



(11) **EP 2 030 700 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
04.03.2009 Bulletin 2009/10

(51) Int Cl.:
B08B 7/00 (2006.01) **B08B 3/08** (2006.01)
D06F 43/00 (2006.01) **D06L 1/02** (2006.01)

(21) Application number: **07017001.4**

(22) Date of filing: **30.08.2007**

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE
SI SK TR**
Designated Extension States:
AL BA HR MK RS

- **Karthäuser, Joachim**
19251 Sollentuna (SE)
- **Lindqvist, Kenneth Stig**
128 38 Skarpnäck (SE)
- **Marcusson, Anders**
181 34 Lidingö (SE)

(71) Applicant: **Linde Aktiengesellschaft**
80807 München (DE)

(74) Representative: **Gellner, Bernd et al**
Patente und Marken
Dr.-Carl-von-Linde-Strasse 6-14
82049 Pullach (DE)

(72) Inventors:
• **Ahlbom, Esko**
75654 Uppsala (SE)

(54) **Method for cleaning**

(57) The present invention relates to a process for cleaning goods comprising the following steps: a) placing the goods to be cleaned in a pressure-resistant cleaning vessel, b) introducing a cleaning solvent into the cleaning vessel, c) removing the residues carrying solvent from the container, d) separating the residues from the solvent, characterised in that, step b and step c are carried out at least twice, therefore leading at least to a first and second cleaning bath, using a halogenated and/or hydrocarbons containing solvent in one cleaning bath, and

using a pressurised fluid containing solvent in another cleaning bath. Furthermore, the present invention relates to a process of the kind mentioned above, characterised in that, step b and step c are carried out at least once, therefore leading at least to one cleaning bath, using a halogenated and/or hydrocarbons containing solvent in combination with a pressurised fluid containing solvent in at least one cleaning bath.

EP 2 030 700 A1

Description

[0001] The present invention relates to a process for cleaning goods comprising the following steps: a) placing the goods to be cleaned in a pressure-resistant cleaning vessel, b) introducing a cleaning solvent into the cleaning vessel, c) removing the residues carrying solvent from the cleaning vessel, d) separating the residues from the solvent.

[0002] In this field the usage of halogenated, e.g. chlorinated, solvents and hydrocarbon containing solvents is very common.

[0003] In recent years, the usage of a pressurised fluid, for example liquid or supercritical carbon dioxide has become known. Furthermore, the usage of organic solvents such as esters or hydrocarbon containing oxygen functionalities has been described in combination with subsequent CO₂ cleaning.

[0004] The following documents give an impression of the state of the art of the last two cleaning methods mentioned: US 4,012,194, US 5,980,648, US 5,759,209 and EP 0 587 169 B1 for CO₂ cleaning and WO 02/086222 A1, WO 02/086223 A1, WO 01/29305 A1 and WO 01/29306 A1 for the usage of organic solvents.

[0005] Whilst halogenated, e.g. chlorinated, solvents as well as hydrocarbons are very effective solvents, their use is to be seen in relation to concerns about their toxicity and flammability. The recovery of these solvents is therefore exceedingly important, but also expensive as well as time and energy consuming.

[0006] Therefore, it is an object of the present invention to provide an improved cleaning process.

[0007] In accordance with the present invention this object is solved by a process for cleaning goods comprising the following steps: a) placing the goods to be cleaned in a pressure-resistant cleaning vessel, b) introducing a cleaning solvent into the cleaning vessel, c) removing the residues carrying solvent from the cleaning vessel, d) separating the residues from the solvent, characterised in that, step b and step c are carried out at least twice, therefore leading at least to a first and second cleaning bath, using a halogenated and/or hydrocarbons containing solvent in one cleaning bath, and using a pressurised fluid containing solvent in another cleaning bath.

[0008] The first and the second cleaning may be carried out in the same cleaning vessel as well as in different cleaning vessels. Thus, it is also possible to place the goods in a first cleaning vessel and to clean the goods with a first cleaning solvent and then transfer the goods to a second cleaning vessel wherein the goods are cleaned with a second cleaning solvent. One of the first or the second cleaning solvent comprises a pressurised fluid whereas the other cleaning solvent comprises a halogenated and/or hydrocarbons containing solvent.

[0009] The object of the present invention is also solved by a process of the kind mentioned above, characterised in that, step b and step c are carried out at least once, therefore leading at least to one cleaning bath, us-

ing a halogenated and/or hydrocarbons containing solvent in combination with a pressurised fluid containing solvent in at least one cleaning bath.

