SPOTLIGHT on

the production of amines in South Africa

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Trochem (Pty) Limited, which is jointly owned by Chemical Holdings Limited and Henkel Corporation of America, recently commissioned the first fatty amine plant to be built in Africa. The plant is capable of producing primary, secondary, and tertiary fatty amines with varying hydrocarbon-chain lengths. These amines are used in the mining industry for the extraction of uranium and as intermediates in the local manufacture of fertilizer anti-caking agents, bitumen emulsifiers, sanitizers, and fabric softeners. Some of the major products that will be produced in the new amine plant are shown in Table I.

TABLE I

SOME OF THE MAJOR AMINE PRODUCTS

Amine	Typical use
Tri-octylamine (Alamine® 336)	Uranium extractant
Di-hydrogenated tallow methylamine	Fabric softener intermediate
Hydrogenated tallow dimethyl-amine	Sanitizer intermediate
Fatty primary amine	Fertilizer anti-caking agent intermediate
Fatty diamines	Emulsifier intermediates

During the first year of operation of the plant, the amines produced will replace between 3 and 4 million rands' worth of imported amines. Vitally important to the South African mining industry is Alamine 336, which is widely used throughout the industry as a uranium extractant. The majority of South Africa's uranium production is obtained by the Purlex solvent-extraction process, which utilizes a solution of 3 to 5 per cent Alamine® 336 in an organic carrier as a solvent extractant. Most uranium plants that do not follow the Purlex route employ the Bufflex route, which uses a smaller solvent-extraction circuit to purify the uranium.

The mixed organic carrier in a Purlex plant normally contains 3 to 5 per cent Alamine 336 and 2 to 3 per cent isodecanol in a medium- to high-flash organic carrier. The isodecanol is added to improve the solubility of the Alamine and the Alamine–uranium complex in the organic carrier. The mechanism for the loading of uranium onto tertiary amines from sulphate media have been given by Fleming[1] as shown in equations (1) to (3).

The loaded uranium can be stripped from the tertiary amine by a number of reagents including sodium chloride, ammonium carbonate, and ammonia–ammonium sulphate. The last stripping mechanism is favoured in South Africa and proceeds as shown in equation (4).

The main raw materials used in the production of amines are fatty alcohols, fatty nitriles, hydrogen, ammonia, formaldehyde, and various catalysts.

Description of the Process

A schematic layout of the main features of amine manufacture is shown in Fig. 1. Owing to the corrosive nature of some of the raw materials and also the need for some of the finished products to be completely free of certain metal contaminants, most of the plant is constructed from 316 stainless steel. The reactor can withstand pressures of over 2900 kPa (400 lb/in^2), which are required for some of the hydrogenations. As both endothermic and exothermic reactions occur in the batch processes, heating and cooling coils have been installed in the reactor. The reactions are carried out under a gas atmosphere; the composition of the atmosphere and the catalyst used vary according to the type of amine being produced.

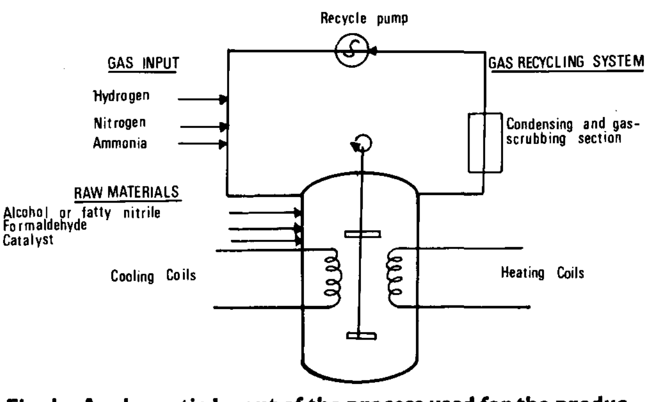

Fig. 1—A schematic layout of the process used for the production of amines

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$$2R_3N + H_2SO_4 \rightleftharpoons (R_3NH^+)_2SO_4^{2-} \quad \ldots (1)$$

$$(R_3NH^+)_2SO_4^{2-} + UO_2(SO_4)_2^{2-} \rightleftharpoons (R_3NH^+)_2\,UO_2(SO_4)_2^{2-} + SO_4^{2-} \quad \ldots (2)$$

$$2(R_3NH^+)_2SO_4^{2-} + UO_2(SO_4)_3^{4-} \rightleftharpoons (R_3NH^+)_4\,UO_2(SO_4)_3^{4-} + 2SO_4^{2-}. \quad \ldots (3)$$

$$(R_3NH^+)_4\,UO_2(SO_4)_3^{4-} + 4NH_4OH \rightleftharpoons 4R_3N + (NH_4)_2SO_4 + (NH_4)_2\,UO_2(SO_4)_2 + 4H_2O. \quad \ldots (4)$$

The batch reaction time varies between 8 and 16 hours, and the progress of the reaction is monitored by the analysis of samples taken from the reactor. Colorimetric titration of the amine is used as an analytical control during production runs, and the final product is analysed by potentiometric titration and gas chromatography. The overall reactions involved in the manufacture of the main products of the amine plant are as follows.

