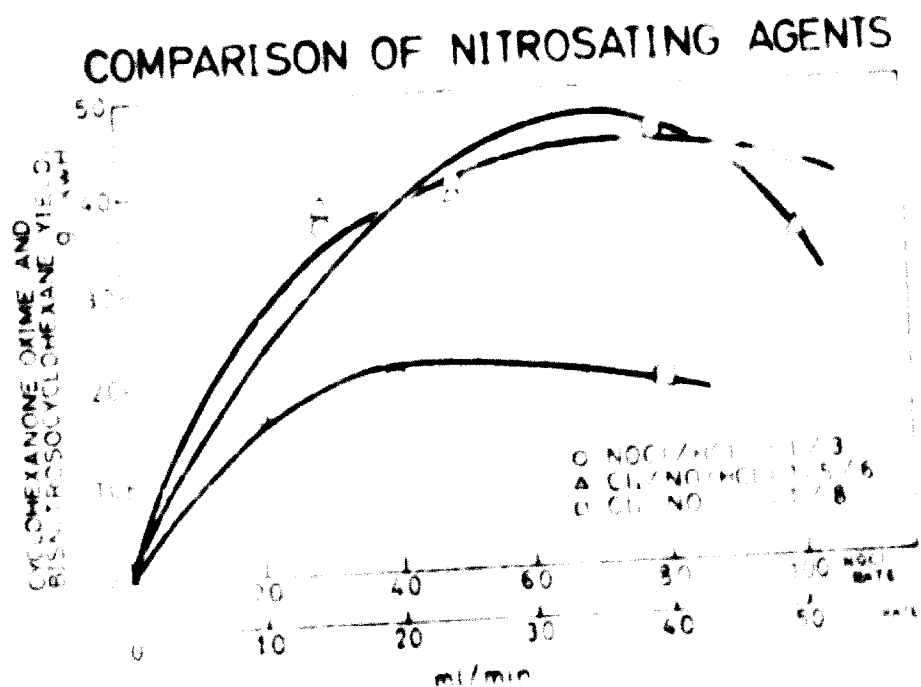
With regard to the type and capacity of a photo-reactor and the arrangement and output of a light source, engineering studies were made from the stand point of the efficiency of utilizing light and economics. As a result of these studies, it has been disclosed that the efficiency of utilizing light is associated with the thickness of the liquid phase between the wall of the reactor and the light source tube. The concentration of an oily substance in the reaction solution composed mainly of the oxime dihydrochloride is also associated with such efficiency. With respect to the photo-reactor, a type of the photo-reactor in which light sources are immersed in the reaction solution was found to be suitable from the stand point of utilizing light most effectively. The schematic diagram of photo-reactor is shown in figure 9. The capacity of the photo-reactors should be determined in consideration of the manufacturing cost and productivity. The present capacity of reactors is about 15 tons per day per unit.

Most of the thermal energy emitted from the light source is removed by lamp-cooling water. The remaining energy together with the heat released by formation of the oxime, is eliminated by cooling with a jacket or coil fitted

to the reactor, thus the reaction temperature is kept constant.

Since highly corrosive substances such as nitrosyl chloride, chlorine chloride, and bromine hydrochloride are involved in the photo-nitrosation, the selection of the reactor materials posed a special problem. Titanium dioxide is not completely resistant to nitrosyl chloride, but completely resistant to chlorine, thus the photo-nitrosation is performed under optimum conditions. Thus the problem of reactor materials has been solved and a reactor made of titanium is now in smooth operation.

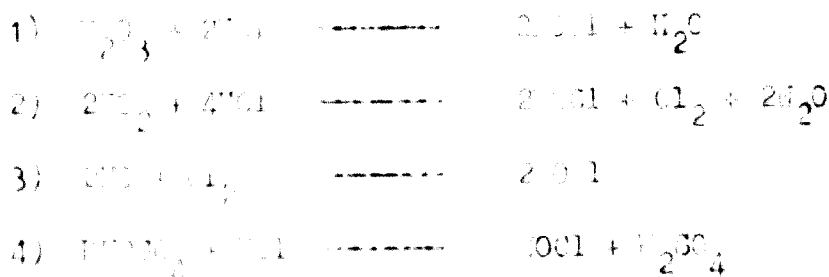
Figure 10



With respect to photo-nitrosating agents, the use of a system of chlorine and nitric oxide or a system of chlorine, nitric oxide and hydrogen chloride in addition to the process involving nitrosyl chloride, are being studied. In the process using chlorine and nitric oxide without addition of hydrogen chloride, a reaction of nitrosocyclohexane to nitro-cyclohexane takes place in preference. The use of a system of chlorine, nitric oxide and hydrogen chloride in the reaction system. In the process using a system of chlorine and nitric oxide diluted with hydrogen chloride as photo-nitrosating agents, the yield of the oxime is as much as that of the nitrosyl chloride process (100%).

