

---

(12) UK Patent Application (19) GB (11) 2 096 133 A

---

(21) Application No **8110574**

(22) Date of filing  
**3 Apr 1981**

(43) Application published  
**13 Oct 1982**

(51) **INT CL<sup>3</sup> C07C 103/44**

(52) Domestic classification  
**C2C 20Y 271 30Y 342  
34Y 579 602 63X 726  
DE FG KY**

(56) Documents cited  
**GB 1335204**

(58) Field of search  
**C2C**

(71) Applicant  
**Croda Chemicals Limited  
Cowick Hall  
Snaith  
Goole  
North Humberside  
DN14 9AA**

(72) Inventor  
**Keith Coupland**

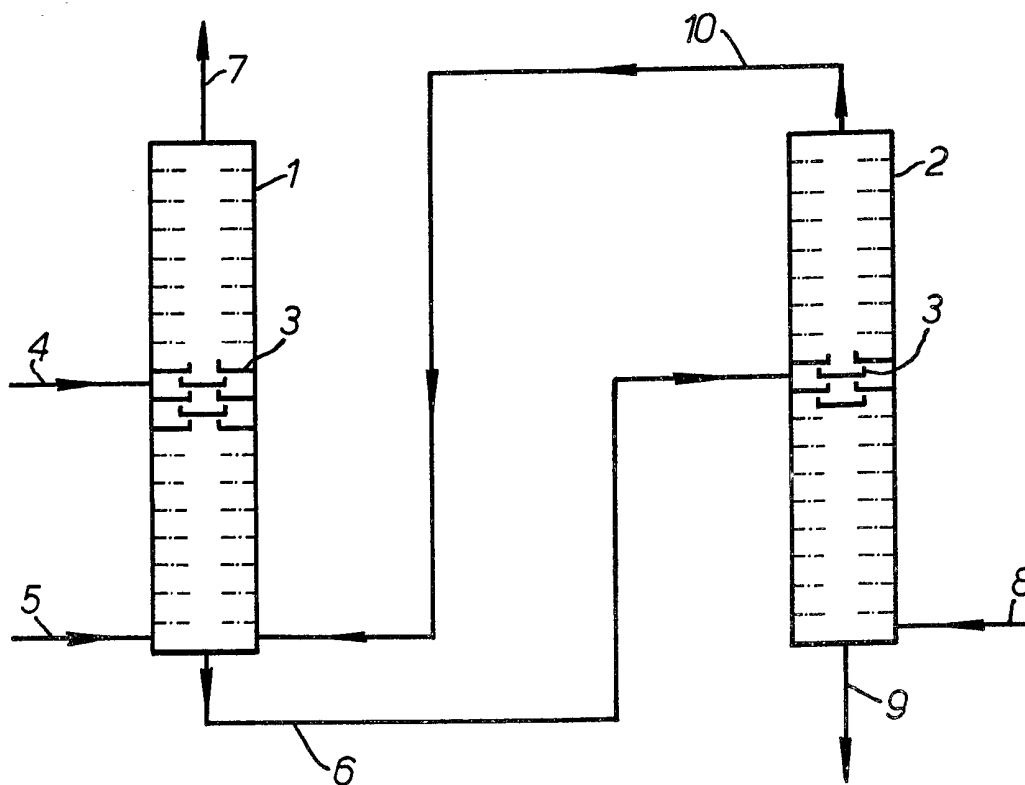
(74) Agents  
**A A Thornton and Co  
Northumberland House  
303-306 High Holborn  
London WC1V 7LE**

(54) **Production of tetraacetylene diamine**

(57) Tetraacetylene diamine (TAED) is made by a continuous process in which ethylene diamine (ED) is first reacted with acetic acid, and the diacetylene diamine produced (DAED) is then reacted with acetic anhydride. Both reactions are preferably conducted in a columnar reactor.

