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**C23C 14/22** (2006.01)

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(71) Applicant: **WASHINGTON STATE UNIVERSITY**  
[US/US]; 423 Neill Hall, Pullman, Washington 99164 (US).(72) Inventors: **LEKOBOW, William Pimakouan**; 1560 NE Merman Drive, #251, Pullman, Washington 99163 (US).  
**ENGLUND, Karl Richard**; 422 N Hayes Streets, Moscow, Idaho 83843 (US). **PEDROW, Patrick Dennis**; 1008 Bor-

der Lane, Moscow, Idaho 83843 (US). **WEMLINGER, Erik Charles**; 1600 NW Hall Drive, Pullman, Washington 99163 (US). **ISLAM, Rokibul**; 1650 NE Merman Drive, #251, Pullman, Washington 99163 (US).

(74) Agent: **LEVIN, Paul D.**; Pepper Hamilton LLP, Suite 5000, 500 Grant Street, Pittsburgh, Pennsylvania 15219-2507 (US).

(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, LT, 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.

[Continued on next page]

## (54) Title: SYSTEMS AND METHODS FOR TREATING MATERIAL SURFACES

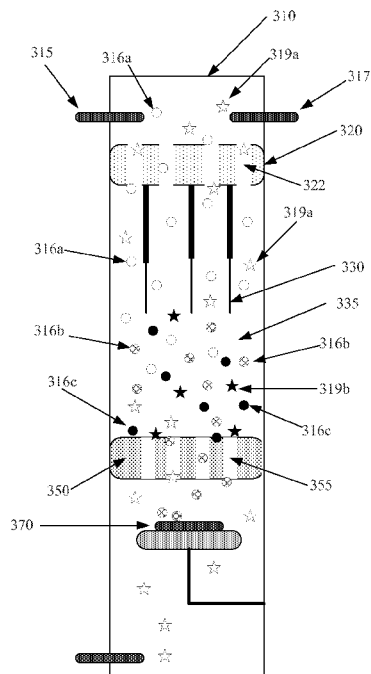


FIG. 3

(57) **Abstract:** A system for treating at least one surface of a material may include a reaction vessel containing a first electrode and a second electrode separated by a gap. A power source may generate an electrical potential across the first electrode and the second electrode. A mixture of a non-reactive fluid and a reactive fluid exposed to the electrical potential may produce a back coronal plasma discharge from the second electrode to the first electrode. The reactive gas may further form a treatment material within the plasma. Depending on the reactive fluid introduced in the reaction vessel, a substrate disposed distally with respect to the second electrode may be coated with the treatment material, thereby increasing the hydrophobic character of the substrate. The treated substrate may be incorporated into a composite composition composed of a hydrophobic matrix.



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# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US14/32058

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - B05B 5/03; C23C 14/22, 16/513 (2014.01)

USPC - 118/50.1, 627; 427/569 CPC: H05H 1/46

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)

IPC(8): B05B 5/03; B05D 3/04, 3/06; B32B 33/00; C23C 14/06, 14/22, 14/50, 16/44, 16/50, 16/513; H05H 1/24 (2014.01)

USPC: 118/50.1, 500, 627, 723R, 729; 204/192.1, 298.02; 239/706; 361/213; 427/248.1, 569 CPC: H05H 1/42, 1/46, 1/2406, 2001/245

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

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

MicroPatent (US-G, US-A, EP-A, EP-B, WO, JP-bib, DE-C,B, DE-A, DE-T, DE-U, GB-A, FR-A); Google Scholar; ProQuest; IP.com; vessel, reactor, chamber, fluid, gas, reactive, acetylene, oxygen, nonreactive, noble, inert, electrical potential, two electrodes, gap, space, distance, treat, coat, substrate, workpiece, surface, hold, support, mesh

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                             | Relevant to claim No.                                              |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------|
| X         | WO 2012/146348 A1 (MASSINES, F et al.) 1 November 2012; paragraphs [0001], [0004], [0023], [0027], [0030]-[0032], [0043], [0045], [0052]; figure 1                             | 1-2, 5-7, 21, 34-37, 40-41, 44-47, 49-52, 54, 56-58, 60-65, 70, 76 |
| ----      |                                                                                                                                                                                | ---                                                                |
| Y         |                                                                                                                                                                                | 3-4, 8-20, 22-33, 38-39, 42-43, 48, 53, 55, 59, 66-69, 77-79       |
| Y         | US 2005/0281957 A1 (COOPER, SC et al.) 22 December 2005; paragraphs [0044], [0058]                                                                                             | 3                                                                  |
| Y         | US 5,330,578 A (SAKAMA, M et al.) 19 July 1994; figure 13; column 7, lines 4-7; column 11, lines 1-5, lines 11-13; column 13, lines 20-26, lines 43-46; column 17, lines 31-33 | 4, 8, 15-16, 43, 48, 66-67, 79                                     |
| Y         | US 2010/0030211 A1 (DAVALOS, R et al.) 4 February 2010; paragraphs [0023], [0036], [0048], [0059], [0065], [0116], [0119]                                                      | 8-14, 38-39                                                        |
| Y         | US 6,068,650 A (HOFMANN, GA et al.) 30 May 2000; column 6, lines 40-45                                                                                                         | 17                                                                 |
| Y         | US 2011/0009807 A1 (KJEKEN, R et al.) 13 January 2011; figure 2; paragraph [0010]; claim 16                                                                                    | 18, 29-30                                                          |
| Y         | US 3,906,274 A (SILVER, HG et al.) 16 September 1975; column 2, lines 57-60; column 4, lines 65-66; column 6, lines 43-49                                                      | 19-20                                                              |
| Y         | US 7,684,735 B2 (INO, T et al.) 23 March 2010; column 4, lines 46-48; column 11, lines 27-28, lines 40-41, lines 50-51, lines 54-55; column 13, lines 33-36                    | 22-26                                                              |

☒ Further documents are listed in the continuation of Box C.



