



(43) International Publication Date
4 October 2012 (04.10.2012)

(51) International Patent Classification:

C03C 3/089 (2006.01) *C03C 3/093* (2006.01)
C03C 3/091 (2006.01) *A61L 2/238* (2006.01)

(21) International Application Number:

PCT/US2012/030704

(22) International Filing Date:

27 March 2012 (27.03.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/468,153 28 March 2011 (28.03.2011) US

(71) Applicant (for all designated States except US): **CORNING INCORPORATED** [US/US]; 1 Riverfront Plaza, Corning, New York 14831 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BORRELLI, Nicholas Francis** [US/US]; 935 West Water Street, Elmira, New York 14905 (US). **PETZOLD, Odessa Natalie** [BZ/US]; 190 Bowlby Road, Elmira, New York 14901 (US). **SCHROEDER, Joseph Francis III** [US/US]; 260 West Third Street, Corning, New York 14830 (US). **SEWARD, Thomas Philip III** [US/US]; 94 Durland Avenue, Elmira, New York 14905 (US). **VERRIER, Florence** [FR/US]; 235 Upper Delevan, Corning, New York 14830 (US). **WEI, Ying** [US/US]; 3433 Conhocton Road, Painted Post, New York 14870 (US).

(74) Agent: **THOMPSON, Tina N.**; Corning Incorporated, Intellectual Property Department, SP-Ti-03-01, Corning, New York 14831 (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, 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, IS, JP, KE, KG, KM, 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, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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,

(54) Title: ANTIMICROBIAL ACTION OF COPPER IN GLASS

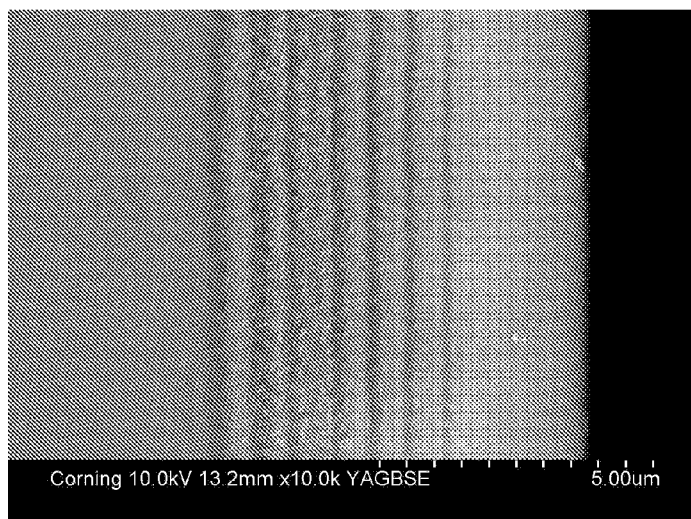


Figure 1

(57) Abstract: The disclosure is directed to glass compositions that incorporate copper into an otherwise homogeneous glass and to a method for making such glass. This incorporation of the copper into the glass composition imparts significant antimicrobial activity to the glass. A method of making a copper-containing glass article comprises: batching a glass batch comprising: 40-85 SiO₂; 10-40 B₂O₃; 1-19 Al₂O₃; 0.1-20 CuO or a selected salt of Cu that is convertible into CuO during melting; 0-20 M₂O, wherein M is Li, Na, K, or combinations thereof; 0-25 RO, wherein R is Ca, Sr, Mg, or combinations thereof; and 0-20 ZnO. melting the batch to form a melted glass; and forming the melted glass to form the copper-containing glass article having antimicrobial properties.





GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD,
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, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

ANTIMICROBIAL ACTION OF COPPER IN GLASS

Cross-Reference To Related Applications

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 of U.S. Provisional Application Serial No. 61/468,153 filed on March 28, 2011 the content of which is relied upon and incorporated herein by reference in its entirety.

Background

Field

[0002] This disclosure is directed to the production of glass whose surfaces have antimicrobial activity, and in particular to glass surfaces containing copper. The disclosure is further directed to a method of making such copper-containing glass and articles from the glass.