GB 2 096 133 A

1/1



## SPECIFICATION

**Production of tetraacetylene diamine**

5 This invention relates to the production of tetraacetylene diamine.

Tetraacetylene diamine (hereinafter abbreviated to "TAED") is useful *inter alia* as a component of cold bleach systems in washing

10 powders. There have been a number of proposals for the production of TAED. One such proposal is described in U.K. patent no. 1335204. This is a two-stage batch process in which, in the first stage, a quantity of

15 ethylene diamine (hereinafter "ED") is reacted with acetic acid to form diacetylene diamine (hereinafter "DAED"). The DAED so made is then acetylated, in the second stage of the process, using an acetylating agent other than

20 acetic acid, examples being ketene and acetic anhydride. Whilst this process is generally satisfactory, it has the disadvantage that it is a batch, rather than continuous, procedure, and where large quantities are involved there can

25 be advantages in continuous operation.

A single stage continuous process for the production of TAED from ED is described in European patent application no. 79102533.1 (publication no. 8369). In this process, ED is

30 reacted with acetic anhydride in a distillation column. Whilst this process has the advantages of being continuous, it has the disadvantage that it utilises a relatively expensive reagent, namely acetic anhydride, for the

35 whole of the acetylation. This is in contrast to the batch process of U.K. 1335204 where acetic anhydride is used only (if at all) in the second stage and the cheaper reactant, acetic acid, is used for the preliminary acetylation of

40 ED to DAED.

We have now devised a process for making TAED from ED on a continuous basis and in which the more expensive acetic anhydride is used for only the second stage of the acetylation. The first stage is effected using (the

45 cheaper) acetic acid, which advantageously may be that obtained as a by-product from the second stage acetylation, among the advantages of this method of operation, over

50 that described in European publication 8369 is that the only waste product from the process is water (although in practice, minor amounts of acetic acid may pass from the first stage acetylation which may be recovered and

55 recycled). If only acetic anhydride were utilised as the acetylating agent (as in European publication 8369), then a stoichiometric amount of acetic acid would be produced, which would have to be reconverted to acetic

60 anhydride to be of further use in the process. This is highly unsatisfactory on the grounds of energy and process costs.

According to the invention, there is provided a continuous process for making TAED

65 which comprises continuously reacting a sup-

ply of ED with a supply of acetic acid to form DAED, continuously removing the by-product water, and continuously reacting the DAED formed with a supply of acetic anhydride to form TAED.

The invention also provides apparatus for carrying out a preferred embodiment of the method of the invention, the apparatus comprising a first and a second columnar reactor,

75 means for supplying ED to a middle region of said first column, a first flash evaporator for acetic acid means for supplying acetic acid vapour from said evaporator to the lower region of said first column, means for removing

80 distillate water from the top region of said first column, means for passing DAED (produced in the first column) from the lower region thereof to the middle region of said

85 second column, a second flash evaporator for acetic anhydride, means for supplying acetic anhydride vapour from said second evaporator to the lower region of said second column, means for removing acetic acid distillate from

90 the top region of said second column, and means for removing TAED (produced in said second column) from the lower region thereof.

The process of the invention is preferably carried out in one or more columnar reactors. The reactors preferably comprise a lower reaction zone which provides contact between the reagents, and an upper portion capable of separating, by distillation, the by-products produced in the reaction. Internal construction of the reactors may be selected from conventional distillation packings, sieve trays and bubble caps, for example. A single column may be used, into which the acetylating agents are injected at different points, with the acetic anhydride being injected at a level

100 below the acetic acid. For example, ED and acetic acid would be injected near the top of the column, and acetic anhydride about half-way down, the TAED product being removed from the bottom of the column, and water

105 and acetic acid being distilled from the top.

Alternatively, and more preferably, two columns can be used, the DAED produced in the first column being continuously transferred to the second column for reaction with acetic anhydride. It is also possible to use three or more columns, the reaction mixture passing sequentially from one column to the next.

