(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 881 995 B9

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**
Note: Bibliography reflects the latest situation

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see page(s) 6, 7

(48) Corrigendum issued on:
22.05.2002 Bulletin 2002/21

(45) Date of publication and mention of the grant of the patent:
07.11.2001 Bulletin 2001/45

(21) Application number: **97905883.1**

(22) Date of filing: **11.02.1997**

(51) Int Cl.[7]: **C03C 3/064**, C03C 4/08, F21V 9/06, A61K 7/42

(86) International application number:
PCT/US97/02078

(87) International publication number:
WO 97/30947 (28.08.1997 Gazette 1997/37)

(54) STRONG UV ABSORBING GLASS

GLAS MIT STARKER UV-ABSORBTION

VERRE A GRANDE ABSORPTION D'UV

(84) Designated Contracting States:
DE FR GB NL

(30) Priority: **21.02.1996 US 11995 P**

(43) Date of publication of application:
09.12.1998 Bulletin 1998/50

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EP 0 881 995 B9

Printed by Jouve, 75001 PARIS (FR)

Description

BACKGROUND OF THE INVENTION

[0001] Recently, a great deal of attention has been directed to the harmful effects of ultraviolet (UV) radiation on humans. Much of the attention has concerned the effect of such radiation on the eye. Accordingly, the value of strong UV absorption by eye glasses has been recognized.

[0002] It is well known that UV radiation can also cause degradation and discoloration in such items as paints, fabrics and plastics. Therefore, strong UV absorption by architectural glazing materials is beneficial. The sun is not the only light source that emits UV. Various types of artificial lighting, such as halogen lamps, may also emit UV radiation. Accordingly, there is an interest in minimizing UV radiation emitted by artificial sources as well. This may be achieved by utilizing UV absorbing glass in the fabrication of lamp envelopes, reflectors and lenses.

[0003] It is common knowledge that photochromic glasses are activated by absorption of UV radiation. The most evident utility of such glasses has been in control of visible light transmission. Inherently, however, they also strongly influence the intensity of UV transmission. This behavior is readily understood in terms of the Grotthus-Draper Law which states that: Only light that is absorbed can produce chemical change.

[0004] Photochromic glasses containing silver halide crystals absorb strongly at wavelengths shorter than 320 nm, but only absorb weakly in the interval between 320 and 400 nm. Even though radiation in the wavelength range of 320-400 nm is much less harmful than that in the shorter wavelength region, for some applications it is desirable to eliminate transmission of this radiation as well. Therefore, several suggestions have been advanced for accomplishing this. For example, it has been proposed to dope the above glasses with ions which provide additional absorption of UV radiation.

[0005] Photochromic glasses containing halides of copper and/or cadmium are also known, but not commercially available. Such glasses were originally disclosed in United States Patent No. 3,325,299 (Araujo I). The transmission cutoff in these glasses occurs at approximately 400 nm, and is much sharper than that in silver halide glasses. Consequently, protection against UV radiation is complete in these glasses without additional doping. The precipitation of the copper halide phase in these glasses is like that of the silver halide phase in the silver halide photochromic glasses. It may require heating of a glass containing in solution the copper and halogen ions of interest. As taught in the patent, the glass is maintained for a short time at a temperature somewhat above the annealing point.

[0006] United States Patent No. 4,166,745 (Araujo II) discloses copper-cadmium photochromic glasses that have a refractive index of 1.52-1.54, and that may be strengthened by an exchange of sodium ions for lithium ions.

[0007] United States Patent No. 4,222,781 (Morse et al.) discloses photochromic glasses based on copper halide wherein good optical clarity and photochromic properties are provided by controlling the alkali metal oxide, the Al_2O_3 and the B_2O_3 concentrations in the base glass, and/or by adding MoO_3 or WO_3 to the composition.