Technical Background

[0003] There is patent and otherwise published literature dealing with antimicrobial action, for example, the antibacterial action of silver both in the ionic form and the nanoparticle form. While antibacterial activity is desirable for many reasons in different applications, a clear distinction is to be made between antibacterial activity and antiviral activity. The distinction is made on the grounds that the mechanism by which metals such as silver alter or kill bacteria may not be the same as the mechanism that metals kill viruses. Moreover, with reference to antiviral activity, the mention of other metals or metal ions other than silver is rare. Articles referring to the antiviral activity of copper, copper alloys and copper ion include J.O. Noyce et al, "Inactivation of influenza A virus on copper versus stainless steel surfaces". Appl. Environ. Microbiol. Vol. 73 (2007) pages 2748–2750; J.L. Sagripanti et al, "Cupric and ferric ions inactivate HIV," AIDS Res Hum Retroviruses Vol. 12 (1996), pages 333–337; and J.L. Sagripanti, "Mechanism of copper-mediated inactivation of herpes simplex virus," Antimicrob. Agents Chemother., Vol. 41 (1997), pages 12–817. These articles discuss antiviral properties of

copper; more specifically, the antiviral action in a Cu^{+2} solution and a metallic copper surface.

[0004] There is a need for glasses with antimicrobial properties in applications such as medical applications wherein surfaces come in contact with humans.

Summary

[0005] Embodiments are directed to glass articles that incorporate copper ions, copper metal, and/or colloidal copper such as copper nanoparticles into an otherwise homogeneous glass and to a method for making such glass articles. This incorporation of the copper into the glass articles promotes significant antimicrobial activity such as antibacterial and/or antiviral activity. One advantage of embodiments described herein is a strong and smooth antiviral glass surface that is useful for a variety of applications where this property is either desirable or necessary. The antimicrobial property is integral to the glass, and is not a coating applied to the surface that will not either wear off or be removed. Applications in which the antiviral glass can be used include medical, healthcare, laboratory shelving and surfaces, and appliance surfaces where antimicrobial function would provide benefit.

[0006] One embodiment is a glass article comprising copper selected from the group consisting of Cu ions, metallic copper, colloidal copper, and combinations thereof dispersed throughout the glass and at a surface of the glass; and the glass having antimicrobial properties.

[0007] Another embodiment is a method of making a copper-containing glass article having antimicrobial properties, the method comprises:

batching a glass batch comprising:

40-85 SiO_2 ;

10-40 B_2O_3 ;

1-19 Al_2O_3 ;

0.1-20 CuO or a selected salt of Cu that is convertible into CuO during melting;

0-20 M_2O , wherein M is Li, Na, K, or combinations thereof;

0-25 RO, wherein R is Ca, Sr, Mg, or combinations thereof; and

0-20 ZnO.

melting the batch to form a melted glass; and
forming the melted glass to form the copper-containing glass article having
antimicrobial properties.

[0008] Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the invention as described in the written description and claims hereof, as well as the appended drawings.

[0009] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary of the invention, and are intended to provide an overview or framework for understanding the nature and character of the invention as it is claimed.

[0010] The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s) of the invention and together with the description serve to explain the principles and operation of the invention.

Brief Description of the Drawings

[0011] The invention can be understood from the following detailed description either alone or together with the accompanying drawing figures.

[0012] Figure 1 is a SEM microphotograph of a glass having a high density of Cu-nanoparticles at the surface and extending into the glass for an approximate distance of 5µm according to one embodiment.

Detailed Description

[0013] Reference will now be made in detail to various embodiments of the invention, examples of which are illustrated in the accompanying drawings. Wherever possible, the same reference numbers will be used throughout the drawings to refer to the same or like parts.

[0014] As used herein the term “antimicrobial,” means an agent or material, or a surface containing the agent or material that will kill or inhibit the growth of at least two different

types of microbes: bacteria, viruses and fungi. The term as used herein does not mean it will kill or inhibit the growth of all species microbes within such families, but that it will kill or inhibit the growth of one or more species of microbes from such families. When an agent is described as being “antibacterial, or “antiviral” or “antifungal,” it means that the agent will kill or inhibit the growth of bacteria, viruses or fungi, respectively.

[0015] As used herein the term “Log Reduction” or “LR” means $-\text{Log}(C_a/C_0)$, where C_a = the colony form unit (CFU) number of the antimicrobial surface containing Cu nanoparticles and C_0 = the colony form unit (CFU) of the control glass surface that does not contain Cu nanoparticles. That is:

$$\text{LR} = -\text{Log}(C_a/C_0),$$

As an example, a Log Reduction of 3 = 99.9% of the bacteria or virus killed and a Log Reduction of 5 = 99.999% of bacteria or virus killed.