In the initial acetylation of ED with acetic acid, the two reactants may be mixed prior to entry into the reaction vessel(s). This reaction is exothermic and the amount of heat evolved may be sufficient to keep the temperature of the reaction mixture at the desired level to distil off the by-product water. To

120 provide some control, however, means for heating the vessel are preferably provided.

In the acetylation of DAED with acetic anhydride, the reaction vessel may be heated to increase the speed of the reaction and to distil

130 off the acetic acid by-product. This acetic acid

can be utilised in the initial acetylation of ED.

In the process of the invention, the amount of acetylating agent present will preferably be in excess of the stoichiometric amount, and indeed an excess can be utilised as a solvent for the acetylated products.

In order that the invention may be more fully understood, one embodiment thereof will now be described, by way of illustration only, with reference to the accompanying drawing which illustrates schematically, in simplified form, one arrangement of two columnar reactors for carrying out the method of the invention.

Referring to the drawing, two columnar reactors, 1 and 2, are arrayed as shown, each being made for example of stainless steel, and each containing, for e.g. bubble cap 33 extending throughout each column (only a few being shown in each column). At about the half-way point in column 1 is an inlet feed 4, for supplying ED to the column. At or close to the foot of the column 1 is an inlet feed 5 for supplying acetic acid vapour to the column from a flash evaporator (not shown). An exit line 6 extends from the bottom of column 1 to about the mid-point of column 2, to transfer DAED, produced in column 1, to column 2 for further reaction. From the top of column 1 an exit line 7 extends to carry away distillate (almost wholly water).

Column 2 is similar to column 1. An inlet 8 is provided, at or close to the foot of the column, for supply of acetic anhydride vapour to the column. An exit line 9 is provided from the bottom of the column to remove TAED product. From the top of the column, an exit line 10 carries acetic acid distillate to the bottom of column 1.

It will be understood that the drawing is highly simplified and various conventional components such as valves, heaters and coolers, have been omitted in the interests of clarity, such components being standard in the design of such plant.

In operation, and after start-up, ED is supplied continuously into column 1 via line 4, and acetic acid vapour is supplied continuously via line 5 (and, optionally, line 10).

DAED is formed in the column as a solution in acetic acid by reaction between the ED and the acetic acid, and the acetic acid solution of DAED collects at the foot of the column. In the upper part of the column, the water by-product from the acetylation reaction distils upwardly and exits through line 7. The approximate temperature profile of the column is 100°C at the top, about 118°C at the mid-point, and about 130°C at the foot.

The acetic acid solution of DAED is fed continuously from the foot of column 1 via line 6 to column 2. Vapourised acetic anhydride is passed into the column via line 8 and travels up the column, meeting and reacting with the DAED to form TAED. Acetic acid

vapour is distilled off from the top of the column via line 10. The approximate temperature profile is about 118°C at the top, 140°C in the middle and 170°C at the foot.

At the foot of the column is a solution consisting principally of TAED in acetic anhydride, approximately 62% acetic anhydride and 32% TAED, the balance being mostly triacetylenediamine. The solution is withdrawn via line 9 and treated to recover the TAED. Preferably, this is effected by chilling the solution whereupon TAED crystallises out. The remaining mother liquid, or part of it, may be recycled to column 2. For example, it may be recycled to the acetic anhydride vapouriser and from there injected into column 2 via line 8.

In column 1, water is distilled off via line 7. To aid in the removal of water, an entraining solvent may be used in column 1, such as diisopropyl ether or a simple ester, e.g. n-butyl acetate or ethyl acetate. The entraining solvent selectively entrains the water but not the acetic acid, ED or DAED, and the solvent travels out of the column with the water, whereafter it may be separated from the water and returned to the column.

When the ED enters column 1, it is initially converted to the diacetate salt, and DAED is formed by dehydration of this salt. A catalyst may be employed to speed up this dehydration reaction. A heterogeneous catalyst may be suspended in the lower half of column 1, for example alumina, silica-alumina or phosphoric acid supported on kieselguhr. Alternatively, a homogeneous catalyst may be dissolved in the liquor in the column, examples being sulphuric acids, zinc acetate and boric acid. Such a catalyst will pass out of the column in admixture with the DAED, and may be separated before the DAED is passed into column 2.