\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"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

08 September 2014 (08.09.2014)

Date of mailing of the international search report

07 OCT 2014

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. 571-273-3201

Authorized officer:

Shane Thomas

PCT Helpdesk: 571-272-4300  
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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/32058

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                        | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Y         | US 2011/0094679 A1 (DONG, CC et al.) 28 April 2011; paragraphs [0009], [0032], [0037], [0060]                             | 27-28, 42             |
| Y         | US 5,683,443 A (MUNSHI, MZA et al.) 4 November 1997; column 9, lines 1, 7-11; column 10, lines 36-39                      | 31-32                 |
| Y         | US 4,048,383 A (CLIFFORD, JE) 13 September 1977; column 17, lines 59-61; column 18, lines 2-4; column 35, lines 37-39     | 31, 33                |
| Y         | US 7,189,436 B2 (KOHLE, GA et al.) 13 March 2007; column 3, lines 15-20; column 15, lines 10-16, lines 23-26, lines 38-39 | 53, 55, 59            |
| Y         | US 2013/0038949 A1 (DAVID, MM et al.) 14 February 2013; paragraphs [0005], [0007], [0013], [0027], [0031]-[0032]          | 61, 68-69             |
| Y         | US 2012/0234696 A1 (MOSLEY, MD et al.) 20 September 2012; figure 1; paragraph [0099], [0133]-[0134]                       | 77-78                 |
| A         | US 2008/0118734 A1 (GOODWIN, AJ et al.) 22 May 2008; entire document                                                      | 1, 50, 76             |
| A         | US 2011/0006040 A1 (SAVAS, SE et al.) 13 January 2011; entire document                                                    | 1, 50, 76             |
| A         | US 5,785,932 A (HELFRITCH, DJ) 28 July 1998; entire document                                                              | 1, 50, 76             |

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US14/32058

## 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:

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 examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-70 and 76-79 are directed toward a system and methods for treating a substrate.

Group II: Claims 71-75 are directed toward composition comprising: a polymer matrix.

---Continued Within the Next Supplemental Box---

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.:  
1-70, 76-79

### 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.

\*\*\*-Continued from Box No. III: Observations where unity of invention is lacking-\*\*\*

The inventions listed as Groups I-II 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: the special technical features of Group I include a system and method for treating a substrate, the system comprising: a reaction vessel comprising a proximal end and a distal end; a source of a non-reactive fluid in fluid communication with the proximal end of the reaction vessel; a source of a reactive fluid in fluid communication with the proximal end of the reaction vessel; a first electrode disposed within the proximal end of the reaction vessel and comprising at least one needle having a needle tip, wherein the at least one needle tip is disposed towards the distal end of the reaction vessel; a second electrode disposed within the reaction vessel and distal end to the at least one needle tip, thereby defining a gap between the at least one needle tip and the second electrode; a power supply in electrical communication with the at least one needle tip and the second electrode and configured to produce an electrical potential between the at least one needle tip and the second electrode; and a substrate holder disposed within the reaction vessel and distal end to the second electrode; contacting the substrate with the substrate holder; introducing a non-reactive fluid into the reaction vessel from the source of the non-reactive fluid; introducing a reactive fluid into the reaction vessel from the source of the reactive fluid; causing the power supply to develop an electrical potential between the at least one needle tip and the second electrode; exposing at least the reactive fluid to the electrical potential, thereby producing a treatment material; and contacting a surface of the substrate with the treatment material, thereby treating the substrate, wherein a fluid pressure within the reaction vessel due at least in part to the non-reactive fluid and the reactive fluid therein is about equal to an ambient gas pressure; and a method of fabricating a system for treating a substrate, which are not present in Group II; the special technical features of Group II include a composition comprising: a polymer matrix; and at least one substrate within the polymer matrix wherein the at least one substrate is coated with a treatment material comprising electrically neutral reactive fluid radicals, which are not present in Group I.

The common technical features of Groups I-II are treating a substrate; contacting the substrate with a treatment material; and the treatment material comprises a reactive material.

These common technical features are disclosed by WO 2012/146348 A1 to Massines, et al. (hereinafter 'Massines'). Massines discloses treating a substrate (treating a substrate using a plasma system; paragraph [0001]); contacting the substrate with a treatment material (a surface of the substrate is in contact with a plasma (treatment material) to plasma treat the substrate; paragraph [0021]); and the treatment material comprises a reactive material (plasma (treatment material) is formed from a process gas that may comprise oxygen (reactive material); paragraphs [0023]-[0024]).

Since the common technical features are previously disclosed by Massines, these common features are not special and so Groups I-II lack unity.