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Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*
— *with information concerning request for restoration of the right of priority in respect of one or more priority claims; the decision of the receiving Office regarding the request for restoration is pending and will be published separately once available (Rules 26bis.3 and 48.2(j))*

(88) Date of publication of the international search report:
30 July 2020 (30.07.2020)

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(54) Title: COMPOUNDS, PROCESSES, AND MACHINERY FOR CONVERTING METHANE GAS INTO METHANE-SULFONIC ACID

(57) Abstract: Improved initiators, solvents, and processing equipment and methods are disclosed for improving the yields and efficiency of a manufacturing process which uses a radical chain reaction to convert methane (CH4), which is a gas under any normal conditions, into methane sulfonic acid (MSA), a liquid. MSA is useful and valuable in its own right, and it also can be processed to create desulfured fuels and other valuable chemicals. A preferred type of initiator combination has been identified, comprising at least two different peroxide sulfate compounds. One will act as a "primary" initiator for the chain reaction, while the other will act as a "chain-lengthening oxidant", which can eliminate chain-terminating species, such as sulfur Dl-oxide, in the MSA-forming reactor.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/29024

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C07C 303/06; C07C 303/44; C07C 309/04 (2019.01)

CPC - C07C 303/06; C07C 309/04

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)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US 2008/0161591 A1 (RICHARDS) 03 July 2008 (03.07.2008); para [0015], [0018], [0023], [0025]-[0026], [0041], [0043]-[0044], [0047], [0054], [0057], [0061], [0069], [0071]-[0076], [0078], [0081], [0084]-[0085], [0087], [0113], [0120], [0131]-[0134], [0136], [0139], [0145]; Figs. 2-3, 5	1-5, 9 ---------- 6, 10-21
X ---- Y	US 2016/0289181 A1 (GRILLO-WERKE AG) 06 October 2016 (06.10.2016); para [0005]-[0006], [0008]-[0009], [0032]	7-8 ---------- 6, 10-11, 15-18, 20-21
Y	US 2012/0138097 A1 (OKORN-SCHMIDT et al.) 07 June 2012 (07.06.2012); para [0004], [0026]	12
Y	US 5,766,491 A (MAZEWSKI et al.) 16 June 1998 (16.06.1998); col 6 ln 37-48	13-14
Y	US 2011/0105802 A1 (VILLA et al.) 05 May 2011 (05.05.2011); para [0006], [0010]-[0011]	19, 21
A	US 2007/0282151 A1 (RICHARDS) 06 December 2007 (06.12.2007); see entire document	1-21
A	US 2006/0100458 A1 (SEN et al.) 11 May 2006 (11.05.2006); see entire document	1-21

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"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)
"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
"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
"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
"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
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
09 December 2019	14 JAN 2020
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Lee Young Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 19/29024

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.:
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:

3. ☐ Claims Nos.:
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:
--Please see attached sheet--

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.:

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 19/29024

Attachment to 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 1-8 directed to a chemical combination or a chemical mixture for initiating and then extending a radical chain reaction which combines methane (CH4) with sulfur trioxide (SO3), in a chemical mixture inside a reactor vessel, in a manner which forms methane-sulfonic acid and to components of said combination or mixture.

Group II: Claims 9-12 and 15-21 directed to a method for preparing or manufacturing methane sulfonic acid via a radical chain reaction.

Group III: Claims 13-14, directed to a reactor assembly for converting methane and sulfur trioxide into methane-sulfonic acid via a radical chain reaction, said reactor assembly comprising a tube enclosure which contains at least one inert baffle-type mixing device inside said tube enclosure, wherein said tube enclosure can be used to process a gas/liquid mixture which flows through said tube enclosure at pressures of at least 500 pounds/square inch, under conditions which do not allow substantial quantities of any chain-terminating species to travel through the tube enclosure in a backflow direction.

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 II includes the technical feature of a method for performing a radical chain reaction which combines methane with sulfur trioxide, not required by Groups I and III.

Group III includes the technical feature of a reactor assembly comprising a tube enclosure which contains at least one inert baffle-type mixing device inside said tube enclosure, wherein said tube enclosure can be used to process a gas/liquid mixture which flows through said tube enclosure at pressures of at least 500 pounds/square inch, under conditions which do not allow substantial quantities of any chain-terminating species to travel through the tube enclosure in a backflow direction, not required by Groups I and II.

Common technical features:

Groups I-III share the technical feature of methanesulfonic acid formed by combining methane and sulfur trioxide in a radical chain reaction.

This shared technical feature, however, does not provide a contribution over the prior art, as being anticipated by US 2008/0161591 A1 to Richards (hereinafter Richards), which discloses methane sulfonic acid formed by combining methane and sulfur trioxide in a radical chain reaction (para [0025]-[0026], Fig 2). As said methanesulfonic acid was known in the art at the time of the invention, this cannot be considered a special technical feature, that would otherwise unify the inventions of Groups I-III.

Groups I and II further share the technical features of:
(i) at least one primary initiator compound having a peroxide bond which can be broken to release radical species capable of efficiently removing hydrogen atoms from methane, thereby creating methyl radicals which will attach to S03 molecules in said chemical mixture; and,
(ii) at least one chain-lengthening oxidant compound, having a peroxide bond which, when broken apart, will release at least one radical species that will efficiently oxidize at least some S02 (sulfur dioxide) molecules present in said chemical mixture, into S03 (sulfur trioxide) molecules, thereby removing chain-terminating S02 molecules from said chemical mixture in said reactor vessel.

These shared technical features, however, do not provide a contribution over the prior art, as being anticipated by Richards, which discloses:
(i) at least one primary initiator compound having a peroxide bond which can be broken to release radical species capable of efficiently removing hydrogen atoms from methane (para [0071]: "reagent supply container 120 contains stabilized anhydrous liquid SO3, or an alternate sulfonating agent that can be converted into Caro's acid and/or Marshall's acid. Both of these reagents are pumped into a suitable acid formation vessel"; also para [0132]: "Marshall's acid at 20.6 mmol (62.5%), sulfuric acid at 19.4 mmol (29.7%), and Caro's acid at 4.4 mmol (7.8%)"; the latter disclosure unequivocally indicates presence of both Marshall's acid, which inherently possesses the aforementioned properties, and Caro's acid), thereby creating methyl radicals which will attach to SO3 molecules in said chemical mixture (para [0025]); and
(ii) at least one chain-lengthening oxidant compound, having a peroxide bond (para [0071], [0132]; Caro's acid), which when broken apart, will release at least one radical species that will efficiently oxidize at least some SO2 (sulfur dioxide) molecules present in said chemical mixture, into SO3 (sulfur trioxide) molecules, thereby removing chain-terminating SO2 molecules (para [0057]; also para [0071] and [0132]: in the formed SO3 - CH4 - Marshall's acid - Caro's acid mixture, the latter ingredient will inherently oxidize unwanted SO2 admixture) from said chemical mixture in said reactor vessel (para [0071]).

As said initiator and chain-lengthening oxidant compound were known in the art at the time of the invention, these cannot be considered special technical features, which would, otherwise unify the inventions of Groups I-II.

The inventions of Groups I-III, thus, lack unity under PCT Rule 13.