[0016] The test method used for determining antibacterial properties of a copper-containing glass was a modified version of the JISZ-2801: 2000 method, which is a Japanese Industrial Standard that was developed to measure the antibacterial activity of copper-containing glass. The antibacterial activity is measured by quantitatively by determining the survival of bacteria cells that have been held in intimate contact with a surface thought to be antibacterial and incubated for 24 hours at 35°C. After the time period has elapsed the cells are counted and compared to a non-treated surface. The test was modified in that for the incubation period was changed to 6 hours at 37°C. After 6 hours the samples were removed from the incubator and the entire testing surface was thoroughly washed with PBS to ensure that all bacteria were removed. The cells and the PBS wash were then transferred to a broth agar plate for overnight culture. After a period of 16-24 hours the bacterial colonies on the agar plate were counted. 150µl of bacterial suspension of concentration 1×10^6 cells/ml was added to the sample plates which can be either a copper-containing glass plate or a control (no copper) plate, covering the plates having a bacterial suspension thereon with the PARAFILM® resulting in PARAFILM® covered plates, and thereafter incubating the bacteria at 37°C for 6 hours as indicated by, and lastly counting the colonies. The samples were tested using E. coli (gram negative) bacteria.

[0017] One embodiment is a glass article comprising copper selected from the group consisting of Cu ions, metallic copper, colloidal copper, and combinations thereof dispersed throughout the glass and at a surface of the glass; and the glass having antimicrobial properties. The copper (whether as the Cu^{+1} , Cu^{+2} , in the reduced state as a Cu nanoparticle) can be at the surface of the glass, a portion of the copper can be embedded or partially embedded in the glass, and/or the copper in any form can be dispersed throughout the glass article, including the surface. The article and the glass can be phosphorus free, for example, free from any intentionally added phosphorus.

[0018] In one embodiment, the copper is in a reduced state; and the glass article has antimicrobial properties, for example, antiviral and/or antibacterial. In one embodiment, the copper is in a reduced state; and the glass article has antiviral properties. In one embodiment, the copper is in a reduced state; and the glass article has antibacterial properties. The reduced copper can be at a depth of in the range of from $2\mu\text{m}$ to $3\mu\text{m}$ from the surface of the glass. In one embodiment, in the reduced copper case, the copper nanoparticles are on the surface and extending to a depth of in the range of from $2\mu\text{m}$ to $3\mu\text{m}$ from the surface of the glass. In one embodiment, the copper is robustly and tenaciously adhered to the surface, that is, the copper on the surface cannot be removed by wiping or cleaning. The article can have a log reduction ≥ 1 , for example, ≥ 2 , for example, ≥ 3 , for example, ≥ 4 .

[0019] In one embodiment, the glass has antibacterial properties. The article can have a log reduction ≥ 1 , for example, ≥ 2 , for example, ≥ 3 , for example, ≥ 4 .

[0020] The glass can be a strengthened glass, for example, an ion-exchanged glass.

[0021] The glass as batched can comprise 0.1 mole% - 20 mole % copper, for example, 1-16 mole %, for example, 5-16 mole %, for example, 5-15 mole %.

[0022] In one embodiment the glass as batched consists essentially of $\text{SiO}_2 = 47 \pm 2$ mole%, $\text{Al}_2\text{O}_3 = 9 \pm 1-1.5$ mole%, $\text{B}_2\text{O}_3 = 27 \pm 3$ mole%, $7-16 \pm 1.5$ mole% for ZnO , and Cu being $0.5-10 \pm 0.2 - 1.5$ mole% as the copper content increases.

[0023] The glass as batched can comprise 10 mole% - 40 mole % B_2O_3 . The glass as batched can comprise a $\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3$ ratio greater than 1, for example, greater than 2, for example, greater than 3. The glass as batched, in one embodiment, comprises in mole percent:

40-85 SiO₂;
10-40 B₂O₃;
1-19 Al₂O₃;
0.1-20 CuO;
0-20 M₂O, wherein M is Li, Na, K, or combinations thereof;
0-25 RO, wherein R is Ca, Sr, Mg, or combinations thereof; and
0-20 ZnO.

[0024] The glass as batched can be phosphorus free.

[0025] In one embodiment, the glass as batched comprises:

40-70 SiO₂;
16-31 B₂O₃;
3-15 Al₂O₃;
5-15 CuO;
0-20 M₂O, wherein M is Li, Na, K, or combinations thereof;
0-25 RO, wherein R is Ca, Sr, Mg, or combinations thereof; and
0-17 ZnO.