[0008] European Publication Number 0 456 351 A2 [U.S. Patent No, 5,145,805] (Tarumi et al) discloses two glass families containing up to 15% copper halide. The non-phosphate family comprises, in percent by weight, 20-85% SiO_2, 2-75% B_2O_3, up to 15% Al_2O_3, up to 30% alkali metal oxides, up to 10% divalent metal oxides and up to 10% of at least one of ZrO_2, La_2O_3, Y_2O_3, Ta_2O_3 and Gd_2O_3. The broad ranges of this disclosure fail to disclose critical features of the present invention.

[0009] There are numerous applications for glasses having the sharp UV cutoff inherent in the copper or copper-cadmium halide glasses. Frequently, however, such applications require avoiding any change in visible absorption such as occurs in photochromic glasses exposed to UV radiation, e.g., sunlight. Many UV materials exhibit yellow color which is unacceptable for certain applications. U.S. 5,322,819 (Araujo III) disclosed a non-photochromic, copper halide containing UV absorbing glass which exhibits a sharp cutoff in transmission in the wavelength interval between visible and UV radiation. Specifically, the Araujo III reference ('819) disclosed a non-photochromic R_2O-B_2O_3-SiO_2 glass which contains a precipitated cuprous or cuprous-cadmium halide crystal phase and has a sharp spectral cutoff at about 400 nm, the glass composition consisting essentially of, in cation percent, 35-73% SiO_2, 15-45% B_2O_3, 0-12% Al_2O_3, the Al_2O_3 being less than 10% when the SiO_2 is over 55%, 0-12% Li_2O, 0-20% Na_2O, 0-12% K_2O, the $Li_2O+Na_2O+K_2O$ being 4.75-20%, 0-5% CaO+BaO+SrO, 0.125-1.0% Cu_2O, 0-1% CdO, 0-5% ZrO_2, 0-0.75% SnO_2, 0-1% As_2O_3, and/or Sb_2O_3, the glass containing 0-1.25% Cl, 0-1.0% Br, 0.25-2.0% Cl+Br and 0-2% F by weight.

[0010] For certain applications such as for protecting the human skin and articles having complex shapes and sizes, currently available UV absorbing glass may not be practical for providing the needed protection. Thus, while the glasses disclosed in the '819 patent have been shown to be very effective in absorbing UV radiation, such glasses are generally available in bulk form, making then impractical for certain applications such as UV absorbing paints and varnishes as well as UV absorbing skin creams for example. Accordingly, it is a principal object of the present invention to provide UV absorbing glass in a form which can be readily utilized in such applications.

SUMMARY OF THE INVENTION

[0011] The object of the present invention is achieved by providing UV absorbing glass in a form suitable for protecting from UV radiation, articles having complicated shapes. Examples suitable forms of the inventive UV absorbing glass material include, (1) a liquid such as a lotion or cream for protecting the skin, (2) paints and varnishes for applying over articles having complicated shapes and sizes, and (3) a solution with which clothing can be impregnated to form UV absorbing clothing.

[0012] Briefly, the invention relates to a strong UV absorbing glass consisting essentially of, in cation percent, 15-30% SiO_2, 50-60% B_2O_3, 2-5% Al_2O_3, 0-6% Li_2O, 0-3.0% Na_2O, 14-20% K_2O, 0.5-1.0% CuO, 0.4-0.7% SnO_2, 0.5-1.5% Cl, and 0.7-1.5% Br.

[0013] In another aspect, the invention relates to a method of making UV absorbing liquid or gel by:

a) providing a UV absorbing glass;
b) grinding the glass into fine powder having average particle size in the range of 1-5 microns; and
c) suspending the fine powder in a matrix to form a liquid.

[0014] In still another aspect, the invention relates to a method of producing essentially haze-free (i.e., transparent), strong UV absorbing glass by:

a) providing a strong UV absorbing glass having a known refractive index, and containing copper and halides;
b) melting the glass;
c) quenching the glass by rolling said glass into a thin roll or ribbon; and
d) heat treating said ribbon to form an essentially haze-free, UV absorbing glass.

The heating process leads to the growth of copper halide crystals in the glass.

