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(21) International Application Number: PCT/US98/18745 (22) International Filing Date: 10 September 1998 (10.09.98) (30) Priority Data: <table border="0"> <tr> <td>60/058,712</td> <td>12 September 1997 (12.09.97)</td> <td>US</td> </tr> <tr> <td>08/948,565</td> <td>10 October 1997 (10.10.97)</td> <td>US</td> </tr> <tr> <td>197 47 355.5</td> <td>27 October 1997 (27.10.97)</td> <td>DE</td> </tr> </table> (71) Applicants (for all designated States except US): OSRAM SYLVANIA INC. [US/US]; 100 Endicott Street, Danvers, MA 01923 (US). SCHOTT GLAS [DE/DE]; Hattenbergstrasse 10, D-55122 Mainz (DE). (72) Inventors; and (75) Inventors/Applicants (for US only): MARLOR, Richard, C. [US/US]; 77 Lothrop Street, Beverly, MA 01915 (US). NAUMANN, Karin [DE/DE]; Gutenbergstrasse 19, D-55270 Ober-Olm (DE). OTT, Franz [DE/DE]; Glaswerk 30, D-95666 Mitterteich (DE). BECKER, Ottmar [DE/DE]; Westendstrasse 30, D-63225 Langen (DE). (74) Agent: HARGEST, Robert, F.; Young & Thompson, 745 South 23rd Street, Arlington, VA 22202 (US).		60/058,712	12 September 1997 (12.09.97)	US	08/948,565	10 October 1997 (10.10.97)	US	197 47 355.5	27 October 1997 (27.10.97)	DE	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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(54) Title: LONG LIFE HALOGEN CYCLE INCANDESCENT LAMP AND GLASS ENVELOPE COMPOSITION (57) Abstract A long life, halogen cycle, incandescent lamp (30) for operation in excess of 85 volts. The lamp comprises a transparent glass envelope (34) having sealed therewithin a tungsten filament (45); a pair of electrical lead-ins (42, 44) connecting the filament and extending exteriorly of the envelope for connection to a supply voltage greater than 100 V; and a fill gas within the envelope, including a halogen, at a pressure of at least three atmospheres. The envelope is constructed of a five component alkaline earth aluminosilicate glass having a composition consisting essentially of, in weight percent from > 58 to about 64 % SiO₂, from about 14 to about 17 % Al₂O₃; from 0 to about 1 % B₂O₃, from 1 to about 6 % MgO, from about 6 to about 12 % CaO, from about 7 to about 17 % BaO and from 0 to about 1.5 % ZrO₂.											

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EE	Estonia						

TITLE**LONG LIFE HALOGEN CYCLE INCANDESCENT LAMP AND GLASS
ENVELOPE COMPOSITION**

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This application claims the benefit of U.S. Provisional application No. 60/058,712, filed September 12, 1997; U. S. Serial No. 08/948,565, filed October 10, 1997; and German Application No. 197 47 355.5, filed October 27, 1997.

10

TECHNICAL FIELD

This invention relates to lamps and more particularly to incandescent halogen lamps. Still more particularly, it relates to a glass for the envelope of halogen lamps.

15 **BACKGROUND ART**

Lamps operating by a tungsten-halogen cycle are known. In operation, tungsten-halogen lamps contain a non-reactive gas filling such as neon, nitrogen, argon, krypton or xenon or a combination thereof, together with a halogen, usually bromine, which combines with the evaporated tungsten escaping from the incandescent filament. An equilibrium concentration is attained by the gaseous species within the lamp between the temperature limits defined by the incandescent filament and the coldest spot in the lamp envelope. The cold spot temperature must be sufficiently high to prevent any tungsten halide from condensing and, providing that this condition is met, a continuous transport cycle operates which keeps the envelope free from tungsten.

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Numerous hard glasses, such as the aluminosilicates, have been employed with tungsten halogen lamps with varying degrees of success. Such glasses include Corning Incorporated nos. 1720, 1724 and 1725; glass nos. 8252 and 8253 available from Schott; no. 180 available from General Electric.

