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[KR/KR]; 102-802 Olympic Apt., Bangi-dong 89,
Songpa-gu, Seoul 138-050 (KR).

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(74) Agent: **PAIK, Nam-Hoon**; 14th Fl., KTB Network Build-
ing 826-14, Yeoksam-dong, Kangnam-ku, Seoul 135-769
(KR).

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(71) Applicant (for all designated States except US): **KOREA
INSTITUTE OF SCIENCE AND TECHNOLOGY**
[KR/KR]; 39-1 Hawolgok 2-dong, Seongbuk-gu, Seoul
136-791 (KR).

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(72) Inventors; and

(75) Inventors/Applicants (for US only): **LEE, Hyun Joo**
[KR/KR]; 106-1403 Songpa Samsung Raemian Apt.,
Songpa-dong 162, Songpa-gu, Seoul 138-170 (KR). **AHN, Byoung Sung** [KR/KR]; 10-207 Changmi Apt.,
Sincheon-dong, Songpa-gu, Seoul 138-240 (KR). **KIM,
Hong Gon** [KR/KR]; 40-704 Gaenari Apt., Yeoksam
2-dong, Gangnam-gu, Seoul 135-986 (KR). **KIM, Hoon
Sik** [KR/KR]; 309-1503 Family Apt., Munjeong-dong,
Songpa-gu, Seoul 138-200 (KR). **LEE, Sang Deuk**

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(54) Title: METHOD OF PREPARING DIALKYL CARBONATES

(57) Abstract: The present invention relates to a process of preparing dialkylcarbonates, and particularly to an improved process of preparing dialkylcarbonates, which comprises performing a reaction between an alcohol compound and a chloroformate derivative in the presence of an imidazole compound, thereby enabling to prepare dialkylcarbonates with high yield in a mild condition without using toxic raw materials and to easily separate impurities.

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METHOD OF PREPARING DIALKYL CARBONATES

TECHNICAL FIELD

The present invention relates to a process of preparing dialkylcarbonates, and particularly to an improved process of preparing dialkylcarbonates, which comprises performing a reaction between an alcohol compound and a chloroformate derivative in the presence of an imidazole compound, thereby enabling to prepare dialkylcarbonates with high yield in a mild condition without using toxic raw materials and to easily separate impurities.

RELATED PRIOR ART

Dialkylcarbonates are widely used mainly for manufacturing special solvents or dyes, plant protection products, monomer or intermediate product for preparing polymers (e.g. polycarbonate), fuel additives and electrolyte solution for lithium secondary battery. As compared to other organic solvent, a dialkylcarbonate has a relatively higher dielectric constant. A dialkylcarbonate also has a lower viscosity than alkylene carbonate, which is known to have a relatively high solubility in an organic material. For these reasons, a dialkylcarbonate is used for electrolyte solution for commercialized lithium secondary battery in combination with alkylene carbonate.

Dialkylcarbonates are generally produced by reacting alkyl alcohol with phosgene. However, the toxicity of phosgene and the corrosiveness of side product (i.e. hydrochloric acid) require a novel process for dialkylcarbonates that may replace the conventional phosgene process.

Japanese patent application publication Nos. 6-25104 and 3-141243 and Korean patent application publication No. 1996-14087 disclose, as an alternative to

the phosgene process, a process for preparing dimethyl carbonates, which comprises steps of: performing a reaction between carbon monoxide and methyl nitrate in the platinum catalyst, and generating methyl nitrate by collecting nitrogen monoxide generated as a side product and reacting the nitrogen monoxide with methyl
5 alcohol. This process solved the problems regarding toxic phosgene and corrosive hydrochloric acid. However, this process still has problems relating to carbon monoxide such as toxicity, pollution, corrosiveness and explosiveness.

U.S. patent Nos. 6458914, 6258923 and 5,599,965 disclose a process for preparing dialkylcarbonates, which comprises the step of passing methyl alcohol
10 and carbon monoxide through Cu-based catalyst bed or performing a slurry reaction with a catalyst. However, this process has drawbacks that a chlorine compound such as palladium chloride and ammonium chloride is further used as a co-catalyst to maintain the activity of catalyst. This process also generates side products that are difficult to be separated from products.

