Analysis of the Impurities in Industrial ε-Caprolactam. Hypothesis of Formation

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Synopsis

Analysis of an industrial ε-caprolactam by gas–liquid chromatography has been carried out using different stationary phases and operating conditions. The impurities in the ε-caprolactam are identified and hypotheses about their formation are presented. In some cases the presence either in cyclohexane or cyclohexanone of the possible impurity-producing compounds is shown.

INTRODUCTION

ε-Caprolactam is being increasingly used in the preparation of synthetic fibers. Polymerization is clearly effected by the impurities present in the monomer. Several authors[1-3] have studied the effect of various impurities in the polymerization, concluding that they affect the viscosity and specific gravity of the polyamide.

ε-Caprolactam is commercially analyzed according to specific parameters as defined by STANDARD GOST 7850-74. These parameters are only relevant from an industrial point of view as they only indicate the commercial quality without due regard for the number, nature, or quantity of the impurities present. Various analytical techniques have been used for their determination, such as thin-layer chromatography,[4-8] infrared spectroscopy,[9-11] gas–liquid chromatography,[12-20] ultraviolet spectroscopy,[21-22] and mass spectrophotometry.[23]

Among the above-mentioned techniques, gas–liquid chromatography is very promising, although not all the problems are solved with it and have to be complemented with others.

ε-Caprolactam impurities can be a result of the reaction of the impurities present in the raw materials (cyclohexane, phenol, toluene, aniline, oleum, and hydroxylamine), products obtained in the intermediate steps (oxidation, hydrogenation, dehydrogenation, oximation, and rearrangement) and products resulting from auxiliary operations (neutralization, extraction, and rectification). The literature on the subject is abundant, showing that the total number of impurities is over 50.

Schaffler,[21] by extraction and cristallization and using ultraviolet spectroscopy, found as impurities cyclohexanone, aniline, octahydrophenazine, o-toluidine, and phenylisonitrile. Octahydrophenazine was also identified by Iogansen[22] in a different ε-caprolactam by the same methods.

Polo Friz,[23] using gas–liquid chromatography and mass spectroscopy, found aniline, cyclohexanone, cyclohexanone oxime, o- and p-toluidine, methylvalerolactam, and octahydrophenazine. Arakelian,[24] using gas–liquid chromatog-

raphy, determined, apart from those previously mentioned, the following impurities: cyclohexylamine, nitrocyclohexane, cyclohexylidenecyclohexanone, and nitrobenzene. Finally, Sokolova,[25] also by gas–liquid chromatography, found butyl- and pentylamine, phenol, phenazine, ϵ-valerolactam, heptamide, methylhexamide, pentylacetamide, and tert-butylpropanamide.

The identification of impurities in an industrial ϵ-caprolactam is a complex matter because of their high number, different nature, and variable amounts. All of them depend upon the raw material used and the production process. The exact knowledge of the impurities present in the product is of great interest, as it allows to establish a hypothesis of formation and hence to act on the process to avoid them.

In the present work, an industrial ϵ-caprolactam was analyzed under different production conditions. The method of analysis was gas–liquid chromatography, using several chromatography columns of various lengths and containing different stationary phases. After identifying the impurities, a hypothesis on their formation is presented.

EXPERIMENTAL

Analysis

The analysis of an industrial ϵ-caprolactam extract produced by oxidation of cyclohexane has been carried out. Gas–liquid chromatography has been used. Of the four different columns used, two were of Carbowax 20M at 20% on Chromosorb W AW; one was 2 m long (A1 column); and the other was 4 m long (A2 column). The other two columns were of FFAP at 13% and H_3PO_4 at 1% on Chromosorb G AW; one was 2 m long (B1 column); and the other was 4 m long (B2 column). The tubes of the four columns were of stainless steel, $\frac{1}{8}$ in. o.d.