30

The 1720, 1724 and 8252 glasses have been used successfully with low voltage applications (i.e., 12v), such as automobile headlamps which operate with wall temperatures below 500°C; however, for line voltage applications, i.e., voltages greater than 85v, with wall temperatures much greater than 500°C, these glasses prove unusable due to an inability to maintain good seals. This condition has been

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attributed to a structural compaction of the glass during operation. The compacted glass results in stresses, which can exceed the breaking strength of the glass, ultimately rupturing the lamp seal.

- 5 Other glasses, such as 1725, 180, and 8253, which all have substantially higher glass strain points, while employable with the higher wall temperatures generated by reduced envelope size and greater voltages, i.e., voltages in excess of 85 volts, will not fail from compaction but ultimately from blackening caused by the tungsten deposition on the inner bulb wall and, subsequently, in a non-passive lamp failure, i.e., the lamp capsule explodes. Ideally, lamp failure should be passive, i.e., by breakage of the filament. Typically, the halogen gas employed is either HBr or CH_3Br . As previously noted, the concentration of the bromine (or other halogen) is critical for controlling the halogen cycle with tungsten. While the glasses enumerated above work well initially, after a given period of time there is a reaction of the alkaline earth cations with the bulb wall, thus depleting the bromine from the halogen cycle. The reaction products typically are BaBr_2 and CaBr_2 , which show as a white haze on the interior of the lamp envelope surface. Halogen lamps are typically designed with this reaction as a limiting factor in lamp performance.
- 10
- 15
- 20 It has been suggested that the alkaline earth reaction with bromine could be decreased by the application of a barrier coating of silica to the interior surface of the lamp envelope (see U.S. Patent No. 5,473,226, assigned to the assignee of the instant invention); however, this solution is costly and not completely effective.
- 25 It would be an advance in the art if a glass could be developed which eliminated or substantially reduced the combination effect of the halogen with the glass material in lamps using power supplies of greater than 85 volts whereby the performance (through increased lumen maintenance) and life of the lamps could be improved; that is, extended to beyond 2500 hours without substantial deterioration in light output.

DISCLOSURE OF INVENTION

It is, therefore, an object of my invention to obviate the disadvantages of the prior art.

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It is another object of my invention to enhance the performance of halogen cycle lamps.

Yet another object of my invention is the provision of a glass for tungsten halogen
10 lamps, which delivers the above results and yet remains economical to manufacture.

These objects have been accomplished, in one aspect of the invention, by providing a long life, halogen cycle, incandescent lamp for operation in excess of 85 volts which comprises: a transparent glass envelope having sealed therewithin a tungsten filament;
15 a pair of electrical lead-ins connecting the filament and extending exteriorly of the envelope for connection to a supply voltage greater than 85 v; and a fill gas within the envelope including a halogen, at a pressure of at least three atmospheres. The envelope is constructed of an alkaline earth aluminosilicate glass having a composition consisting essentially of, in weight percent, from >58 to about 64% SiO₂,
20 from about 14 to about 17.5% Al₂O₃; from 0 to about 1% B₂O₃, from 1 to about 7% MgO, from about 5.5 to about 14% CaO, from about 6 to about 17% BaO, from 0 to about 8% SrO, and from 0 to about 1.5% ZrO₂. Trace amounts of other compounds such as CeO₂, or TiO₂ may be present in amounts less than 1 % by weight. In a preferred aspect of the invention the envelope is constructed of an aluminosilicate
25 glass having a reduced affinity for halogens, comprising, in weight percent: from 59 to about 61% SiO₂, from about 15.3 to about 17.2% Al₂O₃; from about 0.3 to about 0.5% B₂O₃, from 1 to about 6.5% MgO, from about 5.9 to about 13.5% CaO, from about >6.5 to about 9.5% BaO, from 0 to about 8% SrO, from about 0.05 to about 1% ZrO₂, from about 0 to about 0.3% CeO₂, and from about 0 to about 0.5% TiO₂.