Primary amines

Produced from nitriles by catalytic hydrogenation.

$$RCN \xrightarrow[\text{Catalyst}]{H_2\ NH_3} RCH_2NH_2.$$

The ammonia is present to prevent the formation of secondary amines.

Secondary amines

Produced from nitriles by catalytic hydrogenation first to primary and then to secondary amines.

$$2RCN \xrightarrow[\text{Catalyst}]{H_2} 2RCH_2NH_2 \longrightarrow (RCH_2)_2NH + NH_3$$

To increase the rate and yield of the second step the recirculating gases (see Fig. 1) are passed through a water scrubber to remove the ammonia formed.

Tertiary amines

Difatty methyl amines:

Produced by the reaction of secondary amines (produced from nitrile by the reaction given above) with formaldehyde followed by catalytic hydrogenation.

$$(RCH_2)_2NH + H\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \longrightarrow (RCH_2)_2NCH_2OH$$

$$\xrightarrow[\text{Catalyst}]{H_2} (RCH_2)_2NCH_3 + H_2O.$$

Tri-octyl amine:

Produced by amination of alcohols with ammonia and a catalyst under a hydrogen atmosphere.

$$3RCH_2OH + NH_3 \xrightarrow[\text{Catalyst}]{H_2} (RCH_2)_2N\text{-}CH_2R + 3H_2O.$$

The water is condensed out of the system by the recirculating gases passing through the condenser. This facilitates the reaction and prevents the 'poisoning' of the catalyst by the water.

Diamines

Produced by reacting primary amines (produced from nitriles) with acrylonitrile to produce fatty amine propionitriles and then catalytically hydrogenating them in the presence of ammonia.

$$RNH_2 + CH_2{=}CH\text{-}C{\equiv}N \longrightarrow RNHCH_2\text{-}CH_2\text{-}C{\equiv}N$$

$$\xrightarrow[NH_3]{H_2,\ \text{Catalyst}} RNHCH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2.$$

Reference

1. FLEMING, C. A. *The chemistry of uranium recovery from leach solutions.* Johannesburg, South African Institute of Mining and Metallurgy, Vacation School, Uranium Ore Processing, Jul. 1981.

Process control

Sponsored by the South African Institute of Measurement and Control, the Instrument Society of America is bringing a short course in process control to South Africa. This will be the first in a series of courses in instrumentation and process control.

The course, entitled 'Introduction to Process Control', will be held in Johannesburg on 4th and 5th October, 1982, and on 7th and 8th October, 1982. It will be held in Durban on 11th and 12th October, 1982.

This course, which is given regularly throughout the U.S.A., covers the fundamentals of automatic control including process dynamics; emphasis is placed on practical aspects, and a highly mathematical approach is avoided. Participants are given short design projects from actual industrial processes to gain practical experience in applying concepts learnt in the course. Attendees learn how to select manipulated variables and a variety of methods for tuning control systems. Numerous process examples are given throughout the course.

The course will be of interest to engineers and other technical personnel involved in the design, operation, and troubleshooting of process control systems who have little experience with automatic control. Familiarity with algebra is recommended.

The course will be conducted by Dr R. A. Mollenkamp, Associate Professor of Chemical Engineering at the University of Missouri and President of Process Technology Corp. He is the principal investigator for Project Micro CEDS funded by the National Science Foundation to develop microcomputer systems and software to teach process control to practising engineers. Professor Mollenkamp is the author of a number of technical articles, papers, and continuing education texts.

All enquiries about the Johannesburg courses should be directed to Dr A. B. Stewart, Council for Mineral Technology, Randburg (telephone 793-3511) or Mrs Phil du Plessis, Division of Continuing Engineering Education, University of the Witwatersrand, Johannesburg (telephone 716-2538). Information on the Durban courses is available from Mr Alan Hill in Durban (telephone 52-4221).