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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C07D 251/60, 251/62, B01D 39/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 95/25098</b> <b>(43) International Publication Date:</b> 21 September 1995 (21.09.95)
<b>(21) International Application Number:</b> PCT/NL95/00086 <b>(22) International Filing Date:</b> 7 March 1995 (07.03.95) <b>(30) Priority Data:</b> 9400281 15 March 1994 (15.03.94) BE <b>(71) Applicant (for all designated States except US):</b> DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VAN WIJCK, Julius, Gerardus, Theodorus [NL/NL]; Uitbelderstraat 3, NL-6211 SL Maastricht (NL). VAN DE MOESDIJK, Cornelis, Gerardus, Maria [NL/NL]; Op 't Veldje 33, NL-6176 BL Beek (NL). THOELEN, Johan, Jozef, Ghislain [BE/BE]; St. Servaasstraat 22, B-3770 Riemst (BE). <b>(74) Agent:</b> VAN BOKHOVEN, Petrus, Hubertus, Maria; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).		<b>(81) Designated States:</b> AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, JP, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> METHOD FOR THE SEPARATION OF IMPURITIES FROM A HOT SYNTHESIS GAS MIXTURE IN THE PREPARATION OF MELAMINE  <b>(57) Abstract</b>  The invention relates to an improved method for the separation by means of filters of impurities from a hot synthesis gas mixture obtained in the preparation of melamine from urea, involving filters made of sintered, essentially pure chromium, molybdenum, tungsten, or mixtures of these elements.		

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5        METHOD FOR THE SEPARATION OF IMPURITIES FROM A HOT  
      SYNTHESIS GAS MIXTURE IN THE PREPARATION OF MELAMINE

BACKGROUND OF THE INVENTION

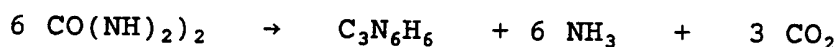
10        1. Field of the invention

      The invention relates to an improved method for  
the separation by means of filters of impurities from a  
hot synthesis gas mixture obtained in the preparation of  
melamine from urea, wherein the improvement is the filters  
comprising at least one element selected from the group  
15 consisting of chromium, molybdenum, and tungsten.

2. Description of the related art

      Hot synthesis gas mixtures containing nitrogen-  
based or carbon-based gas, in general, or ammonia or  
carbon dioxide gas, in particular, or mixtures thereof,  
20 are obtained in the preparation of melamine from urea, in  
which the starting material urea is converted into a hot  
gas mixture containing melamine, ammonia, and carbon  
dioxide by the application of heat and, optionally,  
elevated pressure according to the reaction equation:

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      As the above reaction is generally carried out  
in the presence of a catalyst, the resulting hot synthesis  
30 gas mixture will typically contain impurities such as  
catalyst particles and can also contain other solid  
byproducts such as melem and/or melam. These impurities  
are known to have an adverse effect on the quality of the  
melamine produced.

35        Known catalysts suitable for use in the above  
reaction, include among others aluminium oxide, silica-  
alumina, silicon oxide, titanium oxide, zirconium oxide,  
boron phosphate, or a mixture of two or more of these  
catalysts. The term catalyst as it is used herein is

defined as any material promoting the conversion of the starting material urea into the final product melamine under the reaction conditions applied.

The hot synthesis gas mixture containing  
5 melamine together with ammonia and carbon dioxide gas is formed from the starting material urea at a temperature generally higher than about 325°C and, in general, not exceeding about 500°C. In particular, temperatures between about 370 and about 450°C are preferred. The pressure  
10 applied during the synthesis of the hot gas mixture in the presence of a catalyst is between about 1 and about 30 bar, preferably between about 1 and about 8 bar.

According to conventional methods of separation, the hot synthesis gas mixture containing melamine,  
15 ammonia, and carbon dioxide gas is cooled, and a sublimate of the final product melamine is formed, so that it can be separated from the other gases as a solid. A drawback of this method of separation is that solid catalyst particles and other solid impurities, such as melam and melem, are  
20 also separated from the remaining gases along with the melamine sublimate, contaminating the purity of the final product melamine. The solid impurities mentioned above that are separated from the cooled synthesis gas mixture must then be filtered from the desired final product  
25 melamine. One known method of separation requires dissolving the formed melamine sublimate in water at a temperature between about 80°C and about 100°C. The solid impurities which do not dissolve in the water at that temperature are then removed by filtration and an  
30 essentially pure final product melamine is obtained by evaporation of the water solvent. A drawback of this method of separation, however, is the number of additional process steps (i.e., cooling the hot synthesis gas mixture, forming the sublimate, separation of the solids  
35 from the gases, dissolving the sublimate in solvent, filtering the dissolved sublimate from the undissolved solid impurities, and evaporation of the solvent) that are

needed to obtain the essentially pure final product melamine. A second and preferred method of separation therefore, is direct filtration of the hot synthesis gas mixture as the mixture exits reactor. Hot filtration of the synthesis gas mixture saves the time and expense of performing the additional process steps outlined above, which are necessary to obtain an essentially pure melamine final product from a synthesis gas mixture that is allowed to cool before filtration.

