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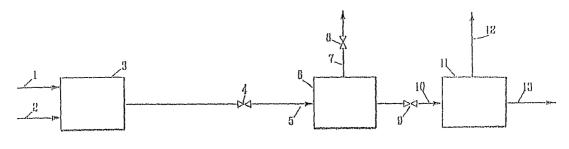


FIG. 1

(57) Abstract: The object of the present invention consists in a process for practically zeroing the ammonia and carbon dioxide losses from the low pressure section of urea plants into the environment. The process simply consists in the recovery and recycling to the urea plant of a quantity of ammonia and carbon dioxide containing vapours, which would represent plant losses. The recovery process is carried out by means of an ejector which sucks said vapours, wherein the motive fluid is a process fluid of the urea plant, without any extra consumption of energy. Said process may be applied either to new or to existing urea plants.

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# Process for the elimination of ammonia and carbon dioxide losses from the low pressure section of urea plants

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## Short description of the invention

The present invention refers to a process for the elimination of ammonia and carbon dioxide losses from urea production plants, more precisely, from their low pressure section into the environment.

Said elimination is carried out by a process essentially consisting in a compression stage by means of an ejector, wherein the motive fluid consists in a process fluid of the urea plant, without any supply of outside energy.

The elimination of ammonia and carbon dioxide losses from a urea plant into the environment represents an important reduction in environmental pollution and also leads to the reduction in urea production cost, if said elimination of ammonia and carbon dioxide losses is carried out in economic manner, as in accordance with the process object of the present invention.

# 20 Background of the invention

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It is known that all the industrial processes for the production of urea are based on the reaction:

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$$2NH_3 + CO_2 = (NH_2)_2 CO + H_2O$$
 (I)

wherein two moles of ammonia and one mole of carbon dioxide give rise to one mole of urea dissolved in one mole of water. From said solution, by water evaporation, urea is obtained as solid product in prilled or granular form.

In reaction(I) reactants  $NH_3$  and  $CO_2$  are obviously indicated as pure raw materials. Practically, however, in industrial plants, both ammonia and carbon dioxide contain impurities such as  $H_2$ ,  $CH_4$ , CO,  $O_2$ , Ar that, as a whole, are generally called "inerts", not because they are chemically thus, but because they are inert in respect to the urea formation reaction.

The "inerts" introduced in a urea plant are represented by the above-mentioned compounds, but also by the passivation air which is introduced in the urea plants in order to prevent corrosion of the materials in contact with the process fluids. In a modern urea plant the conversion of the reactants NH<sub>3</sub> and CO<sub>2</sub> into urea is almost complete even though losses from the plant to the environment are present, which, in the most modern processes, are requested to be lowered to very low values in agreement to the ever more restrictive environmental pollution regulations.

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Said reaction (I) shows the raw materials,  $NH_3$  and  $CO_2$ , and the urea which is obtained as aqueous solution, from which the solid prilled or granular product is obtained by subsequent water evaporation. The reaction does not show, however, that, in the reaction section of the plant, is not quantitative, but it represents an equilibrium depending on pressure, temperature and  $NH_3/CO_2$  and  $H_2O/CO_2$  molar ratios. As a result, in the reaction section a urea solution is obtained which contains a portion of the reactants not transformed into urea, present as free as well as different compounds: among them the ammonium carbamate which is highly corrosive in respect to the construction materials in contact with the process fluids.

An increase in reaction temperature, in order to move towards the right the reaction equilibrium, leads to higher reaction pressures, but, mainly, causes highly corrosive conditions that are not acceptable for the construction materials of plant equipment or the machinery.

According to the various processes the reaction conditions are: temperatures between 170 and 210 °C, pressures between 140 and 240 bar abs.

It is therefore necessary that for the urea plants wherein the reactants  $\mathrm{NH_3}$  and  $\mathrm{CO_2}$  are requested to be practically, totally, transformed into urea, said reactants still present

in the urea solution after the reaction section, free as well as combined, be made free from the same solution and recycled back to the reaction section.

The so called total recycle plants, both conventional and stripping-type ones, are so achieved.

The way by which the purification of the urea solution and the recycling of the reactants not transformed into urea in the reaction section are carried out, characterizes the different urea synthesis processes utilized in industrial plants today.

