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(54) Title: MILD ELECTROCHEMICAL DECARBOXYLATIVE ALKYL-ALKYL COUPLING AND DECARBOXYLATIVE OLEFINATION ENABLED BY RAPID ALTERNATING POLARITY

(57) Abstract: Rapid Alternating Polarity (rAP) is a new electrolysis mode for synthetic organic electrochemistry. As described herein, AC waveforms, particularly rAP, can profoundly alter the reaction outcome of the reduction of carbonyl groups and arenes, exhibiting unprecedented levels of chemoselectivity that is absent when DC is used under otherwise identical reaction conditions. Herein, disclosed are new applications of rAP electrolysis, such as i) rAP -Kolbe electrolysis for the decarboxylative coupling of carboxylic acids; and ii) rAP electrolysis for the decarboxylative olefination of carboxylic acids; both under mild electrochemical conditions.



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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/68403

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 86
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
has been found to be unsearchable because it is an improper omnibus claim, not drafted in accordance with Rule 6.2(a).

3. Claims Nos.: 4-66, 70-85
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
(see supplemental page)

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 23/68403

<p>A. CLASSIFICATION OF SUBJECT MATTER</p> <p>IPC - INV. C07C 2/00, C25B 3/29 (2023.01) ADD. C25B 15/02, C25B 3/23 (2023.01)</p> <p>CPC - INV. C07C 2/00, C25B 3/29</p> <p>ADD. C25B 15/02, C25B 3/23</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC.</p>																			
<p>B. FIELDS SEARCHED</p> <p>Minimum documentation searched (classification system followed by classification symbols) See Search History document</p> <p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched See Search History document</p> <p>Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) See Search History document</p>																			
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p> <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X -- Y</td> <td>US 2016/0097134 A1 (Azad) 07 April 2016 (07.04.2016); abstract, para [0010], [0028], [0147], [0151]</td> <td>1, 3 ----- 2</td> </tr> <tr> <td>Y</td> <td>US 2014/0257002 A1 (EXXONMOBIL RESEARCH AND ENGINEERING COMPANY) 11 September 2014 (11.09.2014); abstract, para [0053]</td> <td>2</td> </tr> <tr> <td>A</td> <td>US 8,961,775 B2 (Altranex Corporation) 24 February 2015 (24.02.2015); entire document</td> <td>1-3</td> </tr> <tr> <td>A</td> <td>Kawamata et al. "Chemoselective Electrosynthesis Using Rapid Alternating Polarity" Journal of the American Chemical Society. 01 October 2021 (01.10.2021) vol 143, pg. 16580-16588; entire document</td> <td>1-3</td> </tr> <tr> <td>A</td> <td>WO 2014/200916 A1 (Azad) 18 December 2014 (18.12.2014); entire document</td> <td>1-3</td> </tr> </tbody> </table>		Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X -- Y	US 2016/0097134 A1 (Azad) 07 April 2016 (07.04.2016); abstract, para [0010], [0028], [0147], [0151]	1, 3 ----- 2	Y	US 2014/0257002 A1 (EXXONMOBIL RESEARCH AND ENGINEERING COMPANY) 11 September 2014 (11.09.2014); abstract, para [0053]	2	A	US 8,961,775 B2 (Altranex Corporation) 24 February 2015 (24.02.2015); entire document	1-3	A	Kawamata et al. "Chemoselective Electrosynthesis Using Rapid Alternating Polarity" Journal of the American Chemical Society. 01 October 2021 (01.10.2021) vol 143, pg. 16580-16588; entire document	1-3	A	WO 2014/200916 A1 (Azad) 18 December 2014 (18.12.2014); entire document	1-3
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<p><input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.</p>																			
<p>* Special categories of cited documents:</p> <table border="0"> <tr> <td>"A" document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"D" document cited by the applicant in the international application</td> <td>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>"E" earlier application or patent but published on or after the international filing date</td> <td>"Y" document of particular relevance; the claimed invention 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</td> </tr> <tr> <td>"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)</td> <td>"&" document member of the same patent family</td> </tr> <tr> <td>"O" document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P" document published prior to the international filing date but later than the priority date claimed</td> <td></td> </tr> </table>		"A" document defining the general state of the art which is not considered to be of particular relevance	"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	"D" document cited by the applicant in the international application	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention 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	"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)	"&" document member of the same patent family	"O" document referring to an oral disclosure, use, exhibition or other means		"P" document published prior to the international filing date but later than the priority date claimed							
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<p>Date of the actual completion of the international search</p> <p>14 November 2023 (14.11.2023)</p>	<p>Date of mailing of the international search report</p> <p>JAN 23 2024</p>																		
<p>Name and mailing address of the ISA/US</p> <p>Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300</p>	<p>Authorized officer</p> <p>Kari Rodriguez</p> <p>Telephone No. PCT Helpdesk: 571-272-4300</p>																		

--continued from Box No. III--

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-3, directed to a method of decarboxylative coupling of carboxylic acids.

Group II: Claims 67-69, directed to a method of decarboxylative olefination of carboxylic acids.

The group of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features:

Group I includes the technical feature of a method of decarboxylative coupling of carboxylic acids, which is not required by any other invention of Group II.

Group II includes the technical feature of a method of decarboxylative olefination of carboxylic acids, which is not required by any other invention of Group I.

Common technical features:

The inventions of Groups I and II share the technical feature of a method of decarboxylative reactions comprising carboxylic acids, wherein a carboxylic acid substrate is subjected to rapid Alternating Polarity (rAP)-Kolbe electrolysis.

These shared technical features, however, do not provide a contribution over the prior art, as being anticipated by WO 2014/200916 A1 to Azad. Azad discloses a method of decarboxylative reactions comprising carboxylic acids (pg. 1, para 1: producing decarboxylated derivatives from carboxylic acids), wherein a carboxylic acid substrate (pg. 40, para 1: Oleic acid) is subjected to rapid Alternating Polarity (rAP)-Kolbe electrolysis (pg. 6, para 1: Kolbe Electrolysis; abstract: polarity reversing electrolysis; pg. 28, para 1: The polarity reversal electrolyses may be performed using a frequency range from 0.001Hz to 3 MHz) (a frequency range from 0.001Hz to 3 MHz is "rapid" as evidenced by instant claim 3).

As said compound was known in the art at the time of the invention, these cannot be considered special technical features that would otherwise unify the inventions of Groups I or II. The inventions of Group I and II thus lack unity under PCT Rule 13.

Item 4. Cont: Claims 4-66, 70-85 have been found to be unsearchable because they are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Claim 86 has been found to be unsearchable because it is an improper omnibus claim, not drafted in accordance with Rule 6.2(a).