15 Korean patent application publication No. 2001-108572 discloses a process for preparing dialkylcarbonates, which comprises the step of performing a reaction between alcohol compound and carbonate gas under high pressure in the presence of cerium oxide (CeO) catalyst. However, this process has drawbacks requiring a harsh reaction condition ($> 160\text{ }^{\circ}\text{C}$ and $> 50\text{ atm}$) and a very low yield of 0.2-0.3%.

20 Japanese patent application publication Nos. 15-342209, 15-342236, 15-342237, 16-8996 and 16-10571 disclose a process for preparing dialkylcarbonates through transesterification reaction between alkylene carbonate and alkyl alcohol by using a hydroxide or a carbonate salt of alkali metal or an oxide of IVA or IVB group metal as a catalyst. Toxic raw materials are not used and corrosive materials
25 are not generated during this process. However, this process requires the use of an additional catalyst and generates ethylene oxide and carbon dioxide as side products

due to the decomposition of alkylene glycol and alkylene carbonate, thus necessitating complex separation and purification steps.

Further, the conventional process mainly focuses on symmetric dialkylcarbonates, and may not be applied to the manufacture of asymmetric
5 dialkylcarbonates.

To solve the aforementioned problems, the present inventors have conducted extensive researches to develop an eco-friendly process for preparing dialkylcarbonates at a mild condition with high yield without using toxic material
10 such as phosgene, carbon monoxide and methyl nitrate, which have been employed in a conventional process.

As a result, the present invention has been completed based on the findings that a target dialkylcarbonate may be manufactured at a relatively lower temperature by performing a reaction between an alcohol compound and a
15 chloroformate derivative in the presence of an imidazole compound.

The present invention prevents the use of toxic raw material such as phosgene and the generation of corrosive material, thus remarkably improving the stability of the process.

Further, according to the present invention, an imidazole compound, which is
20 used as a reaction medium, combines with the generated hydrogen chloride to form an imidazolium. The large differences between the produced dialkylcarbonates and the side products such as the imidazolium in specific gravity and boiling point facilitate the separation of the products by means of a simple purification method such as a layer separation or distillation.

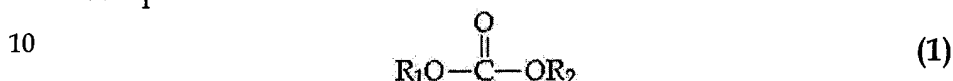
25 Furthermore, the process according to the present invention may be applied to the manufacture of asymmetric dialkylcarbonates as well as symmetric

dialkylcarbonates.

Therefore, the present invention aims to provide a process for preparing dialkylcarbonates at a mild condition with high yield without using toxic materials.

5 DETAILED DESCRIPTION OF INVENTION

The present invention relates to a process of preparing a dialkylcarbonate of Formula 1, which comprises a step of performing a reaction between an alcohol compound and a chloroformate derivative in the presence of an imidazole compound:



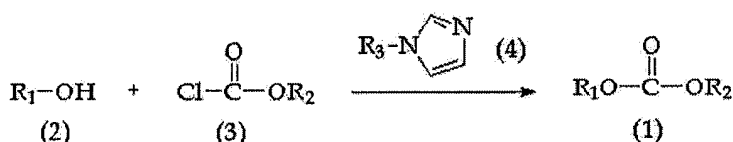
wherein R₁ and R₂, which may be the same or different, are a C₁-C₁₈ fluorinated alkyl group with 1-8 fluorine atom substituents, a C₁-C₁₈ alkyl, a C₁-C₁₈ alkenyl or a phenyl group, respectively.

15 Hereunder is provided a more detailed description of the present invention.

The present invention is characterized in maximizing the yield of a reaction for preparing a dialkylcarbonates of Formula 1 by using an imidazole compound of Formula 4, wherein an alcohol of Formula 2 and a chloroformate derivative of Formula 3 are used as raw materials.