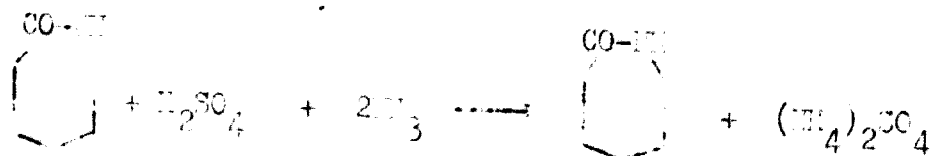
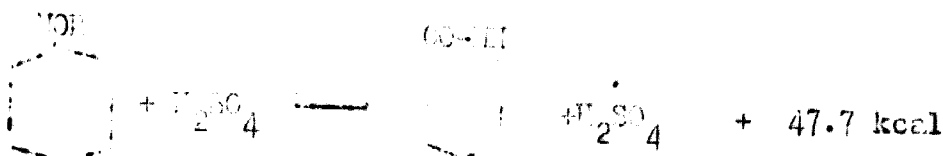
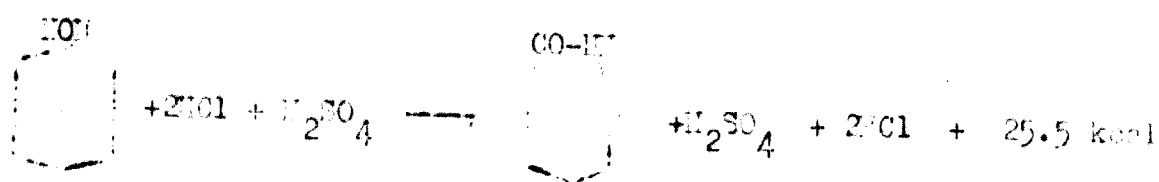
Figure 10). If in this process, the photo-nitrosating agent is introduced to the photo reaction system immediately after being fully diluted with hydrogen chloride, the yield of the acid is reduced to a fraction of the volume required with nitrosyl chloride on the basis of the same concentration of starting material. It is deduced from this fact that in this process the same reaction, formation of nitroso compounds, takes place after formation of nitrosyl chloride. Therefore, it is concluded that the photo-nitrosation with nitric oxide, nitrogen, and hydrogen chloride follows the same principles as applied in the nitrosyl chloride process. However, in the process under study, a proportion of the main reaction products are chlorinated due to the presence of chlorine, resulting in 1-chloro-1-nitrosocyclohexane. Thus this process does not have any advantage over the process using nitrosyl chloride.

Industrial processes for manufacturing nitrosyl chloride involve the following reactions:



For example, in the process in which nitrosyl chloride is produced by the reaction of nitrogen monoxide and hydrogen chloride, the nitrogen monoxide is obtained by air oxidation of ammonia. The nitrogen monoxide, for commercial availability, is governed by the fact that it is highly soluble in water and nitrogen obtained from the ammonia oxidation process is highly impure and the reaction can be separated from the reaction of nitrogen monoxide and hydrogen chloride. In this process, nitrosyl chloride is obtained by the reaction of nitrogen monoxide and hydrogen chloride. The reaction is highly exothermic and sulfur dioxide is a by-product. Consequently a recirculation system of the gas stream is established.

Nitrosyl chloride, which is rearranged into α -chloroaldehyde, is obtained by the reaction of sulfuric acid. Sulfuric acid, laboratory grade, is used at the same time. The reaction scheme is as follows:



The conditions of the rearrangement are practically the same as those used in the case where pure nitro compound is reacted. The rearrangement reaction of cyclohexanone oxime dihydrochloride with sulfuric acid is characterized in that the heat of reaction is reduced due to the release of hydrogen chloride, resulting in slight retardation of the reaction rate.

The yield of B chain rearrangement with sulfuric acid is almost quantitative. Hydrogen chloride is recovered from the reaction rearrangement product and can be recycled to the photo-nitrosation system.

The reaction product is neutralized with ammonia using the conventional method to separate crude β -nitro lactam and ammonium sulfate.

The crude β -nitro lactam obtained can be refined to a high purity by various suitable for polymerization by itself, singly or in proper combination with various conventional refining methods such as extraction, distillation, chemical treatments, and so on.