The different processes have in common the fact that these purification and recycle operations are carried out in one or more subsequent stage(s), at decreasing pressures, the last one being performed in a section operating at low pressure, generally between 1 and 6 bar abs.

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This low pressure section has the task of purifying the urea solution coming from the up-stream sections, by evaporating  $NH_3$  and  $CO_2$  and a certain amount of water. The obtained vapours are condensed and recycled, as aqueous solution, to the up-stream sections, at higher pressures, like the reaction section or an intermediate section, for example a purification and recycle section operating at pressures between 12 and 26 bar abs (medium pressure section).

After this low pressure section, the urea solution, having a concentration of about 70% b.w., is delivered to the final concentration section, operating under vacuum, which separates urea from reaction water (as per reaction (I)) in order to obtain molten urea and then the final solid product, prilled or granular.

At the pressure values between 1 and 6 bar abs, the recycle aqueous ammonia and carbon dioxide solution, obtained in said low pressure section, must be maintained at a relatively low temperature, between 30 and 50 °C in order to avoid losses into the environment, and to make it possible to totally recycle ammonia and carbon dioxide to the reaction section as aqueous solution.

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It is known that in all urea plants this low pressure section is not critical per sé, but it becomes such if in the upstream sections there are some anomalies and, in any case, it may become critical in warm countries, particularly during summer time, when the cooling water temperature is high. In these cases it is in fact difficult to maintain the above temperature of the aqueous solution, with consequent introduction into the environment of some quantities of ammonia and carbon dioxide.

Said losses cause at the same time an environment pollution and a higher cost of the produced urea, taking into account that the ammonia specific consumption substantially affects the urea operating cost.

- At the design stage of a new plant it may be possible to remedy to this inconvenience by remarkably over-designing the low pressure section equipment and/or by foreseeing the dilution, by water addition, of the recycled ammonia and carbon dioxide solution. The first case will result in an increase in the investment cost; in the second case, because of the lower conversion of CO<sub>2</sub> into urea in the reaction section due to the water excess, either a higher investment cost or a higher operating cost, due to the fact that more energy is consumed.
- For existing plants, the conclusions are the same: more equipment (investment cost) and/or more water circulation (higher energy consumption) in order to remedy this inconvenience.

## Disclosure of invention

It is the object of the present invention a process for the elimination of ammonia and carbon dioxide losses from urea plants, more exactly from their low pressure section, into the environment, practically without any energy consumption

In said process an ejector is utilized which sucks the ammonia and carbon dioxide vapours from the low pressure section and compresses them to a higher pressure to such a value that they are not discharged into the environment, but recycled to the urea plant itself. The motive fluid of said ejector consists in the urea solution, which expands from the reaction high pressure section to the medium pressure section operating at 12-26 bar abs, in the plants that foresee this medium pressure section. The motive fluid may also be, as an alternative, the gaseous flow of the plant "inerts", before they leave the plant to the environment. In both cases the vapours consisting in ammonia, carbon dioxide and water vapour (steam) compressed by the motive fluid till the pressure of said medium pressure section where they are easily and practically totally recovered, due to the higher pressure of said section, in respect to the pressure of the low pressure section, as an aqueous solution which is recycled to the plant high pressure reaction section.

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In urea plants without said medium pressure section, for the condensation and the recycle of the compressed ammonia and carbon dioxide containing vapours, downstream the ejector, it is necessary to add a condensation and recycle section, per sé known.

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It may consist in a medium pressure condenser, fed with water and/or with the ammonia and carbon dioxide solution from the low pressure section or in a group absorption column, fed with water and/or with the ammonia and carbon dioxide solution from the low pressure section and a cooler. In both cases the dissolution heat of the recovered ammonia and carbon dioxide, may be removed by cooling water.

The recovered ammonia and carbon dioxide solution in said medium pressure section is recycled to the high pressure reaction section.

From said medium pressure section the "inerts" are introduced to the environment with a content of  $\mathrm{NH}_3$  of few ppm in accordance with the requirements of the most severe environmental pollution regulations.

#### Brief description of the drawings

For a better comprehension of the invention, reference is made to the attached drawings that, in any case, have not to be considered limiting the scope of the invention.

Figure 1 shows the block diagram of a conventional total recycle urea process.