BRIEF DESCRIPTION OF THE DRAWINGS

The single figure is a cross-sectional view of a tungsten halogen lamp employing the
5 invention.

BEST MODE FOR CARRYING OUT THE INVENTION

For a better understanding of the present invention, together with other and further
10 objects, advantages and capabilities thereof, reference is made to the following disclosure and appended claims taken in conjunction with the above-described drawings.

Referring now to the drawings with greater particularity, there is shown in the figure a
15 lamp 30 having a longitudinal axis L and comprising an outer envelope 32 and an inner envelope 34, frame assembly 36, and a base 38. The outer envelope 32 has a neck portion 40. The inner envelope 34 is a tungsten halogen incandescent capsule with a filament 45 therein having electrical lead-ins 42 and 44 connected thereto and extending exteriorly of the body 34 for connection to a source of supply voltage
20 greater than 85v. The capsule 34 in this instance is mounted upon a frame 36.

The capsule 34 is constructed of the glass of this invention and contains a gaseous fill comprised of an inert gas and a halogen. In a preferred embodiment of the invention, the fill comprises 95 % Kr, about 5% N₂ and 0.10 % HBr and is at a pressure of 3-8
25 atmospheres.

The aluminosilicate glass of capsule 34 consists essentially of, in weight percent, from >58 to about 64% SiO₂, from about 14 to about 17.5% Al₂O₃, from 0 to about 1% B₂O₃, from about 1 to about 7% MgO, from about 5.5 to about 14% CaO, from about
30 6 to about 17% BaO, from 0 to about 8% SrO, and from 0 to about 1.5% ZrO₂. In a preferred embodiment of the invention the boron oxide and the zirconium oxide would be eliminated as they have no known effect on lamp operation; however, minor

amounts may be necessary to aid in the melting process. It may also be advisable to include a minor amount of zinc oxide to control liquidus, as well as minor amounts of CeO_2 and/or TiO_2 to control the UV absorption edge. In glasses suitable for use in tanning lamps, up to 2-wt. % Br^- can be added. This will correspond to approximately
5 up to 0.6 wt. % in the finished glass, based on the volatility of the compounds used (e.g., BaBr_2).

Some of the glasses of the invention were tested for bromine depletion against the prior art glasses in the following manner. A fused quartz reaction vessel having a
10 length of about 5 inches and a diameter of about 5 inches was loaded with capsule glass tubing formed from various compositions of glass nos. 8253, 180, 1725, 1724, 1720 and the glass of my invention. The composition of these glasses is shown in Table I.

Table I

	1720	1724	8252	1725	180	8253
Oxides	Corning	Corning	Schott	Corning	GE	Schott
SiO ₂	60.63	57.2	60	63.4	62.1	61.9
Al ₂ O ₃	16.22	16.3	14.5	14.5	14.3	16.2
B ₂ O ₃	5.02	4.35	4.5	0.05	0	0.34
MgO	8.17	5.79	2.0	0.2	0	0.05
CaO	9.45	8.03	10.0	11.2	6.5	12.5
BaO		8.07	9.0	10.4	16.8	7.7
SrO		0		0.2	0.2	0.1
Na ₂ O	0.51	0.038		0.03	0.02	0.08
K ₂ O		0.024		0.02	0.01	0.01
ZrO ₂		0.16		0	0	1.1
Fe ₂ O ₃		0.048		0.041	0.033	0.031
TiO ₂					0.21	
BaO/CaO [moles]		0.37	0.33	0.34	0.95	0.22
MgO/CaO [moles]	1.20	1.00	0.28			
Molar % RO	23.0	22.4	19.2	18.3	16.1	18.5
Physical Properties						
Softening Point [°C]	915	926	940	993	1020	1000
Anneal Point [°C]	712	726	725	778	786	783
Strain Point [°C]	668	674		716	733	733
Thermal Expansion 23-300C [x10 ⁻⁷ /C]	42	44	46	45	43	45
Density [g/cc]	2.52	2.56	2.63	2.72	2.68	2.62