Materials

Table I shows the origin quality and purity of some of the materials used for identification of the impurities. The rest of the materials—heptamide, pentylacetamide, methylhexamide, methylvalerolactam, and octahydrophenazine— not available commercially, were synthesized and purified by normal laboratory methods.[27–30]

Octahydrophenazine was obtained through multiple liquid–liquid extractions

TABLE I
Materials Used

Compound	Manufacturer	Quality	Purity, %
Cyclohexylamine	FEROSA	chromatographic	99
Cyclohexanone		commercial	99.9
Cyclohexanol		commercial	99.9
Aniline	Merck	chromatographic	99
Nitrobenzene	Merck	chromatographic	99
o-Toluidine	Merck	chromatographic	99
p-Toluidine	Merck	chromatographic	99
Cyclohexanone oxime		commercial	99.9

with cyclohexane from the industrial ε-caprolactam extract. Starting with 20 kg of the bottom product of the distillation of ε-caprolactam, a concentrate of 1 kg was obtained. This concentrate was extracted with cyclohexane, and the extract thus obtained was concentrated to one-fourth of its volume by vacuum distillation. The resulting product was washed with water and diluted hydrochloric acid and later dried on anhydrous magnesium sulfate. Removing cyclohexane from the end product by vacuum distillation, 6 g of yellowish crystals with small drops of oil was obtained. After recrystallization in petroleum ether, a product with the infrared and ultraviolet spectra of hydrophenazine was obtained.

RESULTS

A1 Column

The operating conditions used with this column were: chromatograph, Hewlett-Packard 5710 A; column, tube material stainless steel; stationary phase Carbowax 20 M at 20%, solid support Chromosorb W AW DMCS 80/100; length 2 m; external diameter $\frac{1}{8}$ in.

Temperature of injection port, 250°C; of FID, 250°C; of oven, programmed 140°C for 8 min and then at 2°C/min till 180°C.

Carrier gas was nitrogen, 35 cm^3/min.

Sample used was 0.6 μL. Solvent was methyl dichloride. The ε-caprolactam was dissolved in methyldichloride (50% weight).

A2 Column

Operational conditions were the same as in the A1 column, except for the oven temperature, now constant and equal to 180°C, and the column length, now 4 m.

B1 Column

Operational conditions same as in A2, except that the carrier gas flow is now 22 cm^3/min and the stationary phase is FFAP + PO$_4$H$_3$.

B2 Column

Operating conditions identical to B1, column length 4 m.

IDENTIFICATION OF IMPURITIES

A1 Column

A typical chromatogram obtained with this column under the operating conditions described above is represented in Figure 1.

The retention times of the peaks obtained, as well as the nature of those identified, are shown in Table II. In this table, peak number 8 could, in principle, correspond to o- and p-toluidine and cyclohexanone oxime, and very probably to all three, considering that cyclohexanone oxime rarely surpasses 4 ppm.
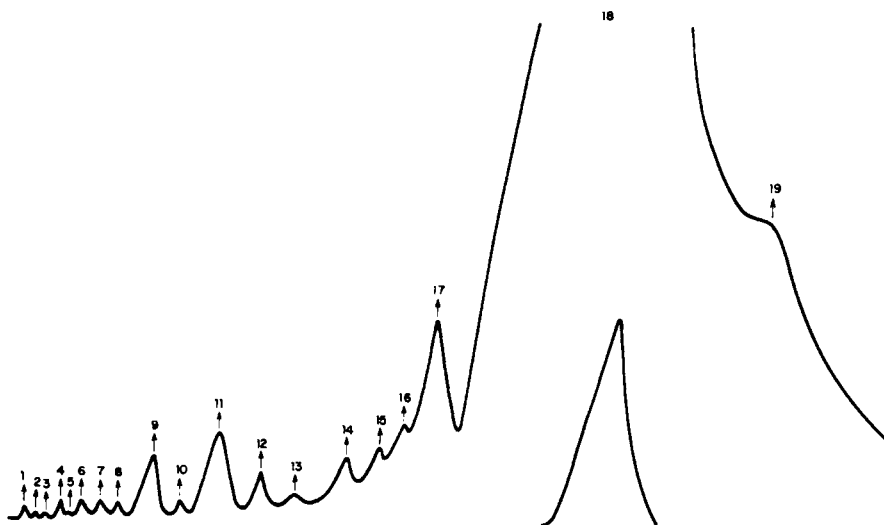
Fig. 1. Chromatogram obtained with column A1.