[0015] Optionally, for applications where it is not practical to apply the roll or ribbon of glass over the article, the UV absorbing glass ribbon can be ground into a fine powder which can subsequently be suspended in a matrix to form a UV absorbing liquid which can then be applied to the surface of the article to be protected. For applications requiring transparency, the refractive index of the matrix is preferably the same or substantially the same as that ofthe UV absorbing glass. A particularly useful matrix for such applications is index matching oil. Examples of applications where use of the liquid form may be useful include, UV absorbing paints and varnishes, UV absorbing body lotions or creams, as a spray for such objects as automobiles and boats, and other similar applications. In a further aspect, the invention relates to a method of making a transparent UV absorbing liquid by:

a) providing a strong UV absorbing glass composition consisting essentially of, in cation percent, 15-30% SiO_2, 50-60% B_2O_3, 2-5% Al_2O_3, 0-6% Li_2O, 0-0.7% Na_2O, 14-20% K_2O, 0.5-1.0% CuO, 0.4-0.7% SnO_2, 0.5-1.5% Cl, and 0.7-1.5% Br,
b) melting the glass;
c) forming the melt into a thin sheet of glass to quench the glass;
d) heat treating the glass to grow tiny crystals of CuCl in the glass;
e) grinding the heat-treated sheet of glass into fine powder having average particle size in the range of 1-5 microns;
f) suspending the fine powder in a transparent liquid to form a transparent UV absorbing liquid.

[0016] In still a further aspect, the invention relates to a method of protecting an article from UV radiation by applying a coating of the inventive UV absorbing liquid on the surface of the article to be protected.

DETAILED DESCRIPTION OF THE INVENTION

[0017] UV absorption in transparent colorless glasses that strongly absorb UV radiation, such as disclosed in U.S. 5,322,819, is due to the suspension of minute crystallites of cuprous halides. Previous attempts to make photochromic plastics by suspending finely ground photochromic glass failed because when the photochromic glass was ground sufficiently fine to make transparent suspensions in organic matrices, no photochromism was observed. Further, the finely ground photochromic glass exhibited a noticeable grey color. Although the reason for this loss of photochromism and color change was never shown, it is widely believed that radiation associated with fast crack propagation during the grinding process photolyzed the silver halide suspended in the glass thereby producing the grey color and destroying photochromism.

[0018] With this background, it was not clear that UV absorbing materials can be made by suspending finely ground powders of UV absorbing glass in a matrix without a similar loss of the UV absorbing properties. Thus, the first part of

the present invention was to determine whether grinding would destroy the cuprous halide particles in UV absorbing glass in the same way silver halide particles were destroyed in photochromic glasses. This is the subject of Example 1 below. As described in the example, grinding does not destroy cuprous halide crystallites. Without intending to be bound by theory, I believe that unlike the situation in photochromic glasses, in these glasses, radiation does not photolyze the crystallites. The sharp UV absorption observed in these glasses correspond to exciton formation. The exciton energy is immediately dissipated in the excitation of lattice modes and the crystal relaxes to its ground state. Thus, even if grinding does generate energetic radiation, photolysis of the cuprous halide is unlikely to pose a problem.

[0019] Another question to be investigated was whether a higher density of cuprous halide particles could be precipitated in glass than had been previously produced. This was important because, unless this could be done, the strength of the UV absorption in thin films would be too weak for many of the intended applications. Accordingly, I have discovered that a family of glasses which contain very high levels of boric oxide and relatively low levels of silica exhibit much stronger UV absorption than currently available UV absorbing glasses. Examples of this family of glasses are described in Table 1 below.