One such method of separation of the synthesis gas mixture, by hot filtration through ceramic filters at the reactor outlet, is disclosed on page 11 of NL-A-6412578. Each ceramic filter generally comprises a group of ceramic tubes, which are commonly known as filter candles. Two important aspects of such filter candles for use as filters in the separation methods disclosed above are the individual strength and porosity of the filter candle. The porosity of the filter candle should be between about 20% and about 70%. However, a drawback of utilizing ceramic filter candles is that when these ceramic filter candles come into contact with hot synthesis gas mixtures, the filter-candle strength decreases rapidly and the filter-candles are increasingly susceptible to breakage, for example, due to the temperature surges that occur with the periodical changes in the operation of a synthesis reactor. As a consequence, ceramic filter candles are used only to a very limited extent for separation methods utilizing hot filtration, because the ceramic filter candles have to be replaced after only a few days of use.

Sintered materials, such as for example AISI 304L, AISI 316L, Hastelloy X and Inconel 600, are also materials known for their use as filters in separation methods for synthesis gas mixtures. However, a filter made of a sintered material as described above, when brought into contact with ammonia and carbon dioxide gases, such as those produced in the preparation of melamine from

urea, also decreases in strength over a short time owing to the formation of nitrides and/or carbonitrides. As a result of which, these sintered materials are used only to a very limited extent as filters in separation methods for synthesis gas mixtures containing ammonia and/or carbon dioxide gases, because these filters have to be replaced frequently.

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#### SUMMARY OF THE INVENTION

It is an object of the present invention to provide a method for the separation of impurities from hot synthesis gas mixtures, in which filters are used that do not decrease rapidly in strength with temperature surges or due to the formation of nitrides and/or carbonitrides in the presence of ammonia (nitrogen-based) or carbon dioxide (carbon-based) gases.

Although much of the disclosure of the present invention is written in terms of using new filter materials to provide a method for improving the separation of impurities from hot synthesis gas mixtures, for example, improving the known separation by filter of impurities obtained in the preparation of melamine from urea, it is a further object of the present invention to provide a filter device that does not decrease rapidly in strength with temperature surges or due to the formation of nitrides and/or carbonitrides.

These objects are accomplished by the use of filters made of sintered, essentially pure chromium, molybdenum, tungsten, or mixtures of at least two of these elements.

#### DETAILED DESCRIPTION OF THE INVENTION

In several embodiments of the present invention, mixtures of chromium and molybdenum, chromium and tungsten, molybdenum and tungsten, or a mixture of all three elements can be used, if desired as the filter materials.

In a preferred embodiment of the present invention, sintered essentially pure chromium is used. The chromium content of the filter of the present invention, referring to the purity level of the chromium, is in general, at least about 95 wt.%, preferably at least about 99 wt.%, and by special preference at least about 99.8 wt.%. Preferably, use is made of the filters of the present invention in the form of filter candles. These filter candles have, in general, a length of about 0.5 m - 2 m and a diameter of about 4 cm - 10 cm.

The use of essentially pure chromium in the filters of the present invention is advantageous because the decrease in strength of the filters due to the formation of nitrides and carbonitrides is much slower with chromium than with the many other known filters which utilize metals such as AISI 304L, AISI 316L, Hastelloy X, and Inconel 600. It has been determined that the filters of the present invention can be used for at least a few months, up to a few years, without their strength decreasing to such an extent that the filters break and have to be replaced.

The decreasing strength of filters, which are used in hot filtration methods to separate synthesis gas mixtures containing ammonia and carbon dioxide gas, is primarily a result of the mechanisms of nitriding and/or carbonitriding. Nitriding is caused by, among other things, the presence of ammonia  $\text{NH}_3$  gas and occurs in particular at temperatures above  $250^\circ\text{C}$ . Carbonitriding is caused by, among other things, the presence of carbon dioxide  $\text{CO}_2$  gas in addition to  $\text{NH}_3$  gas.

