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ETHYLENE AMINES

Production and uses

Ethylene amines (i.e. $NH_2\,(CH_2\,CH_2\,NH)_n\,.\,H$ $n = 1,2\ ...$*) represent a range of polyamines whose market demand has increased recently. A brief survey of their uses and industrial production techniques is given.*

1 — INTRODUCTION

Ethylene amines refer to a series of polyamines in which the molecule is made up of primary, secondary or tertiary amino groups connected through ethylene groups, thus forming linear, cyclic or branched structures.

Almost all these compounds are viscous liquids with an ammonia-like smell and which readily react with various other compounds. Consequently they are used for extensive purposes, that goes from textiles to pharmaceutical chemicals. New applications are likely to be found, taking advantage of their excellent properties.

Although there is no indication of a production line of ethylene amines, at this moment, in Portugal, the petrochemical complex of Sines, will soon produce all the compounds necessary to its production: ethane, ammonia and electrolytic chlorine.

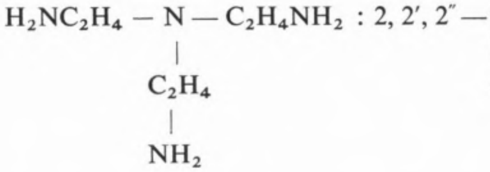
Also, with the chemical industry, today, turning in general increasingly from heavy chemicals to fine chemicals, that guarantee a wide range of market uses, the ethylene amines appear as deserving special attention.

2 — CHEMICAL STRUCTURE AND PROPERTIES

Ethylene amines with linear chemical structure can be expressed generally as $H_2N(C_2H_4NH)_n.H$ with $n = 1, 2, ...$ These include the following compounds:

Ethylene Diamine (EDA): $H_2NC_2H_4NH_2$
Diethylene Triamine (DETA): $H_2N(C_2H_4NH)_2.H$
Tricthylene Tetramine (TETA): $H_2N(C_2H_4NH)_3.H$
Tetraethylene Pentamine(TEPA): $H_2N(C_2H_4NH)_4.H$
Pentaethylene Hexamine(PEHA): $H_2N(C_2H_4NH)_5.H$

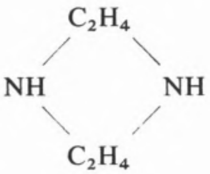
This polyamine series also includes branch-chained structures, such as:

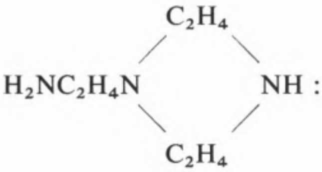


$$H_2NC_2H_4 - \underset{\underset{\underset{NH_2}{|}}{\underset{C_2H_4}{|}}}{N} - C_2H_4NH_2$$

: 2, 2′, 2″ — triamino-
triethyl
amine

and structures containing six atom rings, being 4 of carbon and 2 of nitrogen:


: Piperazine (PIP)


: Aminoethyl Piperazine

Ethylene amines readily dissolve in water and organic solvents, such as acetone, benzene, ethyl ether, and methanol, but hardly dissolve in n-heptane and other chain hydrocarbons. Physical properties of some of these compounds are listed in Table I (1).
In this work the interest is focused in the compounds with a maximum of six amino groups.

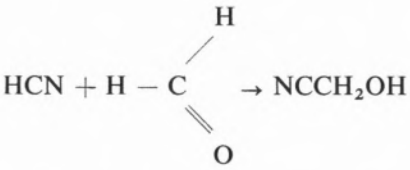
3 — REACTIONS FOR THE SYNTHESIS OF ETHYLENE AMINES

The main reactions to synthesise the ethylene amines, presented in literature, are:

3.1 — In 1914 a German firm patented (3) the production of EDA by catalytic reduction of aminoacetonitrile with hydrogen under pressure, in the presence of nickel suboxide:

$$H_2NCH_2CN + 2H_2 \xrightarrow[Ni]{} H_2NCH_2CH_2NH_2$$

Other patents were presented (4, 5) in which the aminoacetonitrile was prepared by reacting first formaldehyde and hydrogen cyanide, heating the resultant hydroxiacetonitrile with ammonia (aqueous, alcoholic or anhydrous):



$$HCN + H-C(H)=O \rightarrow NCCH_2OH$$

$$NCCH_2OH + NH_3 \rightarrow NCCH_2NH_2 + H_2O$$

The disadvantage of this process is that the aminoacetonitrile is unstable and decomposes with the formation of polymerization and condensation products.