TABLE 1

(In cation %, except for the halides which are given in weight %)					
Oxide	Comparative Glass 1	Glass 2	Glass 3	Glass 4	Glass 5
SiO_2	57.5	22.0	22.0	22.0	22.5
B_2O_3	26.0	55.4	55.4	55.4	55.4
Al_2O_3	2.0	3.0	3.0	3.0	3.0
ZrO_2	3.0	--	--	- -	--
Li_2O	2.5	--	2.0	5.0	2.0
Na_2O	7.5	0.5	0.5	0.5	0.5
K_2O	1.5	19.1	17.1	14.1	17.1
CuO	0.35	0.65	0.65	0.65	0.85
SnO_2	0.2	0.43	0.43	0.43	0.6
Cl	0.75	1.0	1.0	1.0	1.0
Br	1.0	1.0	1.0	1.0	1.0

[0020] It is known that the precipitation of either silver halide or cuprous halide is stimulated by a change in bonding of boron during the heat treatment of the glass. As a result, the amount of halide precipitated tends to increase as the amount of boric oxide in the glass increases. For this reason, the inventive glass composition is preferably low in silica and high in boric oxide.

[0021] Another class of inventive glasses are those having high levels of copper and halides. While strong UV absorption was observed in this class of inventive glass, I have found that as the precipitated cuprous halide increases, the haze level of the glass also increases. This family of strong UV absorbing glasses generally consist of, expressed in cation percent, 15-30% SiO_2, 50-60% B_2O_3, 2-5% Al_2O_3, 0-6% Li_2O, 0-3.0% Na_2O, 14-20% K_2O, 0.5-1.0% CuO, 0.4-0.7% SnO_2, 0.5-1.5% Cl, and 0.7-1.5% Br. It should be noted that the higher the amount of Na_2O, the lower the UV absorption of the glass. In one particularly useful embodiment, the preferred range of Na_2O is in the range of 0.2-0.7%.

[0022] I have discovered that if the glasses are quenched from the melt (for example, by rolling them into thin ribbons), and subsequently heating the rolled glass for very long times at low temperatures, strong UV absorption can be obtained with relatively low levels of haze. This is illustrated in Examples 3 and 4 below. By way of example, one method of rolling the glass is by pouring the melt into a steel plate and rolling the melt with a steel roller. The act of rolling quenches (or quickly cools) the glass and keeps it transparent. Haze is maintained at a low level by avoiding large crystal growths in the glass. The low temperature treatment of the rolled glass allows tiny copper halide crystals (e.g., CuCl) crystals to grow such that strong UV absorption is achieved without haze.

[0023] As stated, the higher the levels of copper and halides, the higher the level of haze in the glass. Thus, it is expected that even stronger UV absorption as those measured in the aforementioned glass composition can be achieved by substantially increasing the amounts of copper and halides in the glass. However, because it is not possible to measure UV absorption level in opaque glasses, I am unable to define the upper limit of copper and halides, or even to determine if such a limit exists for UV absorption purposes. As a result, in those applications where transparency is not essential or even useful, for example, where the UV absorbing glass is to be added to paints, lotions and the like, significantly higher amounts of both copper and halides can be added. For example, it is expected that for such applications, copper in the amount of up to 5% or greater, and halides up to 3% or greater can be used.

[0024] The heat treated rolled glass or ribbon of glass can optionally, be ground into a fine powder having an average particle size, preferably in the range of 1-5 microns. If it is desired to form a UV absorbing liquid for example, the glass powder can be suspended in a matrix such as a liquid, to form a UV absorbing liquid. As contemplated by this invention, the powder may be added for example, to body lotion to make such lotion UV absorbing to thereby protect the skin from UV radiation. In addition, the powder may be added to a paint or varnish to make the paint and varnish UV absorbing. Another contemplated use of the inventive UV absorbing liquid is for example, application to an article of clothing to thereby make such clothing UV absorbing. The above examples of possible uses of the inventive UV absorbing liquid are by way of illustration only, they are not exhaustive. Other similar applications will be obvious to persons skilled in the art.