A2 Column

With this column, chromatograms of the type found in Figure 2 are obtained. In this chromatogram, up to 21 different peaks can be found.   Table III shows the retention times and the nature of the peaks.

A comparison of these results with those obtained from the A1 column shows that the peak assigned to methylvalerolactam in A1 is now divided into three, the first corresponding to methylvalerolactam, and the other two to α- and γ-methylcaprolactam.   Furthermore, peak 8 in A1 is now divided into peaks 11

TABLE II
Results With Column A1

| Peak	t_R, s	Nature
1	20	pentylamine
2	25	hexylamine
3	28	heptylamine
4	33	cyclohexylamine
5	43	cyclohexanone
6	53	cyclohexanol
7	75	unknown
8	90	unknown
9	120	aniline
10	160	nitrobenzene
11	176	o- and p-toluidine and cyclohexanone oxime
12	244	n-pentylacetamide
13	275	unknown
14	340	ϵ-caprolactone
15	420	heptamide
16	560	unknown
17	653	α-methylvalerolactam
18	760	ϵ-caprolactam
19	1710	octahydrophenazine
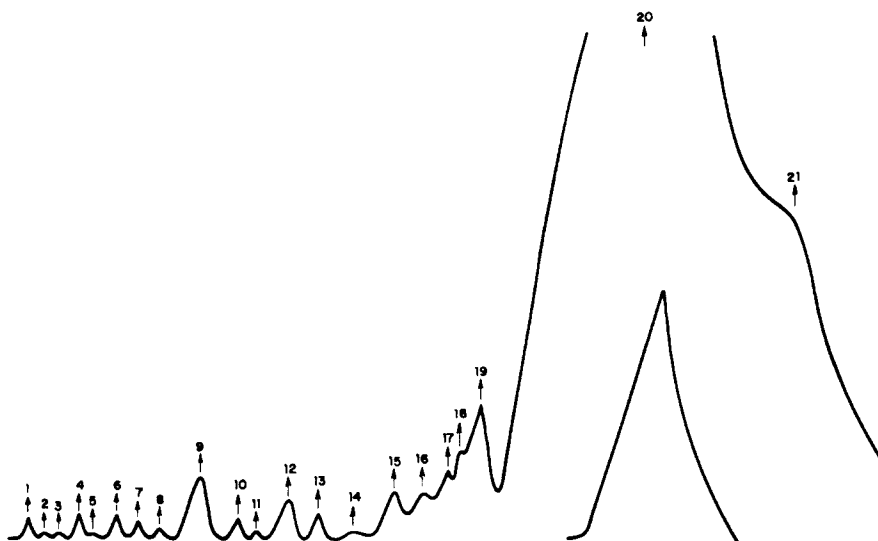
Fig. 2. Chromatogram obtained with column A2.

and 13, the former corresponding to cyclohexanone oxime and the latter to *o*- and *p*-toluidine.

Peaks 18 and 19 in column A2 were assigned to α- and γ-methylcaprolactam because both α- and γ-methylcyclohexanones are present in cyclohexanone. This is further supported by the presence of *o*- and *p*-toluidines in the ε-caprolactam. These impurities can only be formed from the methylcyclohexanones.

TABLE III
Results with Column A2

| Peak	t_R, s	Nature
1	33	pentylamine
2	40	hexylamine
3	47	heptylamine
4	55	cyclohexylamine
5	65	cyclohexanone
6	95	cyclohexanol
7	105	unknown
8	120	unknown
9	135	aniline
10	190	nitrobenzene
11	245	cyclohexanone oxime
12	255	*o*- and *p*-toluidine
13	270	*n*-pentylacetamide
14	370	unknown
15	445	ε-caprolactone
16	510	heptamide
17	805	methylvalerolactam
18	910	α-methylcaprolactam
19	1000	γ-methylcaprolactam
20	1095	ε-caprolactam
21	1865	octahydrophenazine

