



- (51) **International Patent Classification:**
C07C 68/00 (2006.01) C07C 69/96 (2006.01)
- (21) **International Application Number:**
PCT/IN2016/050093
- (22) **International Filing Date:**
23 March 2016 (23.03.2016)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
794/DEL/2015 23 March 2015 (23.03.2015) IN
- (71) **Applicant: COUNCIL OF SCIENTIFIC & INDUSTRIAL RESEARCH [IN/IN];** Anusandhan Bhawan, Rafi Marg, New Delhi 110001 (IN).
- (72) **Inventors: RANADE, Vivek, Vinayak;** National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411008 (IN). **KELKAR, Ashutosh, Anant;** National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411008 (IN). **RANE, Vilas, Hari;** National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411008 (IN). **KINAGE, Anil, Kisan;** National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411008 (IN). **SHINGOTE, Savita, Kiran;** National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411008 (IN). **ROY, Lalita, Sanjib;** National Chemical Laboratory, Dr. Homi Bhabha Road, Pune, Maharashtra 411008 (IN).
- (74) **Agents: CHOPRA, Priyanka et al.;** K & S PARTNERS, 109, Sector 44, National Capital Region, Gurgaon 122003 (IN).

- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

Published:

- with international search report (Art. 21(3))
— with amended claims (Art. 19(1))

(88) Date of publication of the international search report:

27 October 2016

Date of publication of the amended claims:

5 January 2017

(54) **Title:** A PROCESS FOR THE SYNTHESIS OF DIALKYL CARBONATES

(57) **Abstract:** The patent discloses a process for the synthesis of dialkyl carbonates catalysed by a catalyst composition AB oxides, wherein A and B are rare earth metals or A and B are combination of rare earth and transition metals with ratios ranging from 0.5:10 to 10:0.5.



WO 2016/151602 A4

AMENDED CLAIMS
received by the International Bureau on 18 Nov 2016(18.11.2016)

1. A process for the synthesis of dialkyl carbonates catalysed by a catalyst composition AB oxides, comprises the steps of:
 - a. Removing ammonia formed over the period of reaction and cooling the reaction to room temperature to obtain the desired alkyl carbonate; and
 - b. Charging alkyl carbamate and aliphatic alcohol (1:5) in a high pressure reactor, adding the catalyst and heating the reactor to 100-300°C with stirring;wherein A and B are rare earth metals or A and B are mixture of rare earth and transition metals with ratios ranging from 0.5:10 to 10:0.5.
2. The process as claimed in claim 1, wherein dialkyl carbonates are selected from di methyl carbonate (DMC), di ethyl carbonate (DEC), di propyl carbonate (DPC) or di butyl carbonate (DBC).
3. The process as claimed in claim 1, wherein the catalyst is a mixed metal oxide, said metal selected from rare earth/inner transition elements or transition metals.
4. The process as claimed in claim 3, wherein said catalyst is optionally a ternary mixed metal oxide having more than two elements used in combination in the molar ratio a:b:c, where element "a" is in a range of 0.1 to 1; element "b" is in a range of 0.1 to 1-x and element "c" is x, wherein x is in the range of 0.01 to 0.09, wherein said elements are selected from rare earth, transition metals and alkaline earth metals.
5. The process as claimed in claim 3, wherein the element is selected from Zr, Ce, Fe or La.
6. The process as claimed in claim 3, wherein metal oxide is CeZrO.
7. The process as claimed in claim 3, wherein the catalyst is supported or unsupported and the support is selected from carbon, neutral alumina or silica.

8. The process as claimed in claim 1, wherein the process is conducted with CO₂ or N₂ stripping.
9. The process as claimed in claim 1, wherein the process is conducted in batch or continuous mode in an autoclave, packed bed reactor, bubble column reactor or such like.
10. The process as claimed in claim 1, wherein conversion of alkyl carbamate is > 30% and selectivity is more than 30% to the corresponding alkyl carbonate.