[0025] In one preferred embodiment, a transparent UV absorbing liquid was formed by melting a glass composition consisting essentially of, in cation percent, 15-30% SiO_2, 50-60% B_2O_3, 2-5% Al_2O_3, 0-6% Li_2O, 0-3.0% Na_2O, 14-20% K_2O, 0.5-1.0% CuO, 0.4-0.7% SnO_2, 0.5-1.5% Cl, and 0.7-1.5% Br; forming the melt into a thin sheet of glass to quickly quench the glass; heat treating the quenched sheet of glass at a temperature of 525 °C for about 96 hours; grinding the heat treated sheet to an average particle size of 3 microns; and suspending the ground glass in a matrix of index matching oil. A thin film or coating of the resulting transparent UV absorbing liquid can then be applied over the surface of any support or article to be protected from UV absorption. Preferably such coating is in the range of 0.1 to 1 mm in thickness.

[0026] Various aspects of the invention will now be described by reference to the following examples, using the glass compositions given in Table 1.

EXAMPLES

Example 1. The purpose of this experiment was to determine if the process of grinding degraded the strength of the UV absorbance of glass.

[0027] A comparative UV absorbing glass (Glass 1), having the following composition: 57.5% SiO_2, 26% B_2O_3, 2.0% Al_2O_3, 3.0% ZrO_2, 2.5% Li_2O, 7.5% Na_2O, 1.5% K_2O, 0.35% CuO, 0.2% SnO_2, 0.75% Cl, and 1.0% Br, was ground to an average particle size of 3 microns and suspended in index matching oil. The suspension comprised 15 percent by weight ground glass. The density of the oil was 0.88 gms/cc. The density of the glass was assumed to be 2.4 gms/cc. Thus the volume fraction was 0.055. The transmittance spectrum of this material was then measured.

[0028] The absorption coefficient of the bulk glass at 380nm was 112.6 cm^{-1} whereas the absorption coefficient for the ground glass was determined to be 121.9 cm^{-1}. The agreement is within experimental error. Thus, unlike photochromic glasses, UV absorbing glasses can be ground with no degradation of the strength of the UV absorbance.

Example 2. The purpose of this experiment was to determine whether a coating or thin film of the glass suspension of Example 1 would be effective in reducing the UV transmittance of an optical glass having such coating or film applied to its surface.

[0029] A coating of the glass suspension of Example 1, one millimeter thick was applied to the surface of a microscope slide. The UV transmittance of the glass was reduced by about a factor of two.

Example 3. The purpose of this experiment was to show that the quenching of the glass prior to heat treatment is effective in maintaining a low haze level.

[0030] A quenched thin ribbon of the inventive glass (Glass 5) whose composition is given in Table 1 above, was heat treated at 525°C for 72 hours. It was ground down to a thickness of about 0.25 mm, and a standard haze test registered 1.16%.

[0031] A four millimeter thick piece of the same glass given the same heat treatment and then ground to a thickness of about 0.25 mm. A haze of 5.52% was measured.

Example 4. The purpose of this experiment was to demonstrate the efficacy of the inventive glass and heat treatment.

[0032] A quenched thin ribbon of Glass 5 was heat treated at 525 °C for 96 hours. The UV absorption coefficient was found to be 357 cm^{-1}. This represents an improvement by a factor of 3.2 over that of the comparative glass of Example 1.

[0033] As shown by the above examples, the inventive glasses exhibit very strong UV absorption, in many cases, absorption coefficients exceeding 250 cm^{-1} at 385 nm were observed. The observed absorption coefficient is significantly higher than observed in glasses such as Glass I which are intended for use in liquid crystal display, and other

applications. As shown in Example 1, the measured absorption coefficient for such glass was in the region of 100 cm^{-1}.

Example 5. The purpose of this experiment was to determine the effect of grinding on the UV absorbing properties of the inventive glass.

[0034] The glass of Examples 3 and 4 (Glass 5), was ground to an average particle size of 3 microns and suspended in transparent index matching oil so that the suspension comprised about 15 weight percent, ground glass. As in Example 1, the density of the oil was 0.88 gm/cc. The density of Glass 5 is estimated at about 2.4 g/cc, so that the volume fraction of the suspension was about 0.55%. The transmittance spectrum of the matrix was then measured.