The quartz reaction vessel was evacuated, backfilled with a gas consisting of about 80% Kr, 19% N and 1% HBr at a pressure of 1 atmosphere, and sealed. The reaction vessel was placed in an isothermal portion of an oven and heated at 610°C for 500 hours. After cooling, the reaction vessel was opened, the test glass tubing removed, stoppered at one end and filled with deionized water. The opposite end was then stoppered and the capsule tubing were heated to 100°C for one hour to dissolve the water soluble reaction products formed on the inner surfaces of the capsule cylinders. The water content of each of the capsule tubes was then analyzed for bromine, calcium, magnesium, barium, strontium (one of the glass samples had a small amount of CaO replaced by SrO), and sodium. The results are shown in Table II.

Table II

Concentration in original solution in millimoles/liter						
Description	Br	Ba	Ca	Mg	Sr	Na
8253, Partial Substitution of SrO for CaO	0.390	0.036	0.083	0.000	0.062	0.019
GE180, Production Composition	0.388	0.109	0.060	0.000	0.004	0.007
8253, Without ZrO ₂ and B ₂ O ₃	0.348	0.023	0.146	0.000	0.001	0.010
8253D, Production Composition	0.319	0.020	0.135	0.000	0.002	0.011
8253, Without ZrO ₂	0.229	0.018	0.124	0.000	0.001	0.007
8253, Lower Alkali Production Glass	0.189	0.008	0.061	0.000	0.000	0.006
1725, Production Composition	0.154	0.032	0.099	0.000	0.002	0.012
1724, Lab Melt	0.035	0.007	0.008	0.001	0.000	0.003
8253, Partial Substitution of MgO for CaO	0.034	0.007	0.009	0.001	0.000	0.003
1724, Production Composition	0.030	0.006	0.007	0.001	0.000	0.003
1720, Production Composition [0.5 wt% alkali]	0.012	0.000	0.006	0.001	0.000	0.005
8253D, No HBr Treatment [Control]	0.002	0.000	0.004	0.000	0.000	0.002

One of the glasses of this invention is shown in Table II as "8253, Partial Substitution of MgO for CaO". It will be seen that this glass, under identical test conditions, had far less bromine reaction than any of the other high temperature glasses. The lower temperature glasses, i.e., 1720 and 1724, also had low bromine contamination as was expected from their use in low voltage applications; however, as noted above, these glasses cannot be used in high voltage applications because of their low glass strain

points which results in structural compaction and, ultimately, in the lamp failing nonpassively when cracks develop at the inner glass-inlead wire interface.

Other glasses of the invention were prepared as follows:

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EXAMPLES

Alkali-poor variants were used each time for the production of the example glasses, such as quartz sand, aluminum oxide, magnesium carbonate, calcium carbonate and
10 barium carbonate, as well as zirconium sand. If desired, cerium oxide and barium bromide can be added. The well-homogenized mixtures were melted in the laboratory in a Pt/Rh crucible at 1600 - 1650°C, refined and homogenized. The glass was drawn perpendicularly in a laboratory pulling device. The glasses were free of disruptive small crystals. Table III shows an example of a glass (A5) according to an aspect of
15 the invention as well as a comparative example (V1) with their compositions (in wt.% based on the oxides) and their essential properties.

The reboil temperature is indicated, along with the transformation temperature (T_g). The reboil temperature is the temperature at which a visually bubble-free glass sample
20 at room temperature suddenly shows bubble formation at the interface with a metal (sample holder, Mo) when the temperature is increased. The higher this reboil temperature lies, the less the glass tends toward bubble formation when sealed to Mo. In the comparison example the upper cooling point (UCP) is indicated in place of T_g .