Figure 2 shows the block diagram of a conventional total recycle urea process to which the process object of the present invention has been applied.

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Figure 3 shows the block diagram of a stripping-type total recycle urea process, wherein the medium pressure section is present.

Figure 4 shows the block diagram of a stripping-type total recycle urea process wherein the medium pressure section is present, to which the process object of the present invention, in a first alternative, is applied.

Figure 5 shows the block diagram of a stripping-type total recycle urea process, wherein the medium pressure section is present, to which the process object of the present invention, in a second alternative, is applied.

Figure 6 shows the block diagram of a stripping-type total recycle urea process, wherein the medium pressure section is not present.

Figure 7 shows the block diagram of a stripping-type total recycle urea process, wherein the medium pressure section is not present, to which the process object of the present invention is applied together with a medium pressure section, per sé known, for recovering and recycling the ammonia and carbon dioxide vapours, downstream the ejector of the invention.

In the case of a stripping-type total recycle urea process, wherein the medium pressure section is not present (Figure 6),

it is possible, in alternative to the process shown in Figure 7, to add a purification, recovering and recycling medium pressure section, per sé known, together with the process of the present invention. The block diagram would be coincident with the one shown in Figure 4, first alternative, and Figure 5, second alternative.

In the above Figures 1-7 reference numbers have the same meaning as regards both the process stages or the equipment, except where differently indicated.

Ammonia and carbon dioxide are fed to the plant through pipes

(1) and (2) respectively, while the obtained aqueous urea solution is discharged from the plant through pipe (13). Said solution is then concentrated into molten urea, successively transformed in solid prilled or granular urea in other stages not shown in the Figures.

The plant sections operating at high pressure (140-240 bar abs), medium pressure (12-26 bar abs) and low pressure (1-6 bar abs) are indicated by the reference numbers (3) and (14), (6) and (11), respectively.

Section (3) is the high pressure reaction section, wherein ammonia and carbon dioxide react according to equilibrium reaction (I) above indicated.

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In sections (6) and (11), operating respectively at the decreasing pressures above indicated, the urea solution purification with release of reactants, ammonia and carbon dioxide, not transformed into urea, takes place as well as their recovering and recycling to the up-stream respective section towards the reaction section. For purpose of simplification, said recycles are not shown in the attached Figures.

For the stripping-type total recycle urea processes (Figures (3), (4), (5), (6) and (7)) the high pressure section (14) is indicated, wherein the stripping of the urea solution, at the outlet of the reaction section, is carried out, with release of part of the reactants, ammonia and carbon dioxide, not transformed into urea: they are recycled, either in aqueous solution or as vapours to the reaction section (3).

Section (14) is practically operating at the pressure of the reaction section, slightly lower because of the process fluid pressure drops.

The "inerts" enter the urea plant with the reactants ammonia and carbon dioxide and as passivation air, and leave the plant towards the environment from medium pressure section (6) through pipe (7) and expansion valve (8), with the exception of the process shown in Figure 6, wherein, being a stripping-

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type total recycle urea process not provided with the medium pressure section, the "inerts" leave the plant from section (14) (or from section (3)) at high pressure through the expansion valve (15) and pipe (16).

Ammonia and carbon dioxide losses from low pressure section (11) towards the environment are indicated with the reference number of pipe (12) in Figures 1, 3 and 6. The same reference number (12) indicates, on the contrary, in Figures 2, 4, 5 and 7, the pipe through which said ammonia and carbon dioxide (and steam) containing vapours are no more losses, but they are recovered in the urea plant utilizing the process object of the present invention.

The process of the present invention essentially consists in recycling the losses of ammonia and carbon dioxide from the low pressure section of a urea plant by the installation of the ejector (17) which compresses the ammonia and carbon dioxide (and steam) containing vapours which would be lost into the environment, from the low pressure section (11), operating at 1-6 bar abs, to the pressure of medium pressure section (6) operating at 12-26 bar abs. In this section, the ammonia and carbon dioxide (and steam) containing vapours are practically fully condensed and recycled to the high pressure reaction section as aqueous solution.

The motive fluid of said ejector (17) is a plant process fluid which expands from high pressure to the medium pressure.