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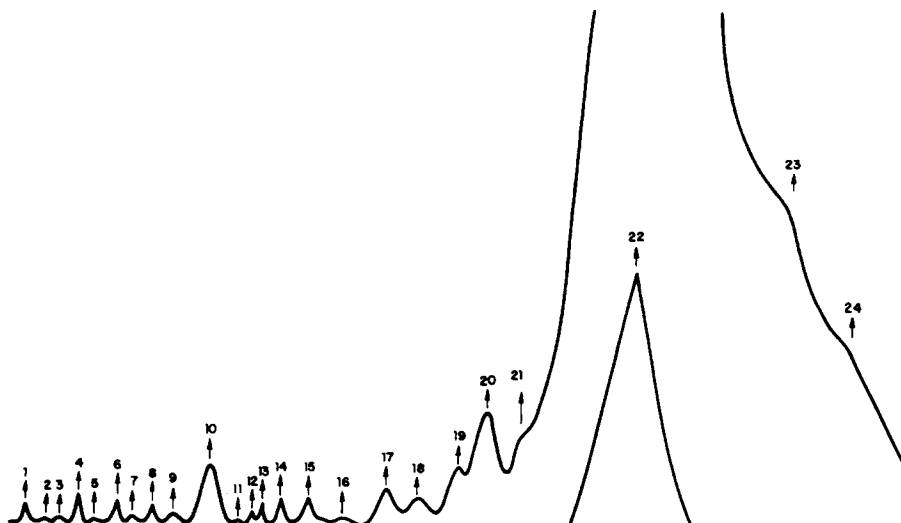
Fig. 3. Chromatogram obtained with column B1.

B1 Column

Figure 3 shows the chromatogram obtained with this column. The nature and retention times of the 24 peaks which can be observed are listed in Table IV.

It is interesting to note the change in the retention time of nitrobenzene

TABLE IV
Results with Column B1

Peak	t_R, s	Nature
1	35	pentylamine
2	40	hexylamine
3	56	heptylamine
4	80	cyclohexylamine
5	90	cyclohexanone
6	135	cyclohexanol
7	160	nitrobenzene
8	250	unknown
9	280	unknown
10	290	aniline
11	325	cyclohexanone oxime
12	345	p-toluidine
13	355	o-toluidine
14	430	n-pentylacetamide
15	495	unknown
16	520	ε-caprolactone
17	590	heptamide
18	615	unknown
19	820	methylvalerolactam
20	905	α-methylcaprolactam
21	1020	γ-methylcaprolactam
22	1350	ε-caprolactam
23	1800	octahydrophenazine
24	1875	adipic imide

compared with that in the columns with Carbowax as stationary phase. Moreover, peak 12 in the A2 column is divided into peaks 12 and 13, corresponding, respectively, to p- and o-toluidine. In the ε-caprolactam samples stored for a long time, a new peak is shown—peak 24—which supposedly corresponds to adipic imide.[32]

B2 Column

Among all the columns tested, this one gives the best results, as shown by the chromatogram in Figure 4. The twenty eight peaks obtained, retention times and nature are given in Table V.

Five peaks appear in the methyllactam area, two more than with the B1 column. There are two new peaks—24 and 25—which apparently correspond, respectively, to β- and γ-methylcaprolactam, for the same reasons mentioned above, that is, the presence of different methylcyclohexanones in the raw material. Two new impurities of unknown nature may be noticed.

HYPOTHESIS ON THE FORMATION OF IMPURITIES

Table VI shows the impurities identified with the raw material from which they are formed and the operation step in the global process in which this happens. This table also includes the conventional quality level affected by each impurity.