[0026] Another embodiment is a method of making a copper-containing glass article having antimicrobial properties, the method comprises:

batching a glass batch comprising:

40-85 SiO₂;
10-40 B₂O₃;
1-19 Al₂O₃;
0.1-20 CuO or a selected salt of Cu that is convertible into CuO during melting;
0-20 M₂O, wherein M is Li, Na, K, or combinations thereof;
0-25 RO, wherein R is Ca, Sr, Mg, or combinations thereof; and
0-20 ZnO.

melting the batch to form a melted glass; and

forming the melted glass to form the copper-containing glass article having antimicrobial properties.

[0027] The method, according to one embodiment, further comprises heating the article in a reducing atmosphere at an elevated temperature in the range of from 250°C to 475°C thereby reducing the copper ions, Cu^{+2} , in the glass as an oxide or other species, to the metal, Cu^0 . The heating can comprise heating the article for a time in the range of from 1 hour to 5 hours, for example, 2 to 5 hours. In one embodiment, the reducing atmosphere comprises hydrogen.

[0028] The method can further comprise strengthening the article after the forming. The strengthening, in one embodiment, comprises ion-exchanging alkali metal ions in the article for alkali metal ions that have a larger ionic radius.

[0029] The exemplary glass compositions can enable the incorporation of high concentrations of copper oxide into easily formed homogeneous glass batches. The examples 1-9 given in Table 1 are exemplary glass batches in mole %, and do not include all the possible compositions spanning a range of glass families, for example, borate glasses, aluminoborosilicate glasses, alkali aluminoborosilicate glasses, soda lime glass. As shown in Table 1, the copper in the glass as batched, determined as the oxide, is in the range of 0.5 mol% to 16 mol%. The compositions in Table 1 are batched compositions. Compositions as shown in Table 1 can have, for example, a variation of ± 2 mole % for SiO_2 , ± 3 mole % for B_2O_3 , ± 1 -1.5 mole % for Al_2O_3 and ZnO will have substantially similar activity.

Examples	1	2	3	4	5	6	7	8	9
SiO_2	47	47	47	47	47	47	47	47	47
Al_2O_3	9	9	9	9	9	9	9	9	9
B_2O_3	27	27	27	27	27	27	27	27	27
CuO	10	5	1	0.5	10	12	14	16	7.5
ZnO	7	12	16	16.5	7	5	3	1	9.5

Table 1.

[0030] After melting the batch materials, the glass may be formed using conventional glass forming methods, for example without limitation, slot draw, fusion draw and/or the float method. The glass article can be a sheet and, in some embodiments, has a thickness in the range of 0.3mm to 5mm, and the length and width can be varied. In other embodiments, the glass article can be arbitrary shapes, for example, conformal to curved

surfaces or in the shape of a tube and, in some embodiments, has a thickness in the range of 0.3mm to 5mm, and the length and width can be varied. Once a glass article is formed, it can be cut into individual articles and further treated or the entire sheet can be further treated and then cut into the articles. In either case the further treatment of the as-made Cu-containing glasses constitutes the next step in which the glass is treated in a hydrogen atmosphere at a temperature of 450°C for 5 hours to reduce the Cu^{+1} , and/or Cu^{+2} in the glass to Cu^0 . The process yields a high density of metallic copper nanoparticles at the glass's surface and extending, for example, 5 μm into the glass as shown in the SEM Micrograph of Figure 1. In Figure 1 the glass surface is to the right. The bright patterns are indicative of copper nanoparticles.

[0031] Glasses containing B_2O_3 have a tendency to phase separate into a borate-rich and borate-poor phase. The Cu likely goes into the borate-rich phase, therefore locally enriching the Cu concentration which can be beneficial. The addition of Al_2O_3 suppresses the phase separation tendency. The role of Zn can also play the same role. The following Tables 2 and 3 show the range of the constituents (B, Al, Zn).

[0032] Table 2 shows exemplary glass batches in mole %, examples 10-15, having $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ and SrO variations at 1% CuO.

Examples	10	11	12	13	14	15
SiO_2	47	47	47	47	47	47
Al_2O_3	9	11	13	15	9	9
B_2O_3	27	25	23	21	27	27
CuO	1	1	1	1	1	1
ZnO	16	16	16	16	7	0
SrO	0	0	0	0	9	16

Table 2.

[0033] Table 3 shows exemplary glass batches in mole %, examples 16-21, having $\text{Al}_2\text{O}_3/\text{B}_2\text{O}_3$ and SrO variations at 5% CuO.