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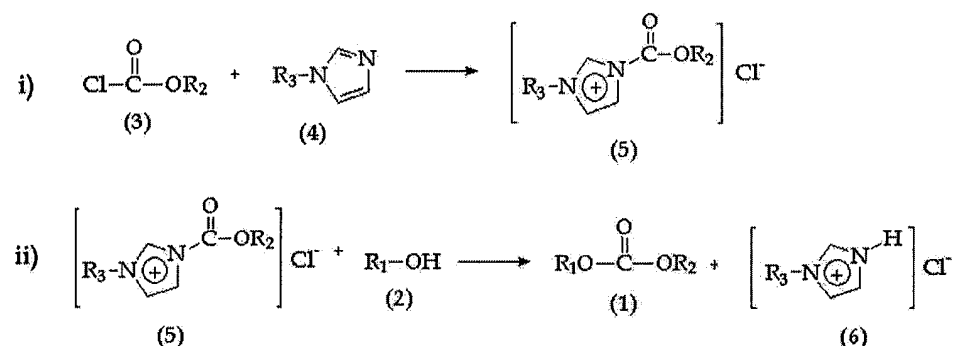
Scheme 1



In scheme 1 above, where R₁ and R₂, which may be the same or different, are a C₁-C₁₈ fluorinated alkyl group with 1-8 fluorine atom substituents, a C₁-C₁₈ alkyl, a C₁-C₁₈ alkenyl or a phenyl group, respectively; and R₃ is a hydrogen atom, a C₁-C₆ alkyl or a C₂-C₆ alkenyl group.

The process of Scheme 1 comprises two steps as shown in Scheme 2 below.

Scheme 2



In Scheme 2, R₁, R₂ and R₃ are same as defined in Scheme 1.

That is, a chloroformate derivative of Formula 3 is reacted with an imidazole compound of Formula 4 to form an ionic liquid, i.e. an imidazolium salt of Formula 5, which is further reacted with an alcohol of Formula 3 to form a target material herein, i.e. a dialkylcarbonate of Formula 1. An imidazolium salt of Formula 6 is also formed as a side product.

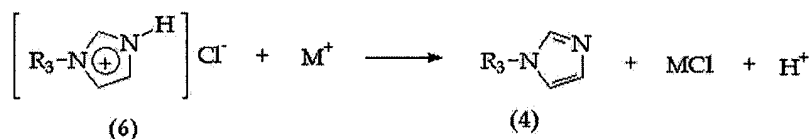
As described above, an imidazole compound of Formula 4 is used as a reaction vehicle in the present invention to produce an intermediate product, which is non-toxic as well as non-corrosive and may thus reduce risks that may occur during the process. Further, due to the use of an imidazole compound, the reaction yield may be highly increased even at a relatively low reaction temperature of

around room temperature. Conventionally, dialkylcarbonates were manufactured at a relatively high temperature of 120-200 °C.

Moreover, both the imidazole compound of Formula 4 and the imidazolium salt of Formula 5 or 6 have a heavier specific gravity and a higher boiling point than the dialkylcarbonate of Formula 1. Thus, the dialkylcarbonate remains in an upper liquid layer, while the intermediate product and the side product are present in a lower liquid layer. Accordingly, the final product may be easily collected using a layer separation method. Moreover, the dialkylcarbonate of Formula 1 may also be obtained with high purity using a simple distillation due to the relatively higher specific gravity than the intermediate product and the side product.

Furthermore, as shown in Scheme 3 below, the side product herein, an imidazolium salt of Formula 6 may be collected after the transformation into an imidazole compound of Formula 4 by adding an appropriate base. Examples of the base include an alkali metal salt, specifically a water-soluble salt of alkali metal such as a sodium hydroxide and a C₁-C₆ sodium alkoxide.

Scheme 3



In Scheme 3, R₃ is as defined as in Scheme 1, and M is an alkali metal.

For the preparation of the dialkylcarbonates herein, 1-1.5 moles of the chloroformate derivative and 1-2 moles of the imidazole compound may be used relative to one mole of the alcohol compound. Preferably, the chloroformate derivative and the imidazole compound may be used in the amount of 1.2 moles and 1.5 moles, respectively, relative to one mole of the alcohol compound. If the amount of the chloroformate or the imidazole compound is less than one mole

relative to one mole of the alcohol compound, the raw material, i.e. the chloroformate derivative may remain unreacted, thus making the separation and purification of the product difficult.