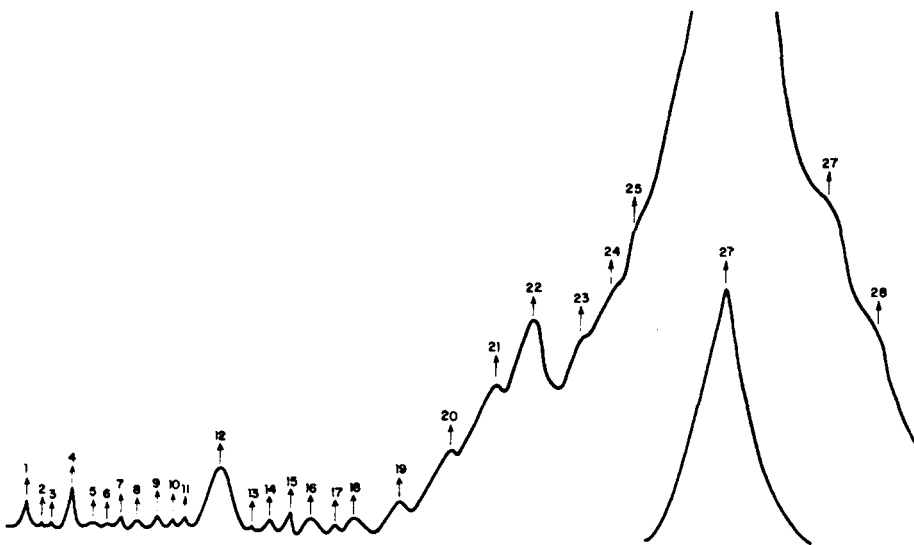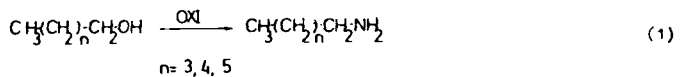Pentylamine, hexylamine, and heptylamine can be formed by a similar process:

$$CH_3(CH_2)_nCH_2OH \xrightarrow{OXI} CH_3(CH_2)_nCH_2NH_2 \qquad (1)$$
$$n = 3, 4, 5$$

Fig. 4. Chromatogram obtained with column B2.

TABLE V
Results with Column B2

Peak	t_R, s	Nature
1	37	pentylamine
2	56	hexylamine
3	65	heptylamine
4	97	cyclohexylamine
5	106	unknown
6	125	cyclohexanone
7	157	cyclohexanol
8	171	nitrobenzene
9	208	unknown
10	268	unknown
11	309	unknown
12	342	aniline
13	410	cyclohexanone oxime
14	425	p-toluidine
15	486	o-toluidine
16	531	n-pentylacetamide
17	573	unknown
18	638	ϵ-caprolactone
19	809	heptamide
20	901	unknown
21	961	methylvalerolactam
22	1049	α-methylcaprolactam
23	1127	γ-methylcaprolactam
24	1233	β-methylcaprolactam
25	1349	δ-methylcaprolactam
26	1413	ϵ-caprolactam
27	1885	octahydrophenazine
28	1950	adipic imide

Cyclohexylamine can be formed from cyclohexanone oxime or cyclohexylamine (formed by reaction between cyclohexanone and hydroxylamine sulfate in the oximation reactor). A more probable scheme for the formation of cyclohexyl-amine is


(2)
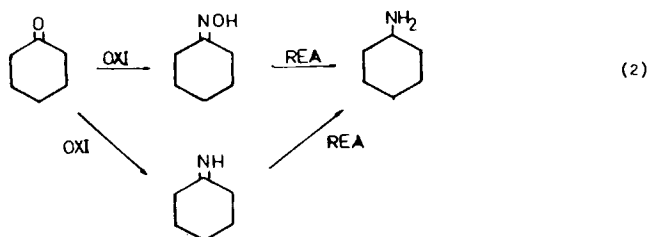
Cyclohexanol can be obtained by reduction of cyclohexanone which has not wholly reacted in the oximation step or because it is already present in the original cyclohexanone as an impurity.

The existence of aniline can be justified asuming that under the rearrangement conditions it is formed by dehydrogenation of the cyclohexylamine.   Under the
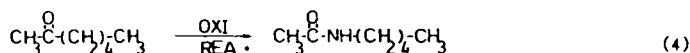
TABLE VI
Origin of the Impurities