Table I

	EDA	PIP	DETA	TETA	TEPA	PEHA
Molecular weight	60.10	86.14	103.17	146.24	189.31	232.38
Solidifying point, °C	10.8	10.60	– 39	– 35	– 30	—
Boiling point, °C at 760 mm Hg	117.2	146.0	206 7	277.5	340.0	260.0 (500 mm Hg)
Vapour pressure, mm Hg at 20 °C	10.0	0.0	0.20	< 0.01	< 0.01	< 0.01
Heat of vapourization, cal/gr	161	—	119	89	80	—
Specific gravity, 20 °C	0.8995	—	0.9542	0.9818	0.9980	1.090
Index of refraction at 20 °C	1.4565	1.446	1.4589	1.4896	1.5076	—
Viscosity, cp at 20 °C	1.60	—	7.14	26.7	96.2	60 (40 °C)
Flash point, °C (open type)	66	—	102	143	184	—

3.2 — The reaction of ethylene oxide and ethanolamine with anhydrous ammonia, in the liquid phase using Raney nickel (6) or nickel and magnesia (7) catalysts, at temperature 180-220 °C, are claimed to produce EDA.

It was reported some years ago that BASF had chosen a catalytic reaction that converts ethanolamine and ammonia into EDA, for a new plant having an output of 2400 tons/annum, and inaugurated in 1971. Water is the only by-product obtained.

3.3 — The liquid phase reaction of ethylene glycol and ammonia in the presence of hydrogen and water:

$$HOCH_2CH_2OH + 2NH_3 \xrightarrow[]{} H_2NC_2H_4NH_2 + 2OH_2$$
$$H_2, H_2O$$

Copper or nickel hydrogenation catalysts, pressures up to 500 p. s. i. g. and temperatures of 200-270 °C are claimed to be effective.

The fact that all the reactions presented so far, produce basically EDA and a very small percentage of ethylene amines of a higher molecular weight, does not make them very attractive once the market demand of the latter (see section 6) is progressing rapidly.

3.4 — EDA and other ethylene amines are claimed to be produced by the amination under pressure of the ethyleneimine; ethyleneimine was obtained, for instance, by treating monoethanolamine with concentrated sulphuric acid, and then treating the resulting acid sulphate of aminoethyl with an excess of OHNa. This process is not economical due to the number of step reactions and to the consumption of SO_4H_2 and OHNa; furthermore, the intermediate ethyleneimine is a very dangerous product due to its toxicity and to the risks of explosive polymerisation that it presents.

3.5 — The ammonolysis of 1,2-dihaloethane was the first reaction used in the synthesis of ethylene amines. Although there were some works in which 1,2-dibromoethane was used (8) the most economical process uses 1,2-dichloroethane (EDC):

$$\underset{(EDC)}{ClC_2H_4Cl} + 2NH_3 \rightarrow \underset{(EDA)}{H_2NC_2H_4NH_2} + 2HCl$$

Besides EDA the reaction produces a great number of other ethylene amines; recent works (2, 9) revealed the existence of at least 24 compounds and, even considering only a maximum of six amino groups for each molecule, it is possible, theoretically, to establish 32 different chemical structures.

4 — INDUSTRIAL PRODUCTION

Almost all the production of ethylene amines in industry is carried out through the ammonolysis of EDC. Ammonia is added into the reactor as a very concentrated aqueous solution (50-65 wt %), obtained by dissolving gaseous ammonia in water, under pressure. In these conditions the reaction with EDC is carried out in a simple phase which avoids problems of mass transfer.

Besides the reaction steps in itself, the production of ethylene amines requires the following operations:

— Liberation of the free ammonia and ethylene amines because the ammonolysis of EDC, in itself, forms amine hydrochlorides.

— When the former step is over a mixture of ethylene amines, ammonia, water and, if ONHa was used to neutralize the hydrochlorides, NaCl will be obtained.

Ammonia, that is generally present in a great excess, can be easily separated (due to its volatility) and recycled to the reactor. A more difficult problem is the separation of watter and NaCl from the ethylene amines; several techniques have been suggested using generally extraction and distillation operations.

The industrial production of ethylene amines is, thus, relatively complex; the flow-sheet presented in fig. 1 (10) is a very good example of the existing plants: The reaction is carried out in the tubular reactor *10*, which is provided with a suitable inlet line *12*. EDC comes from a suitable source such as storage tank *14* and recycle from line *16*, while an aqueous solution of ammonia comes from a storage tank *22*; both are charged to the manifold *20* by way of a line *24*.