Examples	16	17	18	19	20	21
SiO_2	47	47	47	47	47	47
Al_2O_3	9	11	13	15	9	9
B_2O_3	27	25	23	21	27	27
CuO	5	5	5	5	5	5
ZnO	12	12	12	12	6	0
SrO	0	0	0	0	9	16

Table 3.

Antibacterial Testing

[0034] Antibacterial tests were carried out using cultured gram negative *E. coli*; DH5alpha-Invitrogen Catalog No. I8258012, Lot No. 7672225, rendered Kanamycin resistant through a transformation with PucI9 (Invitogen) plasmid). The bacteria culture was started using either LB Kan Broth (Teknova #L8145) or Typtic Soy Broth (Teknova # T1550). Approximately 2µl of liquid bacteria suspension or a pipette tip full of bacteria were streaked from an agar plate and dispensed into a capped tube containing 2-3 ml of broth and incubated overnight at 37°C in a shaking incubator. The next day the bacteria culture was removed from the incubator and washed twice with PBS. The optical density (OD) was measured and the cell culture was diluted to a final bacterial concentration of approximately 1×10^6 CFU/ml. The cells were placed on the selected glass surface, antimicrobial or not antimicrobial (the control) for 6 hours at a temperature of 37°C. The buffers from each well were collected and the plates were twice washed with ice-cold PBS. For each well the buffer and wash were combined and the surface spread-plate method was used for colony counting.

Antiviral Testing

[0035] The antiviral test procedure was carried out using a modified protocol previously described by A. Klibanov. *et al*, *Nature Protocols* (2007). Briefly, Adenovirus Type 5 was diluted to approximately 10^6 PFU/ml in phosphate buffered saline (PBS). Adenovirus solution (10ul) was applied to the glass slide for 2 hours at room temperature. Virus-exposed to the slides are then collected by thorough washes with PBS. Washing suspension containing the viruses were then serially diluted 2-fold with sterilized PBS and 50 µL of each dilution was used to infect HeLa cells grown as a monolayer in a 96 well microplate. After two days, viral titer was calculated by counting the number of infected HeLa cells. Virus titer reduction was calculated as previously described (Standard test method for efficacy of sanitizers recommended for inanimate Non-food contact surfaces, E1153-03, re-approved 2010). The % reduction equals:

$[(\text{number of virus surviving on the glass control} - \text{number of virus surviving on the sample glass}) \times 100] \div \text{number of virus surviving on the glass control}$.

[0036] Exemplary glasses 1, 2, 6, and 9 from Table 1 were hydrogen treated at 450°C for 5 hours and tested for E. coli. The antibacterial results from the JIS Z 2801 test are as follows in Table 4.

Example	CuO	Log reduction
2	5%	log 5
9	7.50%	log 4
1	10%	log 5
6	12%	log5

Table 4.

[0037] Exemplary glasses 2, 5, 6, and 7 from Table 1 were hydrogen treated at 450°C for 5 hours and tested against adenovirus. Exemplary glasses 2, 5, 6, and 7 showed adenovirus log reduction 5 or greater.

[0038] Exemplary glasses as batched 1 and 2 in Table 1, which have been described above as having with significant antibacterial behavior, also exhibit a very potent antiviral activity, with virus titer reduction after 2 hours of exposure reaching 100% (4.5 log reduction) compared to the glass control. Interestingly, when the same glasses that were not subjected to reducing conditions and where Cu is present as a form of ions, the samples did not show significant antiviral activity. However, these same glasses showed antibacterial activity. These results indicate that a high concentration of nano-size metallic copper particles at the surface of the glass is responsible for the strong antiviral activity. Moreover, these results suggest that there is a different mode of action for these Cu glass samples when acting against bacteria versus when acting against viruses. The “kill” mechanisms are different for viruses and bacteria.

[0039] Table 5 shows exemplary glass batches in mole %, examples 22-27, having CuO added to a Pyrex®, an aluminoborosilicate glass, base glass at levels of 0.25, 0.5, 1, 2.5, and 5 mole %.

Examples	22	23	24	25	26	27
SiO ₂	83.27	83.27	83.27	83.27	83.27	83.27
Al ₂ O ₃	1.21	1.21	1.21	1.21	1.21	1.21
B ₂ O ₃	11.53	11.53	11.53	11.53	11.53	11.53
Na ₂ O	3.99	3.99	3.99	3.99	3.99	3.99

CuO	0	0.25	0.5	1	2.5	5.0
R-value	0.24	0.24	0.24	0.24	0.24	0.24

Table 5.