Further, according to the process herein, the reaction may be performed at a lower temperature, i.e. at a temperature of -20 to 50 °C, preferably -10 to 25 °C. In particular, a reaction temperature is preferred to be as low as possible only if the conversion of a raw material, i.e. an alcohol and a chloroformate derivative may be 100%, respectively. However, if the reaction temperature is lower than -20 °C, the reaction rate may be too low, thus resulting in little economical efficiency. The reaction temperature of above 50 °C is not preferred because it may cause products to be decomposed.

Moreover, the reaction of the present invention may be performed in the presence of an appropriate organic solvent. The same kind of a dialkylcarbonate as produced in the process herein may also be used in the present invention as the solvent. The dialkylcarbonate may be used as a solvent in the amount 30-300 wt%, preferably 100-200 wt% relative to the weight of the imidazole compound. In this case, the reaction may be performed more stably at room temperature due to the effect of diluting the raw material, i.e. an imidazole compound and a chloroformate derivative, resulting in effective control of reaction heat. This also facilitates the layer separation between the products, i.e. a dialkylcarbonate and the ionic liquid, i.e. an imidazolium.

EXAMPLES

The present invention is described more specifically by the following Examples. Examples herein are meant only to illustrate the present invention, but the should not be construed as limiting the scope of the claimed invention.

Example 1

20.0 g (0.434 moles) of ethanol was dissolved in 53.5 g (0.651 moles) of 1-methylimidazole, and slowly added dropwise with 49.2 g (0.521 mole) of methyl chloroformate at 0 °C, followed by stirring for 1 hour. The temperature of the reactants was elevated up to the room temperature. Upper layer was separated and subject to the conversion analysis using a gas-liquid chromatography equipped with a capillary column. The conversion of ethanol was 98.6%. The upper layer was distilled at reduced pressure and colorless transparent liquid ethyl methyl carbonate was obtained in the yield of 97.4%.

Ionic liquid imidazolium salt of Formula 5 was instantaneously produced as an intermediate product in the form of white solid when 1-methylimidazole was mixed with methyl chloroformate in the absence of alcohol compound (yield 97%).

¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ (ppm) = 10.10 (s, 1H, CH-Im), 8.15, 7.96 (d, 2H, CH-Im), 4.08 (s, 3H, CH₃-Im), 3.96 (s, 3H, CH₃-O).

The conversion of alcohol compound and the yield of carbonate were calculated using the following Mathematical formulas.

Mathematical formula 1

$$\text{Conversion of alcohol (\%)} = \frac{\text{Moles of reacted alcohol}}{\text{Moles of used alcohol}} \times 100 \quad (1)$$

Mathematical formula 2

$$\text{Yield of carbonate (\%)} = \frac{\text{Moles of produced carbonate}}{\text{Moles of used alcohol}} \times 100 \quad (2)$$

Examples 2-12

5 Dialkylcarbonates were synthesized under the same conditions as in Example 1 except by changing chloroformate derivatives as shown in Table 1. The results are presented in Table 1.

Table 1

Example	Chloroformate derivative	Conversion (%)	Yield of carbonate (%)
1	Methyl chloroformate	98.6	97.4
2	Ethyl chloroformate	95.6	94.1
3	Vinyl chloroformate	89.4	88.0
4	n-Propyl chloroformate	97.1	96.0
5	i-Propyl chloroformate	98.4	96.5
6	Allyl chloroformate	87.3	85.5
7	n-Butyl chloroformate	97.8	95.1
8	i-Butyl chloroformate	92.3	90.4
9	n-Hexyl chloroformate	91.1	90.0
10	Phenyl chloroformate	87.2	83.4
11	n-Heptyl chloroformate	86.4	84.1
12	n-Octyl chloroformate	83.1	79.1

Examples 13-26

Dialkylcarbonates were synthesized under the same conditions as in Example 1 except by changing alcohols as shown in Table 2. The results are presented in Table 2.

5

Table 2

Example	Alcohol	Conversion (%)	Yield of carbonate (%)
1	Ethanol	98.6	97.4
13	Methanol	99.2	97.8
14	n-Propanol	96.4	94.8
15	i-Propanol	98.4	97.3
16	n-Butanol	98.3	96.9
17	i-Butanol	97.9	96.2
18	t-Butanol	93.5	91.0
19	n-Pentanol	96.4	94.8
20	i-Pentanol	94.3	92.6
21	neo-Pentanol	91.3	90.2
22	n-Hexanol	95.5	94.8
23	Phenol	94.5	93.2
24	n-Heptanol	92.4	91.2
25	p-Cresol	95.1	92.9
26	n-Octanol	89.2	88.7

Examples 27-30

Dialkylcarbonates were synthesized under the same conditions as in Example 1 except by changing imidazoles as shown in Table 1. The results are presented in Table 1.