Within reactor *10*, temperatures within the range of about 80 °C to about 140 °C and a pressure within the range of about 500 to about 1,000 p. s. i. g., are used.

The crude reaction mixture is discharged by way of a line *28* leading to a separation zone *32*, where the major portion of the ammonia and some of the water are vapourized for removal overhead by way of a line *34* leading to the aqueous ammonia storage drum *22*. If desired, fresh ammonia for the process may be conveniently added at a replacement rate to the line *34*, for example from a storage tank *36*.

The liquid component is discharged from separation zone *32* by way of a line *40* leading to a combined neutralization and separation zone, designated generally by the number *44*. The neutralization of the amine hydrochlorides is carried out with an aqueous solution of caustic soda, containing 30-60 wt % of OHNa and added through line *45*.

By maintaining the zone *44* at a temperature of about 130 °C, the water and free amines will be volatilized overhead, as formed, and can be removed by way of a line *46* for further processing. The remaining liquid component will be a slurry of sodium chloride in aqueous caustic which may be discharged from the zone *44* by way of a line *48* leading to the centrifuge *52*. Within the centrifuge *52* the slurry is resolved into a solid filtered salt and a filtrate fraction. The filtered salt fraction is preferably washed with wash water charged to the centrifuge *52*, by way of a line *54*. The washed salt is discharged from centrifuge *52*, by way of a conduit *56*, and the filtrate and the wash water are discharged by way of a line *58* leading to a separation zone *62* wherein any entrained amines removed from the zone *44* separate by phase separation.

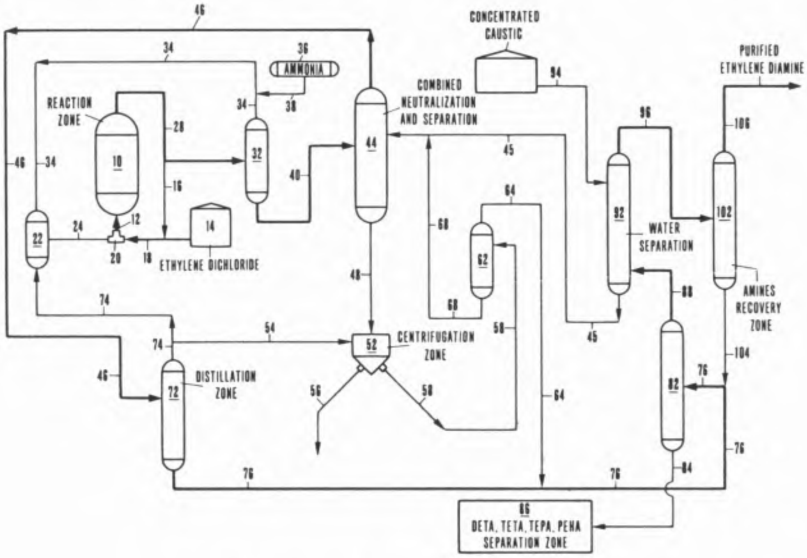


Fig. 1 — Ethylene amines production scheme

The aqueous amine fraction discharged by way of a line *46* is charged to an atmospheric pressure distillation column *72*, wherein the product is separated into an overhead fraction containing all of the ammonia, a significant amount of water and only trace quantitaties of EDA; the ammonia, after liquefaction, may be recycled to the aqueous ammonia storage tank *22*.

The bottom fraction, will contain less than about 30 wt % of water, the balance being amines, and is discharged to an amines recovery zone which may suitably comprise distillation columns *82* and *102*, and water extraction tank *92*, maintained at a temperature of about 70 °C to 100 °C, where it is counter currently contacted with a concentrated aqueous solution of caustic, charged in column *92*, by way of line *94*. This concentrated solution of caustic will desirably contain from about 60 to about 80 wt % of OHNa. As consequence of the counter current extraction step, an EDA extract fraction is formed, fairly pure, which is discharged by way of a line *96* and a caustic raffinate fraction is formed which is discharged by the line *45*. The by-products discharged through line *84* are high molecular weight ethylene amines.

The fraction *96* is charged to a vacuum distillation column *102*, wherein the extract fraction is separated into an overhead EDA fraction which contains only trace quantities of water and other amine impurities and a bottom fraction containing mainly ethylene amines, that is recycled to column *82.*

One of the major problems that an installation such as the one that has been described has to face is the way to control the relative quantities of the several ethylene amines being produced.