25 Tungsten-halogen lamps with high power were prepared from glass tubes in the usual way for a lamp test. These were subjected to a continuous operation at a bulb temperature of 700°C. The time period prior to the beginning of blackening on the

inside of the glass bulb was determined. The value for A5 is also sufficiently good.
In the case of V1, a bulb bulging occurred.

Table III

	A5	V1
SiO ₂	60.7	56.8
Al ₂ O ₃	16.5	16.4
B ₂ O ₃	0.3	4.7
MgO	5.7	5.8
CaO	7.8	7.8
SrO	—	—
BaO	8.0	8.0
ZrO ₂	1.0	—
CeO ₂	—	—
Br	—	—
Na ₂ O	0.011	0.028
K ₂ O	0.006	0.018
H ₂ O (wt.%)	0.01	0.017
$\alpha_{20/2000}$ (10 ⁻⁶ /K)	4.37	4.52
T _g [°C]	781	721 (UCP)
Reboil temp. [°C]	1490	n.d.

Additionally, it is preferred that the sum of the alkaline-earth oxides (RO) not be
below 21 wt.% nor above 24 wt.%. Outside of these ranges both the thermal
expansion and the viscosity have been found to deviate from the desired values.

Further, the weight ratio between the sum of CaO, SrO and MgO, on the one hand,
and BaO on the other hand ((CaO + SrO + MgO) / BaO) shall amount to between 1.45
and 1.75. Preferably, it amounts to between 1.65 and 1.75.

Also, it is believed that the weight ratio of MgO to CaO is important; therefore,
MgO/CaO will be always be greater than 0 and, preferably, less than about 0.8;
otherwise, the crystallization stability of the glass would not be adequate for tube
pulling.

It is believed that the advantages of this invention arise because the ionic transport is
slower for the triple, mixed alkaline earth oxides (BaO, CaO, MgO) than for the

double alkaline earth oxides (BaO, CaO) systems employed in the prior art glasses previously used for high voltage lamps, i.e., GE 180, Corning 1725 or Schott 8253. Also important in the manufacture of the glass of this invention is the elimination or reduction to the absolute minimum of alkali contamination, that is, the presence of sodium, lithium and/or potassium should be kept below 0.05% by weight. Thus, there is provided by this invention a five component alumino-silicate system (SiO₂, Al₂O₃, BaO, CaO, MgO) with distinct advantages over the prior art, namely in its lack of bromine reaction products at the inner surface of a lamp operating under the halogen cycle, thereby permitting longer operation with better maintenance. Additionally, nonpassive failures are reduced or eliminated as the lamp burns cleanly until a normal end of life is achieved.

While there have been shown and described what are at present considered the preferred embodiments of the invention, it will be apparent to those skilled in the art that various changes and modifications can be made herein without departing from the scope of the invention as defined by the appended claims.

CLAIMS

What is claimed is:

- 5 1. A long life, halogen cycle, incandescent lamp for operation in excess of 85 volts comprising: a transparent glass envelope having sealed therewithin a tungsten filament; a pair of electrical lead-ins connecting said filament and extending exteriorly of said envelope for connection to a supply voltage greater than 85 v; and a fill gas within said envelope including a halogen at a pressure of at least three
10 atmospheres, said envelope being constructed of an alkaline earth aluminosilicate glass having a composition consisting essentially of, in weight percent, from >58 to about 64% SiO₂, from about 14 to about 17.5% Al₂O₃; from 0 to about 1% B₂O₃, from 1 to about 7% MgO, from about 5.5 to about 14% CaO, from about 6 to about 17% BaO and from 0 to about 1.5% ZrO₂.
- 15 2. The lamp of claim 1 wherein said halogen is bromine.
3. The lamp of Claim 1 wherein said pressure is up to about 8
20 atmospheres.
4. The lamp of Claim 3 wherein said lamp, when operating, has a wall temperature greater than 500 °C.
5. The lamp of Claim 4 wherein said envelope composition includes a
25 minor amount of ZnO to control liquidus.
6. The lamp of Claim 5 wherein said fill gas includes an inert gas.
7. The lamp of Claim 6 wherein said halogen is bromine.
- 30 8. An aluminosilicate glass having a reduced affinity for halogens, comprising, in weight percent: from >58 to about 64% SiO₂, from about 14 to about

17.5% Al_2O_3 ; from about 0 to about 1% B_2O_3 , from 1 to about 7% MgO , from about 5.5 to about 14% CaO , from about 6 to about 17% BaO , and from 0 to about 8% SrO .