Table 3

Example	Imidazoles	Conversion (%)	Yield of carbonate (%)
1	1-Methylimidazole	98.6	97.4
27	1,2-Dimethylimidazole	99.4	98.1
28	1-Vinylimidazole	95.6	94.8
29	1-Allylimidazole	94.2	92.9
30	1-Butylimidazole	96.1	94.8

Example 31

Lower layer separated in Example 1 was added with 20.84 g (0.521 moles) of sodium hydroxide at room temperature, followed by stirring for 1 hour. 1-Methylimidazole was recovered (recovery 97.6%) by distilling the remaining solution at a reduced pressure after the produced NaCl was filtered.

Examples 32-35

The imidazoles used in Examples 27-30 are recovered by following the same procedure with Example 31. The results are presented in Table 4.

Table 4

Example	Recovered imidazoles	Recovery (%)
31	1-Methylimidazole	97.6%
32	1,2-Dimethylimidazole	96.1

33	1-Vinylimidazole	95.1
34	1-Allylimidazole	94.6
35	1-Butylimidazole	95.9

Example 36

1-Methylimidazole was recovered by following the same procedure as described in Example 31 except by using sodium methoxide (NaOCH_3) instead of sodium hydroxide, and the recovery was 98.5%.

Examples 37-39

Dialkylcarbonates are synthesized under the same conditions as in Examples 1, 2 and 13 except by adding 200 mL of the same kind of the produced dialkylcarbonates as a solvent. The results are presented in Table 5.

Table 5

Ex.	Alcohol	Chloroformate derivative	Added dialkylcarbonate	Conv. (%)	Yield of carbonate (%)
13	Methanol	Methylchloroformate	-	99.2	97.8
37	Methanol	Methylchloroformate	Methylmethyl carbonate	98.8	98.2
1	Ethanol	Methylchloroformate	-	98.6	97.4
38	Ethanol	Methylchloroformate	Methylethyl carbonate	98.4	97.6
2	Ethanol	Ethylchloroformate	-	95.6	94.1
39	Ethanol	Ethylchloroformate	Ethylethyl carbonate	95.2	94.6

Examples 40-54

Dialkylcarbonates are synthesized under the same conditions as in Example 1 except by changing each of the molar ratios of methyl chloroformate and 1-methylimidazole to alcohols as shown in Table 6. The results are presented in Table 6.

Table 6

Example	Molar ratio relative to alcohol		Conversion (%)	Yield (%)
	Methyl chloroformate	1-Methylimidazole		
1	1.5	1.2	98.6	97.4
40	1	1	70.1	63.5
41	1	1.3	79.5	75.2
42	1	1.5	85.3	83.6
43	1	1.7	89.2	87.1
44	1	2	95.2	93.9
45	1.2	1	97.5	82.1
46	1.2	1.3	98.1	89.4
47	1.2	1.5	98.6	97.4
48	1.2	1.7	98.6	97.4
49	1.2	2	98.8	97.5
50	1.5	1	98.4	85.3
51	1.5	1.3	97.4	92.1
52	1.5	1.5	95.5	93.4
53	1.5	1.7	97.4	95.7
54	1.5	2	99.2	98.0

Examples 55-69

Dialkylcarbonates are synthesized under the same conditions as in Example 1 except by changing the reaction temperature as shown in Table 7. The results are presented in Table 7.

Table 7

Example	Reaction temperature (°C)	Conversion (%)	Yield of carbonate (%)
1	0	98.6	97.4
55	-20	81.3	79.7
56	-15	90.2	88.9
57	-10	95.4	94.8
58	-5	98.5	97.4
59	0	98.6	97.4
60	5	98.4	97.0
61	10	98.7	97.1
62	15	98.9	96.7
63	20	99.2	95.4
64	25	98.5	95.2
65	30	97.1	94.3
66	35	95.2	92.0
67	40	90.0	87.2
68	45	82.6	79.3
69	50	70.2	62.4

As described above, a reaction between a chloroformate derivative and an alcohol compound is performed in the presence of an imidazole compound according to the present invention. This method herein may remarkably improve the process stability by preventing the generation of corrosive material, which has been produced as side products in a conventional process. The process herein also facilitates the separation of the products, thus noticeably simplifying the total process.