The molar ratio $NH_3 : EDC$ may be used to a certain extent towards this purpose as Table II (2) shows:

Table II

$NH_3 : EDC$ molar ratio (¹)	EDA	DETA	TETA	TEPA	PEHA
10:1	48.0	25.5	12.3	6.8	2.7
6:1	40.0	22.4	14.9	10.6	5.9
2:1	15.0	22.6	15.9	20.9	14.7

(¹) Temperature = 120 °C.

The snag is that the use of $NH_3 : EDC$ molar ratios smaller than 10 : 1 is seriously hindered by the fact that in those conditions the reaction rate is drastically reduced and the residence time in the reactor becomes uneconomical.

So, in order to increase the relative percentage of the ethylene amines with a higher molecular weight, recycling of EDA, DETA and TETA has been studied as Table III (11) exemplifies.

The negative numbers in the table indicate that the amount of that product recovered was less than the amount fed a srecycle, indicating overall consumption of the product. Thus, it would be possible to recycle a product that is in over-supply to extinction.

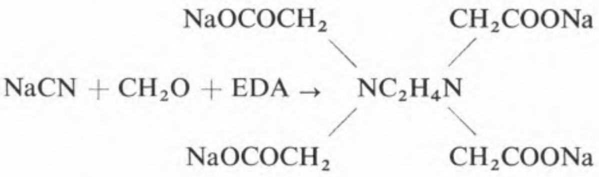
In a similar research area, there have been published recently, several works concerning the reactions of EDA with EDC and DETA with EDC.

5 — PRINCIPAL USES

5.1 — *CHELATING AGENTS*

EDA has proved to be a prolific source of chelating agents which have become also of first-rate importance in analytical chemistry.

The reaction of EDA with sodium cyanide (or chloroacetic acid) and formaldehyde in an alkaline solution provides the sodium salt of the ethylenediaminetetracetic acid:



$$NaCN + CH_2O + EDA \rightarrow \begin{array}{ccc} NaOCOCH_2 & & CH_2COONa \\ & \diagdown \quad \diagup & \\ & NC_2H_4N & \\ & \diagup \quad \diagdown & \\ NaOCOCH_2 & & CH_2COONa \end{array}$$

EDTA is the most widely used organic chelating agent.

Apart from the use in analytical chemistry, chelating agents find their major applications in the manufacture of soaps and detergents, textiles, rubber polymerization and leather processing.

Very recently the use of TETA and TEPA, mainly, has become very popular in the field of electroplating, because it eliminates the use if poisonous cyanide compounds.

5.2 — *TEXTILES*

The ethylene amines and their reactions products find many applications in the textile industry as detergents, surface and finishing agents to improve

Table III

NH_3:EDC molar ratio	15:1	15:1	15:1	15:1
NH_3 conc., wt %	65	65	65	65
Recycle amine (lbs per lb EDC):				
EDA	—	0.551	—	—
DETA	—	—	0.198	—
TETA	—	—	—	0.104
Production rate (lbs per 100 lbs EDC):				
EDA	24.1	−6.2	24.4	25.1
DETA	8.7	14.2	−3.8	7.0
TETA	5.7	12.7	9.9	0.1
TEPA and PEHA	4.9	11.0	8.4	10.2
Residue	2.8	3.7	4.6	3.7

the dye ability, dye fastness, textile strength, elongation, wrinkle resistance and water repellency of textile materials.

The main polyamine derivatives employed with textiles are prepared by reacting the amine with carboxylic acids and derivatives to form the corresponding amides and imidazolines. The amines and their reaction products are usually permanently impregnated into the textile material by the formation of an insoluble salt or resin.

A valuable class of textile resins used to impart wrinkle resistance to cotton fabrics is based on ethylene ureas (imidazoline 2). This material is produced by reacting EDA with carbon dioxide or urea.

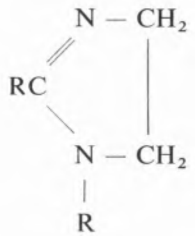
Polyamide resins are made by polycondensation of diamine and dicarboxylic acid or carboxylamine. Well known examples are Nylon 66 and Nylon 6. These resins generally have great strength and excel in wear resistance, lubricating property and oil resistance.

5.3 — *PETROCHEMICAL INDUSTRIES*

Ethylene amines and their reaction products find broad application in the petroleum industry as asphalt additives, reagents in petroleum production and refining and lubricating oil additives. They are also used in the manufacture of plastics mainly to promote fire-resistant compounds.

Wetting and emulsifying agents for asphalt are obtained by condensing carboxylic acids with ethylene amines to form amidoamines and imidazolines:

imidazolines



These agents when added to asphalt for road construction, prevent stripping off the asphalt from the aggregate in the presence of moisture.