[0040] Exemplary glasses were hydrogen treated at 450°C for 5 hours. Antibacterial JIS Z 2801 test was performed using E. coli with exemplary glass 24 and 27 having a log reduction of greater than 1. Exemplary glass 27 had a log reduction of greater than 1.5. Similar results on non-reduced glasses were obtained.

[0041] Table 6 shows exemplary glass batches in mole %, examples 28-33, having CuO added to a Vycor®, an aluminoborosilicate glass batch, at levels of 0.25, 0.5, 1, 2.5 and 5 mole %.

Examples	28	29	30	31	32	33
SiO ₂	64.39	64.39	64.39	64.39	64.39	64.39
Al ₂ O ₃	1.55	1.55	1.55	1.55	1.55	1.55
B ₂ O ₃	26.34	26.34	26.34	26.34	26.34	26.34
Na ₂ O	7.72	7.72	7.72	7.72	7.72	7.72
CuO	0	0.25	0.5	1	2.5	5
R-value	0.23	0.23	0.23	0.23	0.23	0.23

Table 6.

[0042] Exemplary glasses 29, 30, and 31 were hydrogen treated at 450°C for 5 hours and antibacterial tested for E. coli using the JIS Z 2801 test. Exemplary glass 29 had a log reduction of 2.3 to 5, exemplary glass 30 had a log reduction of 5, and exemplary glass 31 had a log reduction of 3.5. Non-reduced glasses had similar results.

[0043] Exemplary glass 29 was hydrogen treated at 450°C for 1 or 2 hours. In the antiviral testing using adenovirus, the log reduction was about 2.

[0044] Table 7 shows exemplary glass batches, in mole %, examples 34-39, having CuO added to a borosilicate glass batch, at levels as shown in Table 7.

Examples	34	35	36	37	38	39
SiO ₂	71.94	71.97	71.61	71.36	71.33	70.87
Al ₂ O ₃	0	0	3.3	5.47	5.61	7.79
B ₂ O ₃	25.1	25.06	22.15	20.22	20.1	18.55
Li ₂ O	2.54	2.55	2.52	2.52	2.54	2.52
K ₂ O	0.42	0.42	0.42	0.42	0.42	0.42
CuO	5.85	8.65	5.82	5.81	8.56	8.51
R-value	0.12	0.12	-0.02	-0.13	-0.13	-0.26

Table 7.

[0045] Exemplary glass 39 was hydrogen treated at 450°C for 5 hours and antibacterial tested for E. coli. Exemplary glass 39 had a log reduction of 5 in the JIS Z 2801 test results.

[0046] Exemplary glass 36 was hydrogen treated at 450°C for 5 hours and antiviral tested with adenovirus with a log reduction of 5.

[0047] Table 8 shows exemplary glass batches, in mole %, examples 40-45, having CuO added to an aluminoborosilicate glass batch, at levels as shown in Table 8.

Examples	40	41	42	43	44	45
SiO ₂	63.8	63.8	63.8	63.8	63.8	63.8
B ₂ O ₃	17.2	17.2	17.2	17.2	17.2	17.2
Al ₂ O ₃	6.1	6.1	6.1	6.1	6.1	6.1
Na ₂ O	1.8	1.8	1.8	1.8	1.8	1.8
Li ₂ O	4.16	4.16	4.16	4.16	4.16	4.16
K ₂ O	6.81	6.81	6.81	6.81	6.81	6.81
CuO	0	0.5	1	2.5	5	7.5
SnO ₂	0.01	0.01	0.01	0.01	0.01	0.01
R-value	0.39					
Anneal	485 C					

Table 8.

[0048] Exemplary glass 45 was hydrogen treated at 450°C for 5 hours and antibacterial tested for E. coli. Exemplary glass 45 had a log reduction of 5 in the test. Non-reduced glass 45 had similar results.

[0049] Exemplary glass 45 was antiviral tested with adenovirus and had a log reduction of 2.

[0050] Table 9 shows antiviral testing results for exemplary glasses 2, 6, 7, 33, 36, and 45. Exemplary glass 7, 2, 6, 36 and 33 had extremely strong and broad antiviral activity. Moreover, exemplary glass 2 killed 5 log of HSV very fast (5 min).

Example Number	Mole % Cu	Antiviral activity (log reduction/time)			
		Adenovirus	HIV-1	Influenza A	HSV
45	7.5	2/2h	1.5/1 h	NT	NT
7	3	5/2h	NT	TBD	3.8/1h
2	5	5/2h	5.32/1h	TBD	5/5min
6	10 or 12	5/2h	3.92/1h	2.5/30min	5/1h
36	5.8	5/2h			
33	5	4.3/2h			

Table 9.