[0010] The inventive processes both combine in a very advantageous way the techniques of cleaning with halogenated, especially chlorinated, solvents and/or hydrocarbon solvents with pressurised fluid cleaning techniques. For example, less impact by reduced need of solvents of the first mentioned type and less losses of such solvents and less energy consumption of the processes are to be mentioned as great advantages.

[0011] It has to be stressed that there is a very broad variety of combining different cleaning bathes containing solvents from a wide range of combinations or single substances to solve the object of the present invention.

[0012] Chlorinated solvents, especially perchloroethylene (PER) are given as examples for the halogenated solvents that can be used in the present invention. Iso-paraffins (german abbreviation: KWL) are an example for the hydrocarbon containing solvents that can be used in the present invention.

[0013] The present invention achieves a significant reduction in the amount of halogenated, especially chlorinated, solvents and/or hydrocarbon solvents needed to achieve an equal or even improved residues (impurities, dirt) removal effect compared to the cleaning processes known. This reduction is very favorable in terms of achieving a process with less environmental impact.

[0014] According to step c of the present invention an efficient removal of solvent from the goods to be cleaned is achieved and very favorable for the inventive process.

[0015] In order to achieve a good solvent recovery, it is very favorable to use a pressurised fluid containing solvent, because of the possibility to recover the pressurised fluid by distillation. This recovery method enhances the ability of the system to work with much more than one cleaning bath.

[0016] Furthermore, the pressurised fluid can be used to take out the halogenated and/or hydrocarbons containing solvents from the goods, if the order of the cleaning bathes is such, that a pressurised fluid containing bath takes place after a cleaning bath containing halogenated and/or hydrocarbons containing solvents. This is a further advantage of using the inventive combination, especially because the pressurised fluid has a very good cleaning effect in addition.

[0017] The order of the cleaning bathes using one or more of the mentioned solvents according to the present invention can be freely chosen and combined in numerous ways and so adapted to a broad variety of cleaning duties. Also the modes of solvent recovery can be chosen from a wide range of possibilities and be adapted to the needs of every combination of cleaning bathes.

[0018] According to a preferred embodiment of the present invention the pressurised fluid is liquid carbon dioxide and/or supercritical carbon dioxide. The cleaning ability of liquid or supercritical carbon dioxide is known to be very good and increases for supercritical carbon

dioxide.

[0019] The recovery of CO₂ by distillation is easy to manage. Therefore, the use of CO₂ is very favorable, especially in view of combining a few cleaning cycles, i.e. using a few cleaning bathes one after another, which normally takes place in one cleaning vessel.

[0020] According to a preferred embodiment of the present invention the goods to be cleaned are garments. The present invention is suitable for cleaning of textile as well as leather garments.

[0021] According to an alternative embodiment of the present invention the goods to be cleaned contain metal, plastic, stone and/or glass material. The goods can be metal, plastic, stone and/or glass objects as well as objects containing parts of the mentioned materials. Further examples for goods to be cleaned are industrial parts or medical devices.

[0022] According to an embodiment of the present invention the goods to be cleaned are contaminated by chemical substances, organic residues and/or particles resting on the surface or within the structure of the goods. The residues can also be called impurities or dirt of any kind.

[0023] According to a preferred embodiment of the present invention in at least one cleaning bath a mixture of a pressurised fluid with halogenated and/or hydrocarbons containing solvent is used. The mixing of said substances in one cleaning bath is especially advantageous in view of the cleaning quality.

[0024] According to an embodiment of the present invention every cleaning bath is operated at an elevated pressure, i.e. a pressure at least above atmospheric pressure.

[0025] According to a very advantageous embodiment of the present invention the final cleaning bath, e.g. the second cleaning bath, is carried out using CO₂ in a concentration of at least 90% in weight of the whole solvent amount of the cleaning bath, preferably at least 95%, even more preferably at least 99%, the remainder being CO₂ or a detergent.

[0026] According to an preferred embodiment of the present invention the process is carried out using a pressure within the cleaning vessel of at least 30 bar, preferably of more than 40 bar, even more preferably of more than 50 bar. The cleaning efficiency is especially good under high pressure.

[0027] According to an alternative embodiment of the present invention, which might be very useful for special applications, the process is carried out using a pressure within the cleaning vessel of less than 30 bar, preferably of less than 20 bar, even more preferably of between 2 and 10 bar. This embodiment works with moderately elevated pressure and therefore is able to save costs in view of the necessary pressure resistance of the components, e.g. the cleaning vessel.