The reaction products of TEPA and polybutenylsuccinic anhydride are claimed to be effective as smoke inhibitors for diesel fuels; treated with polyisobutenyl succinimide, TEPA is used as corrosion and icing inhibitor for gasoline.

5.4 — *RUBBER*

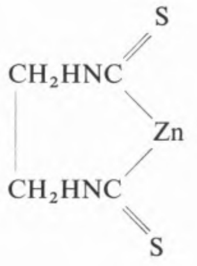
It is known that amino groups are effective in preventing aging of rubber. This naturally applies to ethylene amines. Chiefly used in this area was EDA. Bayer of Germany has the vulcanization-accelerator T. R., while ICI offers the age resister DED.

The higher members of the ethylene amines series have also proved to be useful in the rubber industry as activators, catalysts, curing agents, stabilizers, and modifiers in the polymerization and vulcanization of natural and synthetic rubber.

5.5 — *AGRICULTURAL CHEMICALS*

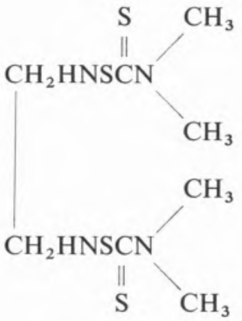
EDA is used as raw material for the pesticides Disen and Monox, which have the following chemical structures:

Disen



;

Monox



Both of them are said to be non-toxic to man and animals, and have no ill effect on crops.

5.6 — *PAPER AND CELLULOSE*

The wet strength of paper can be greatly increased by the addition of the thermoplastic resin prepared from ethylene amines, formaldehyde and urea; resins obtained from TETA or TEPA, maleate esters, and epichlorohydrin are used as floculation agents for paper and improve very much both the wet tensile strength and dry tensile strength.

5.7 — *PHARMACEUTICAL AND COSMETICAL PRODUCTS*

TETA was used to stabilize enzyme preparations; the stabilization of enzyme preparations is of the greatest importance in the production of cosmetics and detergents.

EDA and TEPA are used to produce zircornium complexes that are claimed to be effective as antiperspirants with high activity, very low irritation potential to the human skin, and exhibiting virtually no fabric damage.

A 2:5 copolymer of TEPA and epichlorohydrin was studied for hypolipidemic and hypocholesteromic actions in various animals. The results obtained with rats, rabbits and chickens proved that this copolymer was highly effective for this purpose.

6 — *MARKET EVOLUTION FORECAST*

In 1968, the demand for ethylene amines in the U. K. was estimated at 3500 tons/annum, but no manufacturing units existed in this country and the product was thus imported from the United States and Continental Europe. Later it was announced that B. P. Chemicals was going to build a 7000 tons/annum ethylene amines plant in their petrochemical complex at Baglan Bay in South Wales. The production started in 1971 but some months later was suspended due to great technological difficulties.

Although there are no numbers available, it is believed that the United States with Dow Chemicals Company and Jefferson Chemicals Company (and certainly a few others) are the biggest world producers.

It is interesting to see the evolution of the demand for ethylene amines in the Japanese market, because it is believed, it reproduces the development in the major western industrialized countries, from which no figures were obtainable.

Table IV

Annual demand in tons [1]

	1966	1971
EDA	1,380	1,900
DETA	480	1,450
TETA	180	520
TEPA	200	610
PEHA	—	70
Total	2,240	4,550

As table IV suggests, in making forecasts EDA and higer amines must be considered separately.

The use pattern for EDA is 37% for agricultural chemicals, 17% for chelating agents (EDTA), and 25% for other uses. This means that agricultural chemicals and chelating agents account for about 60% of the total consumption. Not much can be expected in this field, natural increase being just about the only hope for the future.

A brighter outlook is promised for fields where higher ethylene amines are chiefly employed e. g. polyamide resins, surface active agents, and additives for lubricating oils. In addition there is a good chance of finding new applications. Thus a growth rate of 10 to 20% may be expected, which means that higher molecular weight ethylene amines will continue to grow in demand at a faster rate than EDA, and will probably in the very near future face a shortage.

Faced with this situation, special concern must be given in working out and establishing a production system whereby the ratio of outputs of different ethylene amines can be made to conform with market requeriments.

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RESUMO

As etileno-aminas (P.e. $H_2N(CH_2CH_2)_n.H$ $n = 1,2 \ldots$*) constituem um grupo de poliaminas cuja procura no mercado tem aumentado nos últimos anos Apresenta-se uma breve resenha das suas utilizações e técnicas de produção industrial.*