The aforementioned ionic liquid, i.e. imidazolium salt of Formula 6, which is produced as a side product in the process herein, is not corrosive because it is of a salt state substantially without a boiling point. The imidazolium salt may also be easily separated from the product, i.e. dialkylcarbonates. Furthermore, the imidazolium salt may be transformed into the initial imidazole compound by the treatment of an appropriate base such as sodium hydroxide, and easily collected for the recovery. For this reason, the process herein may be applied to a mass production and a continuous process.

CLAIMS

What is claimed is:

1. A process of preparing a dialkylcarbonate of Formula 1, which comprises performing a reaction between an alcohol compound and a chloroformate derivative in the presence of an imidazole compound:



wherein R₁ and R₂, which may be the same or different, are a C₁-C₁₈ alkyl group having 1-8 fluorine atom, a C₁-C₁₈ alkyl, a C₁-C₁₈ alkenyl or a phenyl group, respectively.

2. The process of claim 1, wherein the chloroformate derivative and the imidazole compound are used in the amount of 1-1.5 moles and 1-2 moles, respectively, relative to one mole of the alcohol compound.
3. The process of claim 1, wherein the reaction is performed at a temperature of from -20 to 50 °C.

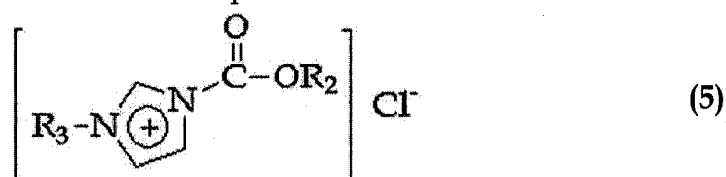
4. The process of claim 1, wherein the imidazole compound has a structure of Formula 4:



wherein R₃ is a hydrogen atom, a C₁-C₆ alkyl or a C₂-C₆ alkenyl group.

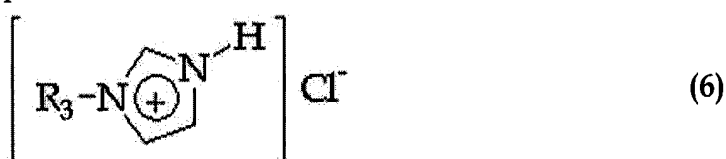
5. The process of claim 1, wherein the reaction is performed in a solvent of a dialkylcarbonate, which is the same with the product of the reaction.

6. The process of claim 1, wherein an imidazolium salt of Formula 5 is produced as an intermediate product in the reaction:



wherein R₃ is a hydrogen atom, a C₁-C₆ alkyl or a C₂-C₆ alkenyl group.

7. The process of claim 1, wherein an imidazole salt of Formula 6 is produced as a product:



wherein R₃ is a hydrogen atom, a C₁-C₆ alkyl or a C₂-C₆ alkenyl group.

8. The process of claim 7, wherein the imidazolium salt is reacted with an alkali metal salt to produce an imidazole compound.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2006/005347**A. CLASSIFICATION OF SUBJECT MATTER***C07C 51/27(2006.01)i*

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)

IPC8: C07C, C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean Patents and Applications for Inventions since 1975Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
STN(REG, CAplus)**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005277782 A1 (Enitecnologie S.p.A.) 15 December 2005 See the whole document	1-8
A	JP 06092905 A (Nippon Polyurethane Kogyo Kk) 5 April 1994 See the whole document	1-8
A	Kondo, Kiyoshi et al., 'Selenium catalyzed synthesis of carbonates. Reaction of alkoxide with carbon monoxide and oxygen in the presence of selenium', Bulletin of the Chemical Society of Japan, 48(1), pp. 108-11, 1975 See the whole document	1-8
A	GB 1385002 A (Societe Nationale des Poudres et Explosifs) 26 February 1975 See the whole document -----End of documents-----	1-8



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