[0028] Concerning the pressure in the cleaning vessel it should be mentioned, that it is very easy to operate at moderately elevated pressure (i.e. Pressure above at-

mospheric pressure) for an hydrocarbons containing cleaning bath. When CO₂ is added it can be used to increase the pressure. When liquid carbon dioxide is added in such an amount, that it will be present in liquid form in the cleaning bath, the pressure will be above 35 bar, preferably above 40 bar and even more preferably above 50 bar.

[0029] According to an embodiment of the present invention the goods to be cleaned and/or the cleaning vessel are heated. For example, this method will increase the cleaning efficiency. For example, the goods to be cleaned and/or the cleaning vessel is heated when recovering gaseous CO₂.

[0030] According to an embodiment of the present invention a solvent recovery system is used showing a recovery rate of at least 98%, preferably of at least 99%. Due to the reduced amount of halogenated or hydrocarbon containing solvents the recovery system for this substances can be of a smaller scale than usual. In certain embodiments one recovery system may be in service for more than one cleaning vessels, eventually situated at a different location. The pressurised fluid is best recovered by distillation.

[0031] According to an embodiment of the present invention the solvent recovery system uses a vacuum pump to increase the solvent recovery rate. It may be especially advantageous to combine the heating up of the goods to be cleaned and/or the cleaning vessel with the use of the vacuum pump. For example, the goods to be cleaned and/or the cleaning vessel is heated when recovering gaseous CO₂ and the vacuum pump is used after the recovery of gaseous CO₂ in order to increase the removing rate of all other solvents from the goods to be cleaned.

[0032] According to an embodiment of the present invention two recovery systems may be in use, one for halogenated and/or hydrocarbons containing solvents and one for pressurised fluid containing solvents. For example, a high pressure recovery system for CO₂ can be used first, followed by a recovery system for halogenated and/or hydrocarbons containing solvents, which can be of high pressure or of low pressure type. Gaseous CO₂ can also be recovered in a low pressure system, but liquid CO₂ needs a high pressure recovery system. The residues (impurities, dirt, e.g.) can be recovered, i.e. separated from the solvents, in any recovery system, but most effectively this takes place in the last recovery system used.

[0033] According to a preferred embodiment of the present invention the final cleaning bath is heated to a temperature in the range of zero to 100°C, preferably not exceeding 40°C, even more preferably not exceeding 30°C. This feature is especially advantageous for cleaning delicate garments and/or when it is important to further improve the removing and/or recovery rate for the halogenated and/or hydrocarbons containing solvents.

[0034] The present invention is very advantageous in view of many aspects, a few of them given below:

The combination of the use of halogenated and/or hydrocarbon containing solvents with pressurised fluid as a solvent, especially liquid or supercritical carbon dioxide, allows the reduction of the amount of the first two. The subsequent increase of the amount of CO₂ used is easy to handle, e.g. due to the possibility of recovering CO₂ by means of distillation having a comparatively low energy consumption and due to the fact that CO₂ is an easy to handle non toxic substance.

[0035] The inventive cleaning process utilises only a very small amount of toxic and/or flammable solvents, especially compared to known cleaning processes using halogenated and/or hydrocarbon containing solvents. Therefore, need and emission rate to the environment as well as content of solvent remaining on the goods to be cleaned are significantly improved, which means all these amounts are significantly reduced. The working conditions in general are therefore improved. Legislative demands like the German BimschV and the Californian Clean Air Act are easily satisfied.

[0036] The cleaning quality as a result of the inventive process is very good. The cleaned goods are essentially free of residues, which means essentially no solvents can be found on or in the goods after the cleaning process is finished.

[0037] Operating at the mentioned low temperatures, e.g. at a temperature between 10 and 40°C, reduces the risk for discolouration of delicate garments and other thermal degradation which might occur to some goods at high temperatures.

[0038] Embodiments of the present invention are described in greater detail below.

Example 1:

[0039] Garment or metal parts are cleaned by using perchloroethylene (PER). The goods to be cleaned are placed in a pressure-resistant vessel. Also other auxiliary components are adapted for operation under elevated pressure. First PER liquid is introduced into the cleaning vessel. The residues carrying PER liquid is then removed from the cleaning vessel. Pressurised CO₂ is introduced into the cleaning vessel forming the second cleaning bath. The CO₂ is used to dissolve solvent residues. Loaded with dissolved solvent the CO₂ is removed from the cleaning vessel and led to a recovery system. In the recovery vessel or system pure CO₂ is recovered, e.g. and preferably by means of distillation.

[0040] Both, the cleaning process and the solvent recovery, i.e. the separation of the solvent from the goods as well as the separation of the residues from the solvent, may be carried out more than once and in various sequences.