[0035] The observed absorption coefficient was 178 cm^{-1}. In this liquid state, the improvement over the UV absorption of the comparative glass of Example 1, dropped to a factor of 1.5. It is not known why the UV absorption coefficient of glass differs in the suspension (Example 5), from the value measured in bulk (Examples 3 and 4).

[0036] As contemplated by the invention, this liquid combination of UV absorbing glass and a matrix such as the transparent index matching oil, can be applied to the surface of any article to protect the article from UV radiation. For transparent applications, the matrix should have the same index as the glass to ensure transparency.

Claims

1. Strong UV absorbing glass, the glass composition consisting essentially of, in cation percent, 15-30% SiO_2, 50-60% B_2O_3, 2-5% Al_2O_3, 0-6% Li_2O, 0-3.0% Na_2O, 14-20% K_2O, 0.5-1.0% CuO, 0.4-0.7% SnO_2, 0.5-1.5% Cl and 0.7-1.5% Br.

2. A UV absorbing glass according to Claim 1, wherein the amount of Na_2O is in the range of 0.2-0.7%.

3. A UV absorbing material comprising a suspension of finely divided particles of the UV absorbing glass according to Claim 1 or 2 in a matrix.

4. A UV absorbing material according to Claim 3, wherein the UV absorbing glass is a transparent glass.

5. A UV absorbing material according to Claim 3 or 4, wherein the matrix is a liquid having a refractive index which is substantially equal to the refractive index of the UV absorbing glass.

6. A UV absorbing material according to any of Claims 3 to 5, wherein the matrix is a gel.

7. An article comprising a thin film or coating of a UV absorbing material as claimed in any of Claims 3 to 6 applied onto a support.

8. An article according to Claim 7, wherein the film or coating is in the range of 0.1 to 1 mm in thickness.

9. A method of producing essentially haze-free, strong UV absorbing glass by:

   a) providing a glass composition consisting essentially of, in cation percent, 15-30% SiO_2, 50-60% B_2O_3, 2-5% Al_2O_3, 0-6% Li_2O, 0.2-0.7% Na_2O, 14-20% K_2O, 0.5-1.0% CuO, 0.4-0.7% SnO_2, 0.5-1.5% Cl and 0.7-1.5% Br;
   b) melting the glass;
   c) quenching the glass by rolling said glass into a thin ribbon; and
   d) heat treating said ribbon to form an essentially haze-free, UV absorbing glass.

10. A method according to Claim 9, wherein the ribbon is heat treated at a temperature in the range of 500 to 550°C for a time period in the range of 60 to 100 hours.

Patentansprüche

1. Stark UV-absorbierendes Glas, wobei die Glaszusammensetzung, in Kation-Prozent, weitgehend aus 15 - 30% SiO_2, 50 - 60% B_2O_3, 2 - 5% Al_2O_3, 0 - 6% Li_2O, 0 - 3,0% Na_2O, 14 - 20% K_2O, 0,5 - 1,0% CuO, 0,4 - 0,7% SnO_2, 0,5 - 1,5% Cl und 0,7-1,5% Br besteht.

2. UV-absorbierendes Glas nach Anspruch 1, wobei die Na_2O-Menge im Bereich von 0,2 - 0,7% liegt.

3. UV-absorbierendes Material, das eine Suspension fein verteilter Teilchen des UV-absorbierenden Glases nach Anspruch 1 oder 2 in einer Matrix aufweist.

4. UV-absorbierendes Material nach Anspruch 3, wobei das UV-absorbierende Glas ein transparentes Glas ist.

5. UV-absorbierendes Material nach Anspruch 3 oder 4, wobei die Matrix eine Flüssigkeit mit einem Brechungsindex ist, der weitgehend gleich dem Brechungsindex des UV-absorbierenden Glases ist.

6. UV-absorbierendes Material nach einem der Ansprüche 3 - 5, wobei die Matrix ein Gel ist.

7. Gegenstand, der einen dünnen Film oder Schicht eines UV-absorbierenden Materials nach einem der Ansprüche 3 - 6, aufgebracht auf eine Unterlage, aufweist.