[0051] In one embodiment, the glass as batched has an R-value of less than 1. The role of R-value in the borosilicate glasses may influence the antimicrobial behavior and the ability to precipitate the copper nanoparticles within the volume of the glass, as opposed to on the surface, where it can be wiped off. R-value provides an indication of the number of NBOs (non-bridging oxygens) in the glass structure.

[0052] R-value is defined as the ratio of (total alkali minus alumina)/boric oxide, in either mole or cation percent. It is undefined in the absence of alkali oxides.

[0053] R-values are included in the tables above, where appropriate. High positive R-values, especially around 1 or greater, seem undesirable.

[0054] While typical embodiments have been set forth for the purpose of illustration, the foregoing description should not be deemed to be a limitation on the scope of the disclosure or the appended claims. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of this disclosure or the appended claims.

Claims

We claim,

1. A glass article comprising copper selected from the group consisting of Cu ions, metallic copper, colloidal copper, copper nanoparticles, and combinations thereof dispersed throughout the glass and at a surface of the glass; and the glass having antimicrobial properties.
2. The article according to claim 1, wherein the glass is phosphorus free.
3. The article according to claim 1, wherein the copper is in a reduced state; and the glass has antimicrobial properties.
4. The article according to claim 3, wherein the reduced copper is at a depth of in the range of from 2 μ m to 3 μ m from the surface of the glass.
5. The article according to claim 3, having a log reduction ≥ 1 .
6. The article according to claim 1, wherein the glass has antibacterial properties.
7. The article according to claim 6, having a log reduction ≥ 1 .
8. The article according to claim 1, wherein the glass is a strengthened glass.
9. The article according to claim 1, wherein the glass as batched comprises 0.1 mole% - 20 mole % copper.
10. The article according to claim 1, wherein the glass as batched comprises 10 mole% - 40 mole % B₂O₃.
11. The article according to claim 1, wherein the glass as batched comprises a B₂O₃/Al₂O₃ ratio greater than 1.

12. The article according to claim 1, wherein the glass as batched has an R-value of less than 1.

13. The article according to claim 1, wherein the glass comprises copper nanoparticles and wherein the nanoparticles are robustly adhered to the surface.

14. The article according to claim 1, wherein the glass as batched comprises in mole percent:

40-85 SiO₂;

10-40 B₂O₃;

0-19 Al₂O₃;

0.1-20 CuO;

0-20 M₂O, wherein M is Li, Na, K, or combinations thereof;

0-25 RO, wherein R is Ca, Sr, Mg, or combinations thereof; and

0-20 ZnO.

15. The article according to claim 14, wherein the glass as batched comprises 1-19 Al₂O₃.

16. The article according to claim 14, wherein the glass as batched comprises:

40-70 SiO₂;

16-31 B₂O₃;

3-15 Al₂O₃;

5-15 CuO;

0-20 M₂O, wherein M is Li, Na, K, or combinations thereof;

0-25 RO, wherein R is Ca, Sr, Mg, or combinations thereof; and

0-17 ZnO.

17. The article according to claim 14, wherein the glass as batched is phosphorus free.

18. The article according to claim 1, wherein the glass is an aluminoborosilicate or borosilicate glass.

19. The article according to claim 1, wherein the glass consists essentially of $\text{SiO}_2 = 47 \pm 2$ mole%, $\text{Al}_2\text{O}_3 = 9 \pm 1$ -1.5 mole%, $\text{B}_2\text{O}_3 = 27 \pm 3$ mole%, 7-16 ± 1.5 mole% for ZnO, and Cu being 0.5-10 ± 0.2 - 1.5 mole% as the copper content increases.

20. A method of making a copper-containing glass article having antimicrobial properties, the method comprising:

batching a glass batch comprising:

40-85 SiO_2 ;

10-40 B_2O_3 ;

1-19 Al_2O_3 ;

0.1-20 CuO or a selected salt of Cu that is convertible into CuO during melting;

0-20 M_2O , wherein M is Li, Na, K, or combinations thereof;

0-25 RO, wherein R is Ca, Sr, Mg, or combinations thereof; and

0-20 ZnO.

melting the batch to form a melted glass; and

forming the melted glass to form the copper-containing glass article having antimicrobial properties.

21. The method according to claim 20, further comprising heating the article in a reducing atmosphere at an elevated temperature in the range of from 250°C to 475°C thereby reducing the copper ions, Cu^{+2} , in the glass as an oxide or other species, to the metal, Cu^0 .