9. The glass of Claim 8 wherein said composition has up to about 1%
5 B_2O_3 .

10. The glass of Claim 9 wherein said composition has up to about 1.5%
 ZrO_2 .

10 11. The glass of Claim 10 wherein a minor amount of ZnO replaces a
minor amount of CaO to control the liquidus.

12. An alkaline-earth aluminosilicate glass consisting essentially of, in
wt.% based on the oxides, >58 to about 64% SiO_2 , from about 14 to about 17.5%
15 Al_2O_3 ; from 0 to about 1% B_2O_3 , from 1 to about 7% MgO , from about 5.5 to about
14% CaO , from about 6 to about 17% BaO , from 0 to about 1.5% ZrO_2 , and from 0 to
about 8% SrO .

13. The glass of Claim 12 wherein the sum of the alkaline-earth oxides is
20 not below 21 wt.% nor above 24 wt.%.

14. The glass of Claim 12 wherein the weight ratio of $(\text{CaO} + \text{SrO} +$
 $\text{MgO})/\text{BaO}$ is between 1.45 and 1.75.

25 15. The glass of Claim 14 wherein said weight ratio is between 1.65 and
1.75.

16. The glass of Claim 14 wherein said glass has an alkali oxide content of
< 0.03 wt.% and a water content of < 0.02 wt.%.

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17. The lamp of Claim 1 wherein said B_2O_3 is present in an amount of 0.2
to 0.7 wt.%.

18. The lamp of Claim 1 wherein the amount of ZrO_2 is from 0.05 to 1 wt.%.

5 19. An aluminosilicate glass having a reduced affinity for halogens, comprising, in weight percent: from >58 to about 64% SiO_2 , from about 14 to about 17.5% Al_2O_3 ; from about 0 to about 1% B_2O_3 , from 1 to about 7% MgO , from about 5.5 to about 14% CaO , from about 6 to about 17% BaO , from about 0 to about 8% SrO , from about 0 to about 1.5% ZrO_2 , from about 0 to about 0.3% CeO_2 , and from
10 about 0 to about 0.5% TiO_2 .

20. An aluminosilicate glass having a reduced affinity for halogens, comprising, in weight percent: from 59 to about 61% SiO_2 , from about 15.3 to about
15 17.2% Al_2O_3 ; from about 0.3 to about 0.05% B_2O_3 , from 1 to about 6.5% MgO , from about 5.9 to about 13.5% CaO , from about >6.5 to about 9.5% BaO , from about 0 to about 8% SrO , from about 0.05 to about 1% ZrO_2 , from about 0 to about 0.3% CeO_2 , and from about 0 to about 0.5% TiO_2 .

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21. An aluminosilicate glass having a reduced affinity for halogens, comprising, in weight percent: about 60.7% SiO_2 , about 16.5% Al_2O_3 ; about 0.3% B_2O_3 , about 5.7% MgO , about 7.8% CaO , about 8% BaO , about 1% ZrO_2 , from about 0 to about 0.3% CeO_2 , and from about 0 to about 0.5% TiO_2 .

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22. The lamp of Claim 1 wherein said envelope also includes from >0 to about 8% SrO .

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/18745

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01K 1/50

US CL : 313/579, 636

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)

U.S. : 313/579, 636, 570, 567

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)

U.S. PTO (APS): HALOGEN, CYCLE, INCANDESCENT, LAMP, COMPOSITION, ALUMINOSILICATE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

RONALD E. DELGIZZI

Telephone No. (703) 305-4900