[0041] A very good cleaning quality is achieved and the cleaned goods are essentially free of the PER typical odour. The PER liquid used in the first cleaning bath as

well as the PER liquid extracted by the help of CO₂ out of the second cleaning bath is separated from residues such as contaminants, e.g. dirt or other substances which were cleaned off the goods and other extracted substances. In this way the unwanted residues like contaminants and dirt are collected in concentrated form. The separated solvents can be reused.

Example 2:

[0042] Example 2 is also an example for cleaning garments or metal parts. Instead of the use of PER isoparaffins (German abbreviation: KWL) are used. The other features of the cleaning process remain unchanged as described in example 1.

Example 3:

[0043] Goods to be cleaned with the help of PER or isoparaffins in the presence of CO₂ already in the first cleaning bath.

[0044] The goods to be cleaned are placed in a pressure-resistant vessel. Also other auxiliary components are adapted for operation under elevated pressure. First PER or isoparaffin liquid is introduced into the cleaning vessel. CO₂ is already added as dense medium or solvent into the first cleaning bath. The concentration of CO₂ is advised to be preferably between 1 and 99,8%, more preferably between 10 and 99%, even more preferably between 50 and 98% (percentage given on weight basis).

[0045] The residues carrying solvent mixture is then removed from the cleaning vessel.

[0046] Pressurised CO₂ is introduced into the cleaning vessel forming the second cleaning bath. The CO₂ is used to dissolve solvent residues. Loaded with dissolved solvent the CO₂ is removed from the cleaning vessel and led to a recovery system. In the recovery vessel or system pure CO₂ is recovered, e.g. and preferably by means of distillation.

[0047] The amount of PER or isoparaffins used is considerably smaller than in example 1 and 2. Subsequently cleaned goods are free of any solvent and any solvent odour.

[0048] All other features are similar to example 1.

Example 4:

[0049] Goods to be cleaned with the help of PER and isoparaffins in the presence of CO₂ already in the first cleaning bath. All other features are similar to example 3.

Example 5:

[0050] Example 5 stresses that example 3 and 4 could also be limited to one cleaning bath, i.e. the first cleaning bath, and still achieve a very good cleaning quality.

Example 6:

[0051] In example 6 the cleaning process starts with a first cleaning bath containing CO₂ in gaseous form and not containing any halogenated and/or hydrocarbons containing solvents in the first cleaning bath. One or more of this substances are used in subsequent cleaning bathes.

Example 7:

[0052] Example 7 is similar to example 6, but liquid CO₂ is present in the first cleaning bath. This option may be very advantageous in order to get rid of a significant amount of dirt right at the beginning of the cleaning process.

[0053] In general, for all examples, it should be mentioned again that the amounts of different solvents present in the cleaning bathes can be chosen in the range of 0 to 100%. The amounts used differ in view of the cleaning ability and the recovery properties of the substances.

Claims

1. Process for cleaning goods comprising the following steps: a) placing the goods to be cleaned in a pressure-resistant cleaning vessel, b) introducing a cleaning solvent into the cleaning vessel, c) removing the residues carrying solvent from the cleaning vessel, d) separating the residues from the solvent, **characterised in that**, step b and step c are carried out at least twice, therefore leading at least to a first and second cleaning bath, using a halogenated and/or hydrocarbons containing solvent in one cleaning bath, and using a pressurised fluid containing solvent in another cleaning bath.
2. Process for cleaning goods comprising the following steps: a) placing the goods to be cleaned in a pressure-resistant cleaning vessel, b) introducing a cleaning solvent into the cleaning vessel, c) removing the residues carrying solvent from the cleaning vessel, d) separating the residues from the solvent, **characterised in that**, step b and step c are carried out at least once, therefore leading at least to one cleaning bath, using a halogenated and/or hydrocarbons containing solvent in combination with a pressurised fluid containing solvent in at least one cleaning bath.
3. Process according to claim 1 or 2, **characterised in that**, the pressurised fluid is liquid carbon dioxide and/or supercritical carbon dioxide.
4. Process according to any of claims 1 to 3, **characterised in that**, the goods to be cleaned are gar-

ments.