8. Gegenstand nach Anspruch 7, wobei der Film oder die Schicht eine Dicke im Bereich von 0,1 - 1 mm aufweist.

9. Verfahren zur Herstellung weitgehend trübungsfreier, stark UV-absorbierender Gläser, mittels:

   a) Bereitstellen einer Glaszusammensetzung, die weitgehend, in Kation-Prozent, aus 15 - 30% SiO_2, 50 - 60% B_2O_3, 2 - 5% Al_2O_3, 0,6% Li_2O, 0 - 3,0% Na_2O, 14 - 20% K_2O, 0,5 - 1,0% CuO, 0,4 - 0,7% SnO_2, 0,5 - 1,5% Cl und 0,7-1,5% Br besteht;
   b) Schmelzen des Glases;
   c) Quenchen bzw. Abschrecken des Glases durch Rollen des Glases zu einem dünnen Band; und
   d) Wärmebehandlung des Bandes, um ein weitgehend trübungsfreies, UV-absorbierendes Glas zu bilden.

10. Verfahren nach Anspruch 9, wobei das Band bei einer Temperatur im Bereich von 500 - 550°C für einen Zeitraum von 60 - 100 Stunden wärmebehandelt wird.

Revendications

1. Verre absorbant fortement l'ultraviolet, la composition du verre étant essentiellement constituée, en pourcentages de cations, de 15 à 30 % SiO_2, 50 à 60 % B_2O_3, 2 à 5 % d'Al_2O_3, 0-6 % de Li_2O, 0 à 3,0 de Na_2O, 14 à 20 % de K_2O, 0,5 à 1,0 % de CuO, 0,4 à 0,7 % de SnO_2, 0,5 à 1,5 % de Cl et 0,7 à 1,5 Br.

2. Un verre absorbant l'ultraviolet selon la revendication 1, dans lequel la proportion de Na_2O se situe dans l'intervalle de 0,2 à 0,7 %.

3. Un matériau absorbant l'ultraviolet comprenant une suspension de particules finement divisées du verre absorbant l'ultraviolet selon la revendication 1 ou 2 dans une matrice.

4. Un matériau absorbant l'ultraviolet selon la revendication 3, dans lequel le verre absorbant l'ultraviolet est un verre transparent.

5. Un matériau absorbant l'ultraviolet selon la revendication 3 ou 4, dans lequel la matrice est un liquide ayant un indice de réfraction qui est sensiblement égal à l'indice de réfraction du verre absorbant l'ultraviolet.

6. Un matériau absorbant l'ultraviolet selon l'une quelconque des revendications 3 à 5, dans lequel la matrice est un gel.

7. Un article comprenant un mince film ou revêtement d'un matériau absorbant l'ultraviolet selon l'une quelconque des revendications 3 à 6 appliqué sur un support.

8. Un article selon la revendication 7, dans lequel le film ou revêtement présente une épaisseur se situant dans l'intervalle de 0,1 à 1 mm.

9. Un procédé de production d'un verre absorbant fortement l'ultraviolet et sensiblement exempt de trouble par les

opérations consistant :

a) à obtenir une composition de verre essentiellement constituée, en pourcentages de cations, de 15 à 30 % SiO_2, 50 à 60 % B_2O_3, 2 à 5 % d'Al_2O_3, 0 à 6 % de Li_2O, 0,2 à 0,7 % de Na_2O, 14 à 20 % de K_2O, 0,5 à 1,0 % de CuO, 0,4 à 0,7 % de SnO_2, 0,5 à 1,5 % de Cl et 0,7 à 1,5 de Br ;
b) à fondre le verre ;
c) à tremper le verre en laminant ledit verre en un ruban mince; et
d) à traiter thermiquement ledit ruban pour former un verre absorbant l'ultraviolet qui est sensiblement exempt de trouble.

10. Un procédé selon la revendication 9, dans lequel le ruban est traité thermiquement à une température se situant dans l'intervalle de 500 à 550 °C pendant une durée se situant dans l'intervalle de 60 à 100 heures.