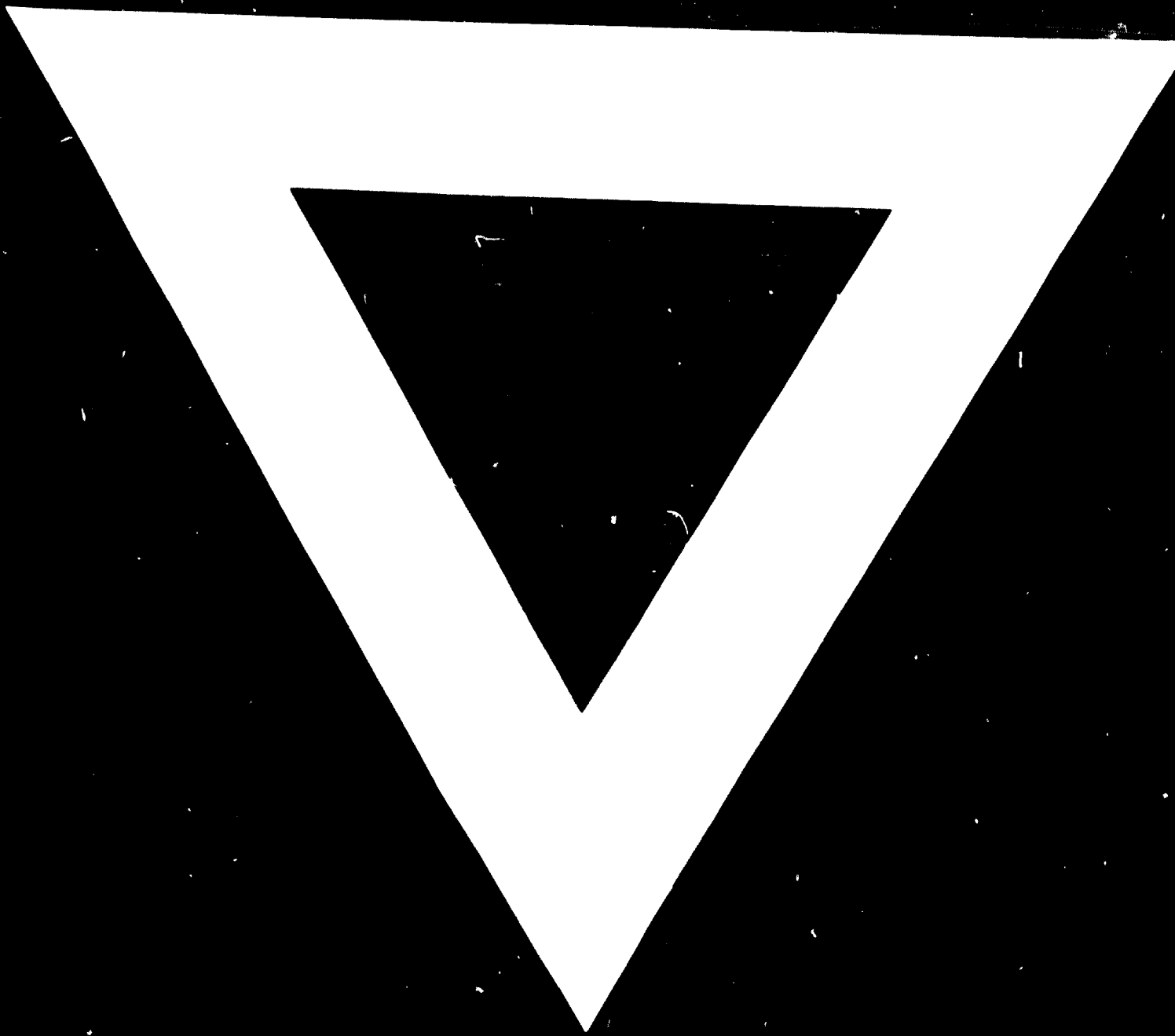
Conclusion

The distinctive feature of the PNC process lies in the photochemical synthetic reaction in the first step. Since the nitro group is introduced directly into cyclohexane to form the oxime, the reaction process is the shortest as compared with those involved in other processes. In conventional process which uses phenol or cyclohexane as the starting material requires

at least four steps of reaction whereas the photochemical process has made it possible to reduce the reaction steps to two. In the conventional method, ammonium sulfate was produced by weight 4 to 5 times as much as that of ϵ -caprolactam produced. By contrast, the photochemical process has reduced the by-product ammonium sulfate to about 1/10 the amount produced in the conventional process. It also uses inexpensive nitrosyl chloride as a nitrogen source instead of costly hydroxylamine. Thus it has played an important role in improving the economics of the manufacture of ϵ -caprolactam.

The above process is the first application of a photochemical reaction on large industrial scale. The technical knowledge and experience gained in developing this process will be very useful in commercializing future photochemical processes. The photochemical process of lauro lactam, the new material for nylon 12, has already been developed at Nagoya plant on semi-commercial scale.





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