5. Process according to any of claims 1 to 4, **characterised in that**, the goods to be cleaned contain metal, plastic, stone and/or glass material.
6. Process according to any of claims 1 to 5, **characterised in that**, the goods to be cleaned are contaminated by chemical substances, organic residues and/or particles resting on the surface or within the structure of the goods.
7. Process according to any of claims 1 to 6, **characterised in that**, in at least one cleaning bath a mixture of a pressurised fluid with halogenated and/or hydrocarbons containing solvent is used.
8. Process according to any of claims 1 to 7, **characterised in that**, every cleaning bath is operated at an elevated pressure, i.e. a pressure at least above atmospheric pressure.
9. Process according to any of claims 1 to 8, **characterised in that**, the final cleaning bath, e.g. the second cleaning bath, is carried out using CO₂ in a concentration of at least 90% in weight of the whole solvent amount of the cleaning bath, preferably at least 95%, even more preferably at least 99%, the remainder being CO₂ or a detergent.
10. Process according to any of claims 1 to 9, **characterised in that**, the goods to be cleaned and/or the cleaning vessel are heated.
11. Process according to any of claims 1 to 10, **characterised in that**, a solvent recovery system is used showing a recovery rate of at least 98%, preferably of at least 99%.
12. Process according to claim 11, **characterised in that**, the solvent recovery system uses a vacuum pump to increase the solvent recovery rate.
13. Process according to any of claims 1 to 12, **characterised in that**, the final cleaning bath is heated to a temperature in the range of zero to 100°C, preferably not exceeding 40°C, even more preferably not exceeding 30°C.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 01 7001

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
D,X	WO 01/29305 A (RACETTE ET AL) 26 April 2001 (2001-04-26) * abstract * * page 1, line 7 - line 17 * * page 3, line 1 - line 9 * * page 5, line 14 - line 26 * * page 6, line 2 - page 7, line 5 * * page 8, line 9 - line 19 * * page 9, line 6 - page 10, line 2 * * page 13, line 3 - page 17, line 9 * * page 17, line 30 - page 21, line 14 * * claims * * figures *	1-13	INV. B08B7/00 B08B3/08 D06F43/00 D06L1/02
X	----- US 5 377 705 A (SMITH, JR. ET AL) 3 January 1995 (1995-01-03) * abstract * * column 1, line 15 - line 18 * * column 3, line 61 - column 4, line 8 * * column 4, line 34 - column 5, line 59 * * column 6, line 17 - line 20 * * column 6, line 37 - column 7, line 32 * * claims * * figures *	1-13	TECHNICAL FIELDS SEARCHED (IPC) B08B D06F D06L B01D
X	----- US 5 417 768 A (SMITH, JR. ET AL) 23 May 1995 (1995-05-23) * abstract * * column 1, line 7 - line 40 * * column 1, line 50 - line 56 * * column 1, line 64 - column 2, line 25 * * column 2, line 30 - column 3, line 4 * * column 3, line 11 - line 15 * * column 3, line 35 - line 51 * * column 3, line 56 - column 6, line 11 * * claims * * figure * ----- -/--	1-6,8-13	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 15 January 2008	Examiner van der Zee, Willem
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

1
EPO FORM 1503 03.82 (P04C01)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 07 01 7001

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X A	GB 2 311 992 A (BESPAK PLC) 15 October 1997 (1997-10-15) * abstract * * page 1, line 5 - line 11 * * page 4, line 10 - page 6, line 18 * * claims * -----	1-6,9, 11-13 8,10	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 15 January 2008	Examiner van der Zee, Willem
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

1
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 07 01 7001

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

15-01-2008

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0129305	A	26-04-2001	AT	337427 T	15-09-2006
			AU	778581 B2	09-12-2004
			AU	8021700 A	30-04-2001
			BR	0014772 A	10-06-2003
			CA	2388500 A1	26-04-2001
			DE	60030304 T2	23-08-2007
			EP	1224351 A1	24-07-2002
			ES	2270877 T3	16-04-2007
			JP	2003512111 T	02-04-2003
			MX	PA02003817 A	06-09-2004
			NO	20021764 A	14-06-2002
			NZ	518788 A	26-09-2003
			NZ	526305 A	24-03-2005
			US	2002100124 A1	01-08-2002
			US	6355072 B1	12-03-2002
			US	2002011258 A1	31-01-2002
			US	2002010965 A1	31-01-2002

US 5377705	A	03-01-1995	NONE		

US 5417768	A	23-05-1995	US	5509431 A	23-04-1996

GB 2311992	A	15-10-1997	AU	2516597 A	29-10-1997
			DE	69700551 D1	28-10-1999
			DE	69700551 T2	30-12-1999
			EP	0892825 A1	27-01-1999
			WO	9738044 A1	16-10-1997
			US	6241828 B1	05-06-2001

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 4012194 A [0004]
- US 5980648 A [0004]
- US 5759209 A [0004]
- EP 0587169 B1 [0004]
- WO 02086222 A1 [0004]
- WO 02086223 A1 [0004]
- WO 0129305 A1 [0004]
- WO 0129306 A1 [0004]