Instead of feed ED as such in to column 1, it is possible to feed a mixture of ED and acetic acid in which mixture some reaction may already have occurred.

#### CLAIMS:

1. A continuous process for making TAED which comprises continuously reacting a supply of acetic acid, to form DAED whilst continuously removing the by-product water, and continuously reacting the DAED formed with a supply of acetic anhydride to form TAED.

2. A process according to claim 1 which is carried out in one or more columns.

3. A process according to claim 2, wherein the process is carried out in two columns, in the first of which the ED is reacted with acetic acid to form DAED, and in the second of which the DAED from the first column is reacted with acetic anhydride to form TAED.

4. A process according to claim 3, wherein the first column is a bubble cap column into a middle region of which ED is injected,

and acetic acid vapour is supplied to the lower part of the column.

5. A process according to claim 3 or 4, wherein the ED and acetic acid are supplied to the first column to provide therein a mole ratio of ED to acetic acid of greater than 1:2.

6. A process according to claim 3, 4 or 5, wherein a water-entraining solvent is injected into the first column to assist in the distillation of water therefrom.

7. A process according to any of claims 3 to 6, wherein a catalyst is provided in the first column to promote dehydration of ethylene diamine diacetate formed therein.

8. A process according to any of claims 3 to 7, wherein a solution of DAED in acetic acid is continuously withdrawn from the bottom of the first column and injected into the second column.

9. A process according to claim 8, wherein the said solution is injected into the middle region of the second column and acetic acid vapour is injected into the lower portion of the column.

10. A process according to any of claims 3 to 9, wherein the second column is a bubble cap column.

11. A process according to any of claims 3 to 10, wherein acetic acid by-product of the reaction of DAED with acetic anhydride is recycled from the second column to augment the supply of acetic acid reacting with ED in the first column.

12. A process according to claim 11, wherein the acetic acid by-product is distilled from the top of the second column and at least part thereof is injected into the lower portion of the first column.

13. A process according to any of claims 3 to 12, wherein a hot solution of TAED in acetic anhydride is removed from the bottom of the second column.

14. A process according to claim 13, wherein the said solution is chilled and the precipitated TAED separated from the mother liquor.

15. A process according to claim 14, wherein the mother liquor or part thereof is recycled to the second column.

16. A process according to claims 9 and 15, wherein the mother liquor is re-introduced into the second column in association with the acetic acid vapour.

17. A process according to any of claims 3 to 16, wherein the ED is fed into the first column as a preformed mixture thereof with acetic acid, and wherein further acetic acid is supplied to the column.

18. A continuous process for making TAED substantially as herein described with reference to the accompanying drawing.

19. TAED made by a process as claimed in any preceding claim.

20. Apparatus for carrying out the method of claim 3, which comprises a first and a

second columnar reactor, means for supplying ED to a middle region of said first column, a first flash evaporator for acetic acid, means for supplying acetic acid vapour from said evaporator to the lower region of said first column, means for removing distillate water from the top region of said first column, means for passing DAED (produced in the first column) from the lower region thereof to the middle region of said second column, a second flash evaporator for acetic anhydride, means for supplying acetic anhydride vapour from said second evaporator to the lower region of said second column, means for removing acetic acid distillate from the top region of said second column, and means for removing TAED (produced in said second column) from the lower region thereof.

21. Apparatus according to claim 20, wherein means are provided for supplying the acetic acid distillate from the second column to the lower region of the first column.

22. Apparatus according to claim 20 or 21, which also includes means for chilling the TAED removed from the second column, means for separating the chilled TAED from accompanying mother liquors, and means for returning the said mother liquors to the second column.

23. Apparatus for carrying out the process of claim 3, substantially as herein described with reference to the accompanying drawing.