It has been discovered that the filter materials of the present invention, particularly chromium, are remarkably less susceptible to attack by, for example,  $\text{NH}_3$  and  $\text{CO}_2$  gas at temperatures above  $250^\circ\text{C}$ , than the heretofore known materials utilized in similar filters. As there are other parts of equipment, in general, that can potentially come into contact with  $\text{NH}_3$  and  $\text{CO}_2$  gas at

temperatures above 250°C, beneficial use can also be made of the material of the present invention, particularly essentially pure chromium, in order to protect these various other equipment parts. . Examples, besides  
5 reactors for the preparation of melamine, include, without limitation, reactors for the preparation of acrylonitrile, urea, or ammonia. Valves, flanges, reducers, and bends in process lines are some examples, without limitation, of items that are particularly suited for replacement of  
10 steel with materials of the present invention, in particular essentially pure chromium.

The improved method of separation according to the present invention is illustrated by the following non-restrictive examples.

15

#### Example I

A side-stream from a melamine reactor was directed to a pilot reactor where filters containing filter candles, corresponding to Table 1, with a length of  
20 1 m and a diameter of 6 cm, were tested at a temperature of 390°C and a pressure of 7 bar. Six tests were conducted with each filter containing six filter candles.

The composition of the melamine gas mixture was as follows: 86 vol.% NH<sub>3</sub>, 8 vol.% CO<sub>2</sub>, 3 vol.% N<sub>2</sub>, 3 vol.%  
25 melamine and low concentrations of isocyanic acid and cyanide. The pressure drop across the filter housing was used to determine when one or more filter candles had broken. After a pressure drop across the filter housing was observed, the filter housing was immediately opened  
30 and the filter was checked to determine how many filter candles had broken. The results of these tests are presented in Table 1.



Table 1

Test No.	Candle type (SiC = silicium carbide)	Number of broken candles	Days of operation before the filter was opened
1	SiC candle	2	2
2	SiC candle	6	8
3	SiC candle	1	4
4	SiC candle	3	6
5	Chromium candle	0	14
6	Chromium candle	0	14

Example II

Test specimens with the following dimensions were cut from filter candles of various types corresponding to the materials listed in Table 2: length: 50 mm; width: 10 mm, and thickness: 6 mm. The weight of each of the specimens was about 10 grams. The specimens were suspended in an aggressive atmosphere in an exposure furnace at a temperature of 390°C and 450°C and kept there for more than a week. The composition of the aggressive gas atmosphere was as follows: 86 vol.% NH<sub>3</sub>, 8 vol.% CO<sub>2</sub>, 3 vol.% melamine, 3 vol.% N<sub>2</sub> and trace amounts of isocyanic acid and cyanamide. Nitriding of the specimens resulted in a mass increase of the specimens, and was measured as the weight increase of the test specimens in micrograms per square centimeter per hour. The test specimens were cut from filter candles made of sintered chromium, solid chromium and stainless steel (AISI 304L). The results are presented in Table 2.

Table 2: Results of the exposure experiments

	Material	Exposure temperature, in °C	Weight increase, in $\mu\text{g}/\text{cm}^2/\text{hour}$
5	Sintered chromium	450	4.2
	Sintered chromium	390	0.25
	Sintered chromium	390	0.43
	Sintered chromium	390	0.12
10	Solid chromium	450	0.046
	Solid chromium	450	0.097
	Stainless steel	390	3.0
	Stainless steel	450	15

C L A I M S

1. An improved method for the separation by means of  
filters of impurities from a hot synthesis gas  
mixture obtained in the preparation of melamine from  
urea, wherein the improvement is the filters  
comprising at least one element selected from the  
group consisting of sintered, essentially pure  
chromium, molybdenum, and tungsten.
2. The improved method according to claim 1,  
wherein the filters consist of sintered, essentially  
pure chromium.
3. The improved method according to claim 2, wherein the  
chromium content is at least about 99 wt.%.
4. The improved method according to claim 2, wherein the  
chromium content is at least about 99.8 wt.%.
5. The improved method according to claim 1, wherein the  
filters comprise filter candles.
6. Method for the separation of impurities from a hot  
synthesis gas mixture in the preparation of melamine  
as substantially described in the description and the  
examples.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 95/00086

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C07D251/60 C07D251/62 B01D39/20

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)

IPC 6 C07D B01D

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)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BE,A,654 779 (AMERICAN CYANAMID COMPANY) 23 April 1965 & NL,A,6 412 587 cited in the application ---	1-6
A	US,A,4 591 644 (STAMICARBON B.V.) 27 May 1986 ---	1-6
A	GB,A,1 153 107 (TOYO KOATSU INDUSTRIES, INCORPORATED) 21 May 1969 -----	1-6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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11 April 1995

Date of mailing of the international search report

26. 04. 95

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International Application No

PCT/NL 95/00086

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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