Said fluid can therefore be the urea solution exiting the high pressure section (3), in case of a conventional total recycle process, as indicated in Figure 2.

In case of stripping-type total recycle urea process, provided with a medium pressure section (6) (Figure 3), there are two alternatives for the choice of the ejector motive fluid. A first alternative (Figure 4) consists in the utilization of all or a portion of the urea solution which expands through the expansion valve (4) from the high pressure section (14) to the pressure of the medium pressure (6). In the ejector (17) ammonia, carbon dioxide and steam containing vapours are sucked through pipe (12) and compressed to the pressure of the medium pressure (6), wherein ammonia and carbon dioxide reactants are condensed and recycled to the reaction section (3) as aqueous solution.

In a second alternative, in case of a stripping-type total recycle process, provided with the medium pressure section (6), the present invention foresees the use of the "inerts" as motive fluid for the ejector (17). Said "inerts" leave the high pressure purification and recycle section (14) through the expansion valve (15) and, through pipe (16), they enter

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the ejector (17), which sucks the ammonia, carbon dioxide and steam containing vapours through pipe (12), and compresses them to the pressure of the medium pressure (6) wherein they are almost fully recovered and recycled to the reaction section (3) as agueous solution.

In the case of a stripping-type total recycle process (Figure 6), not provided with a medium pressure section, the process of the invention may still be advantageously used with the ejector (17) (Figure 7) which sucks the ammonia, carbon dioxide and steam containing vapours through the pipe (12) and compresses them to a pressure of the same order of that one of the medium pressure section of the other above mentioned processes. At this pressure ammonia and carbon dioxide are easily, and almost fully, condensed in section 18 and recycled to the reaction section (3). The motive fluid of said ejector (17) is represented by the "inerts" gaseous fluid which expands from the high pressure to the above-considered pressure.

The condensation of the ammonia, carbon dioxide and steam containing vapours from the low pressure section takes place in section (18), essentially consisting, for example, in a condenser or in a condensation column with cooler, both fed with the ammonia and carbon dioxide solution from the low

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pressure section and/or water through pipe (19) and an appropriate pump for the recycle. The dissolution heat of ammonia and carbon dioxide may be removed by cooling water.

The "inerts" so cleaned flow to the environment through pipe (7) and expansion valve (8).

As an alternative, a medium pressure section may be introduced, complete of purification, condensation and recycle sections, in a stripping-type total recycle process, not provided with it, so achieving the process above described in Figures 4 and 5.

Figures 1 to 6 show also the expansion valve (4) and pipe (5) between the high pressure section (14) and medium pressure section (6), the expansion valve (9) and pipe (10) between the medium pressure section (6) and low pressure section (11).

15 In Figure 7, valve 4 and pipe 10 connect the high pressure section 14 with the low pressure section 11.

As highlighted by the above description, the elimination of ammonia and carbon dioxide losses from the low pressure section of a urea plant is carried out, according to the process of the present invention, without any increase of energy consumptions of said plant, but simply using the pressure difference of certain typical fluids present in the considered urea process.

The process of the present invention can be used either for new or for existing urea plants.

Examples of two embodiments of the present invention are indicated in the following; they refer to the application of the process of the invention to two different urea plants based on the stripping-type total recycle process provided with the medium pressure section. In the two examples, as motive fluid, a different process fluid was used, as described in the above mentioned two alternatives.

Said examples have the aim to better illustrate the invention, without however limiting it.

#### Example 1

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In a urea plant having the capacity of 2200 T/D, located in a warm climate country, a continuous loss of ammonia and carbon dioxide containing vapours, from the low pressure section of the plant into the environment, was present. This loss was rather limited during the cold months, but during the warm months the ammonia loss was quantified as 750 Kg/h. In order to reduce this loss, which represented at the same time an economic loss and a serious pollution problem, one or more of the following remedies should have been taken: to remarkably reduce the plant capacity; to boost the low pressure section by adding some heat exchangers, with a considerable investment

cost; to dilute the ammonia and carbon dioxide aqueous solution, obtained in the low pressure section, with a high quantity of water, with consequent energy consumption increases and difficulties also in maintaining the plant capacity.

The process of the invention was applied to this plant by installing an ejector wherein the motive fluid was a portion of the urea solution (200  $m^3/h$ ) expanding from high pressure section (14) (159 bar abs) to medium pressure section (6) (18,5 bar abs).