| Impurity	Origin	Formation	Quality level affected
Pentylamine	pentanol	OXI and REA	
Hexylamine	hexanol	OXI and REA	
Heptylamine	heptanol	OXI and REA	
Cyclohexylamine	cyclohexanone	OXI and REA	
Cyclohexanone	cyclohexanone	Unreacted	PN and UV[32-34]
Cyclohexanol	cyclohexanone cyclohexanol	Unreacted	PN[32-34]
Aniline	cyclohexanone	OXI and REA	PN, VB, and UV[32-34]
Nitrobenzene	cyclohexanone	OXI and REA	UV[33]
Cyclohexanone oxime	cyclohexanone oxime	Unreacted	PN, VB, and UV[33-34]
o- and p-Toluidine	methylcyclohexanones	OXI and REA	VB and UV
n-Pentylacetamide	2-heptanone	OXI and REA	VB
ε-Caprolactone	cyclohexanol	REA	
Heptamide	heptanol	REA	
Methylvalerolactam	methylcyclohexanone	OXI and REA	PN, VB, and UV
Methylcaprolactams	methylcyclohexanones	OXI and REA	
Octahydrophenazine	cyclohexanone oxime	REA	PN, VB, and UV[34]
Adipic imide	ε-caprolactam	oxidation	PN, UV, CO, and AL

same conditions aniline could oxidize forming nitrobenzene:

(3)
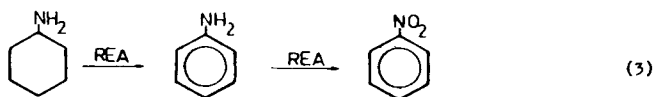
N-Pentylacetamide can be formed from 2-heptanone—an impurity of the cyclohexanone fed to the oximation step—in the oximation and rearrangement reactors. The most probable formation reaction is

$$CH_3\text{-}\overset{O}{\underset{}{C}}\text{-}(CH_2)_4\text{-}CH_3 \xrightarrow[\text{REA}]{\text{OXI}} CH_3\text{-}\overset{O}{\underset{}{C}}\text{-}NH\text{-}(CH_2)_4\text{-}CH_3$$

(4)

Heptamide can be formed from the heptanoic acid formed by oximation from heptanol in the rearrangement reactor:

$$CH_3(CH_2)_5CH_2OH \xrightarrow{REA} CH_3(CH_2)_5COOH \xrightarrow{REA} CH_3(CH_2)_5\overset{O}{\underset{}{C}}\text{-}NH_2$$
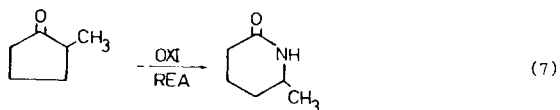
(5)
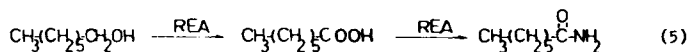
ε-Caprolactam seems to be formed from hydroxylcaproic acid previously formed from cyclohexanol in the rearrangement reactor:

(6)
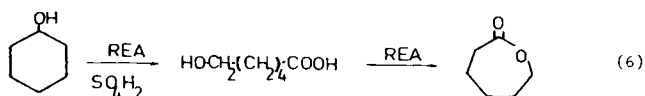
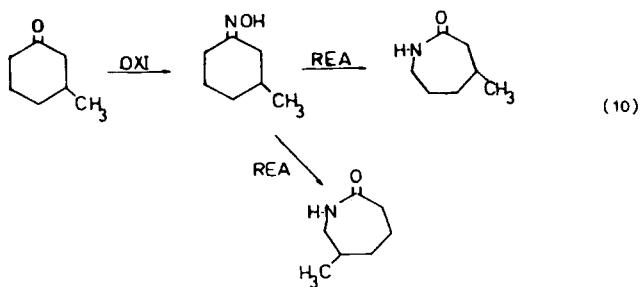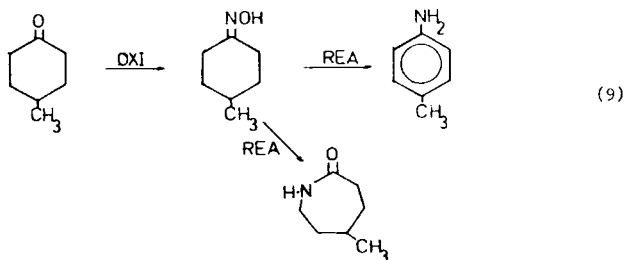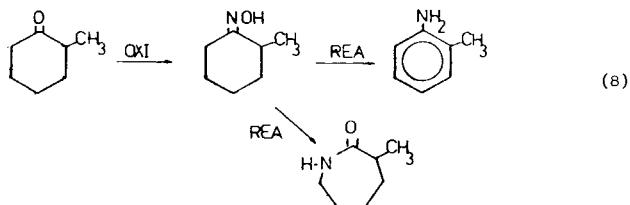ε-methylvalerolactam is very probably formed from ε-methylcyclopentanone,