22. The method according to claim 21, wherein the heating comprises heating the article for a time in the range of from 2 hours to 5 hours.

23. The method according to claim 20, further comprising strengthening the article after the forming.

24. The method according to claim 23, wherein the strengthening comprises ion-exchanging alkali metal ions in the article for alkali metal ions that have a larger ionic radius.

1/1

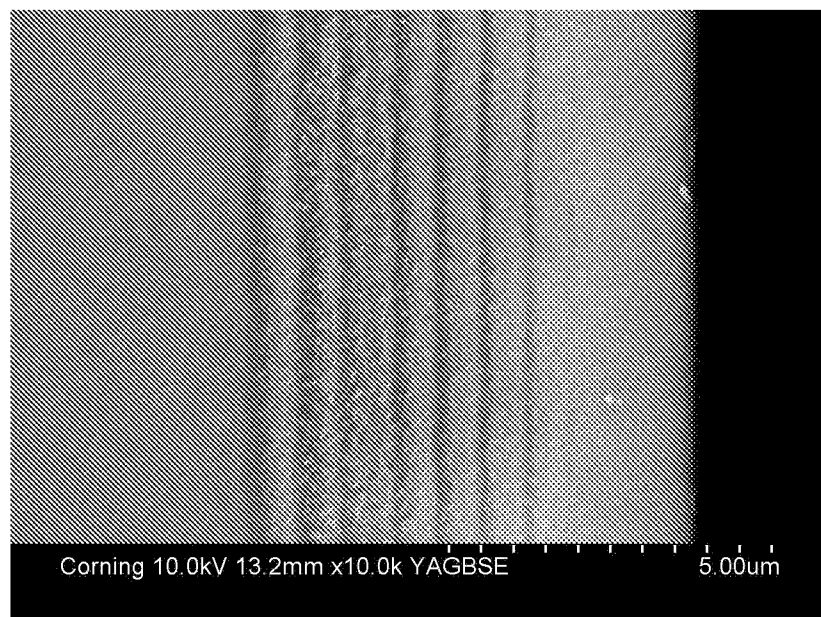


Figure 1

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/030704

A. CLASSIFICATION OF SUBJECT MATTER

INV. C03C3/089 C03C3/091 C03C3/093 A61L2/238
ADD.

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)

C03C A61L

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 3 146436 A (U H I SYST KK) 21 June 1991 (1991-06-21)	1,2,6,7, 9-11,14, 15,17, 18,20
A	abstract page 208; table 1 page 211; table 4	3-5,8, 13,16, 19,21-24
X	JP 10 218641 A (NIPPON GLASS FIBER CO LTD) 18 August 1998 (1998-08-18)	1,2,6,7, 9-11,14, 15,17, 18,20
A	abstract paragraph [0072] - paragraph [0073] claim 1	3-5,8, 13,16, 19,21-24
	----- -/-	



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

"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

26 June 2012

Date of mailing of the international search report

04/07/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Picard, Sybille

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/030704

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 2002 0009963 A (KANG WON HO [KR]) 2 February 2002 (2002-02-02)	1,6,7,9
A	abstract claim 1 example 1 figure 1	2-5,8, 10,11, 13-24
A	----- EP 1 449 816 A1 (GEMTRON CORP [US]) 25 August 2004 (2004-08-25) abstract claims 1-3 -----	1-11, 13-24

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/030704

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.: 12
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:
see FURTHER INFORMATION sheet PCT/ISA/210
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:

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 an 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.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 12

The additional feature of claim 12 is the R- value, however R is not defined in claim 12 or in any upper claim. R appears in claim 14 but it is unclear if it would have or not the same meaning. Furthermore, the "R -value" is not defined and therefore cannot be compared with the prior art. As a consequence, no search on that claim could be made.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/030704

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 3146436	A	21-06-1991	JP 2015755 C 19-02-1996
			JP 3146436 A 21-06-1991
			JP 7014825 B 22-02-1995

JP 10218641	A	18-08-1998	NONE

KR 20020009963	A	02-02-2002	NONE

EP 1449816	A1	25-08-2004	BR PI0400578 A 04-10-2005
			CA 2458425 A1 20-08-2004
			CN 1557756 A 29-12-2004
			EP 1449816 A1 25-08-2004
			JP 2004250327 A 09-09-2004
			KR 20040075283 A 27-08-2004
			MX PA04001649 A 25-08-2004
			US 2004166173 A1 26-08-2004