The use of the ejector (17) according to the invention allowed, with a small investment cost and without any extra energy consumption, to eliminate the reactant loss.

The pay-back time of this investment was about 5 months.

#### 15 Example 2

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In an urea plant having the capacity of 1800 T/D, located in a warm climate country, an ammonia and carbon dioxide containing vapour loss from the low pressure section to the environment, was ascertained.

As an annual average the loss was estimated to be about 600 Kg/h of ammonia. The applicable remedies, all uneconomic, were those mentioned above in Example 1.

The process of the invention was applied to this plant by installing an ejector (17) wherein the motive fluid consisted in the "inerts" expanding from the high pressure section (14) (155 bar abs) to the medium pressure section (6) (19 bar abs). The ammonia loss was practically set to zero with a small investment cost and without any extra energy consumption.

The pay-back time of this investment was about 4 months.

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## Claims

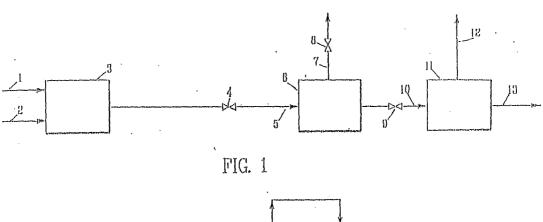
- 1. Process for zeroing the ammonia and carbon dioxide losses from the low pressure section of a plant for the production of urea from ammonia and carbon dioxide, said plant essentially consisting in a reaction section 5 operating at the temperature of 170-210 °C and pressure of 140-240 bar abs and in one or more subsequent section(s) for operating at decreasing pressures, each purification, condensation and recycle of the reactants not transformed into urea, one of which, the low pressure 10 section, operating at 1-6 bar abs, characterized by the fact that the ammonia and carbon dioxide containing vapours, which are the losses into the environment from the low pressure section are sucked by an ejector and compressed to the pressure of a section at a pressure 15 intermediate between those of the high and low pressure sections of the urea plant, condensed and then recycled to the reaction section, "the motive fluid in said ejector being a process fluid of the urea plant itself.
- 2. Process according to claim 1, characterized by the fact that the intermediate section is the medium pressure section existing in the urea plant.

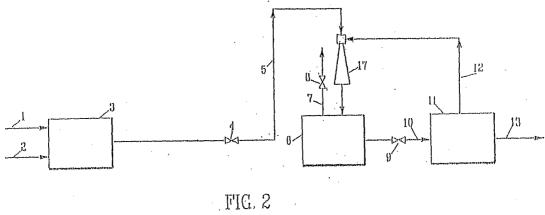
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- 3. Process according to claim 1, characterized by the fact that the intermediate section is an ammonia and carbon dioxide containing vapours condensation and recycle thereof medium pressure section added to the urea plant downstream the ejector of the invention.
- 4. Process according to claim 3, characterized by the fact that the condensation and recycle intermediate section added to the urea plant is composed by a condenser and a pump.
- 5. Process according to claim 3, characterized by the fact that the intermediate section of condensation and recycle added to the urea plant, is composed by an absorption column, a heat exchanger and a pump.
- 6. Process according to claim 2, characterized by the fact that the motive fluid of the ejector consists in the urea solution expanding from high to medium pressure section of the urea plant.
  - 7. Process according to claim 2, characterized by the fact that the motive fluid of the ejector consists of a portion of the urea solution expanding from the high to the medium pressure section of the urea plant.

8. Process according to claim 2, characterized by the fact that the motive fluid of the ejector consists in the

- "inerts" expanding from high to medium pressure section of the urea plant.
- 9. Process according to claim from 3 to 5, characterized by the fact that the motive fluid of the ejector consists in the "inerts" expanding from the pressure of the high pressure section to the pressure of the medium pressure added section.