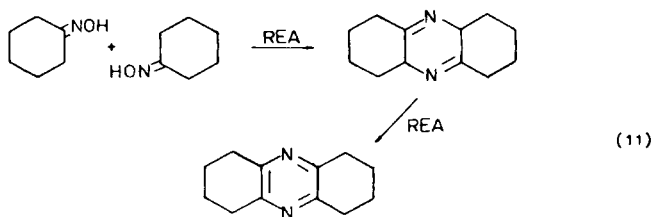an impurity of cyclohexanone, in the oximation and rearrangement steps:

$$\text{(image: reaction scheme)} \qquad (7)$$

Both the o- and p-toluidines, as well as the methylcaprolactams, must be formed from methylcyclohexanones according to the following reactions:

$$\text{(image: reaction scheme)} \qquad (8)$$

$$\text{(image: reaction scheme)} \qquad (9)$$

$$\text{(image: reaction scheme)} \qquad (10)$$

The octahydrophenazine is probably formed from cyclohexanone oxime in the rearrangement reactor as follows:

$$\text{(image: reaction scheme)} \qquad (11)$$

Finally, the adipic imide is formed as follows:

$$\text{(12)}$$
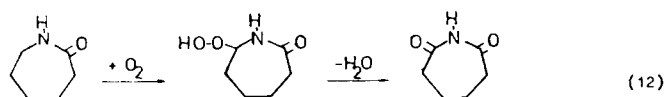
With respect to the above-mentioned hypothesis, most raw materials from which the impurities are supposedly formed have been identified in the cyclohexanone fed to the oximation step. The analyses have been carried out by gas–liquid chromatography employing two different columns:

C Column. Polypropylenglycol at 25% on Chromosorb W AW-DMCS 80/100, 8 ft long and $\frac{1}{8}$ in. in diameter, at the following operating conditions: nitrogen flow 25 cm^3/min; injection port temperature 250°C; FID temperature 250°C; oven temperature programmed at 70°C for 16 min and then at 8°C/min till 150°C.

D Column. TCEPE at 5% on Chromosorb P-DMCS 100/120, 12.5 ft long and $\frac{1}{8}$ in. in diameter, at the following operating conditions; nitrogen flow 23 cm^3/min; injection port temperature 250°C; FID temperature 250°C; oven temperature programmed at 50°C for 8 min and then at 4°C/min till 150°C.

The retention times, in seconds, of the different compounds identified are shown in Table VII. When the retention times for two different compounds cannot be distinguished, they are marked with a key. The use of the two different columns C and D allows separation of those compounds.

The raw materials from which the impurities of cyclohexanone have been formed have also been identified to be present in cyclohexane before oxidation. In Table VIII the retention times of these compounds are shown. Column C in the already mentioned conditions, except for the oven temperature, now constant and equal to 75°C, was used.

TABLE VII
Identified Compounds in Cyclohexanone

Compound	t_R, s	
	C Column	D Column
2-Heptanone	1362	1412
Methylcyclopentanone	1456*	1581
n-Pentanol	1477*	1350
2-Methylcyclohexanone	1543	1865
Cyclohexanone	1560	1824
3-Methylcyclohexanone	1588†	1966‡
4-Methylcyclohexanone	1588†	2020
n-Hexanol	1655	1652
Cyclohexanol	1720	1760
n-Heptanol	1950	1980‡

TABLE VIII
Identified Compounds in Cyclohexane

Compound	t_R, s
n-Pentane	95
n-Hexane	170
Methylcyclopentane	230
Methylcyclohexane	450

Nomenclature

AL   alkalinity
VB   volatile bases content, ppm
CO   color, APHA units
OXI   oximation step
PN   permanganate number, s
REA   rearrangement step
t_R retention time, s
UV   ultraviolet absorption

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