10. Use of the process of the invention according to claims from 1 to 9, either for new or for existing urea plants.







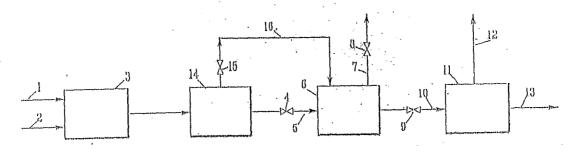
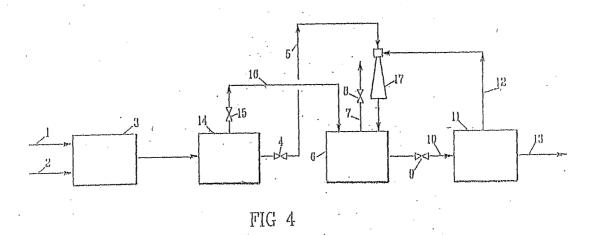
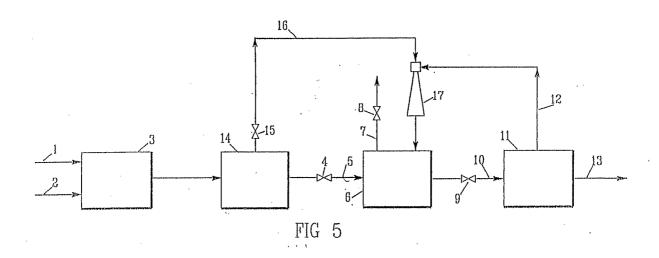
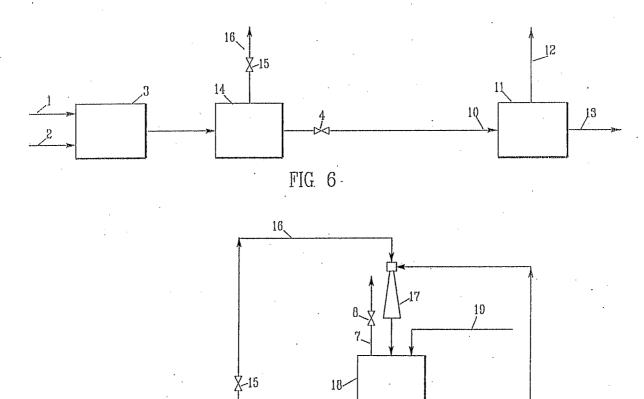
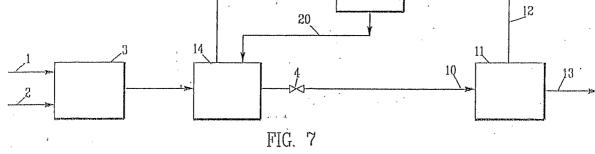


FIG. 3









# INTERNATIONAL SEARCH REPORT

International application No PCT/IT2007/000099

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C273/04 C07C273/16								
According to International Patent Classification (IPC) or to both national classification and IPC								
B. FIELDS SEARCHED								
Minimum documentation searched (classification system followed by classification symbols)								
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched								
Electronic data base consulted during the international search (name of data base and, where practical, search terms used)								
EPO-Internal, WPI Data								
C. DOCUMENTS CONSIDERED TO BE RELEVANT								
Category*	Citation of document, with indication, where appropriate, of the rele	evant passages	Relevant to claim No.					
X	WO 02/46145 A (DSM NV [NL]; MEESSEN JOZEF HUBERT [NL]; JONCKERS KEES [NL]) 13 June 2002 (2002-06-13) claims 1-6 page 5, line 23 - line 25 page 5, line 31 - page 6, line 7 page 6, line 12 - line 29 page 3, line 17 - line 19 page 3, line 27 - line 31 US 3 357 901 A (EIJI OTSUKA ET AL) 12 December 1967 (1967-12-12) column 2, line 16 - line 35 column 2, line 44 - line 48 column 3, line 65 - column 4, line 29		1-10					
Furti	ner documents are listed in the continuation of Box C.	X See patent family annex.						
* Special categories of cited documents:  *A* document defining the general state of the art which is not considered to be of particular relevance  *E* earlier document but published on or after the international filing date  *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  *O* document published prior to the international filing date but later than the priority date claimed  *P* document published prior to the international filing date but later than the priority date claimed  *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention cannot be considered novel or cannot be considered to involve an inventive step when the document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  **E* document member of the same patent family								
Date of the actual completion of the international search  Date of mailing of the international search report								
11 October 2007		18/10/2007						
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European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Fitz, Wolfgang						

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Information on patent family members

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