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(54) Titre : VITRE GRIS NEUTRE A FAIBLE TRANSMISSION DE LUMIERE
 (54) Title: LOW LIGHT TRANSMISSION NEUTRAL GRAY GLASS

(57) **Abrégé/Abstract:**

The invention relates to a glass comprised of silicon, sodium and calcium of neutral grey colour with low light transmission (less than 20 %). The glass reduces the solar energy transmission such as for example the transmission of near infrared radiation (less than 14 %) and to a large extent the transmission of ultraviolet radiation transmission (less than 12 %). This glass comprises the following components expressed in percentages by weight Fe₂O₃ between 1.20 and 2.0 %; FeO between 18 and 28 % (reduction percentage); Co₃O₄ between 0.020 and 0.030 %; selenium between 0.0025 and 0.010 %; CuO between 0.0050 and 0.050 %. The glass of the invention avoids using colorant compounds such as nickel, chromium and manganese.



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<p>(21) Solicitud internacional: PCT/MX98/00053</p> <p>(22) Fecha de la presentación internacional: 2 de Diciembre de 1998 (02.12.98)</p> <p>(30) Datos relativos a la prioridad: 08/982,612 2 de Diciembre de 1997 US (02.12.97)</p> <p>(71) Solicitante: VIDRIO PLANO DE MEXICO, S.A. DE C.V. [MX/MX]; Ex-Hacienda de la Santa Cruz, San Juan Ixhuatepec, Tlalnepantla, México 54180 (MX).</p> <p>(72) Inventores: SCHEFFLER HUDLET, Herbert; Ojo de Agua No. 52, Club de Golf Hacienda, Atizapán de Zaragoza, México 52959 (MX). CABRERA LLANOS, Roberto Marcos; Avenida Revolución No. 207, 111-24, Plazas Ecatepec, Ecatepec, México 55220 (MX). CID AGUILAR, José Guadalupe; Avenida Morelos Poniente No. 39, San Cristóbal Centro, Ecatepec, México 55000 (MX). PINTO NEGROE, Rafael Enrique; Norte 25 No. 41, Colonia Nueva Vallejo, Segunda Sección, México, D.F. 07720 (MX).</p> <p>(74) Mandatarios: VELA GUZMAN, Angel etc.; Avenida Roble No. 660, Colonia Valle del Campestre, Garza García, Nuevo León 66265 (MX).</p>		<p>(81) Estados designados: CA, MX, Patente europea (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Publicada <i>Con informe de búsqueda internacional. Antes de la expiración del plazo previsto para la modificación de las reivindicaciones, será publicada nuevamente si se reciben modificaciones.</i></p>
<p>(54) Title: LOW LIGHT-TRANSMITTING NEUTRAL GREY GLASS COMPOSITION</p> <p>(54) Título: COMPOSICION DE VIDRIO GRIS NEUTRO DE BAJA TRANSMISION DE LUZ</p> <p>(57) Abstract</p> <p>The invention relates to a glass comprised of silicon, sodium and calcium of neutral grey colour with low light transmission (less than 20 %). The glass reduces the solar energy transmission such as for example the transmission of near infrared radiation (less than 14 %) and to a large extent the transmission of ultraviolet radiation transmission (less than 12 %). This glass comprises the following components expressed in percentages by weight: Fe₂O₃ between 1.20 and 2.0 %; FeO between 18 and 28 % (reduction percentage); Co₃O₄ between 0.020 and 0.030 %; selenium between 0.0025 and 0.010 %; CuO between 0.0050 and 0.050 %. The glass of the invention avoids using colorant compounds such as nickel, chromium and manganese.</p> <p>(57) Resumen</p> <p>Un vidrio sílico-sódico-cálcico de color gris neutro que tiene una baja transmisión de luz (menor a 20 %), que reduce la transmisión de energía solar, tal como la transmisión de radiación infrarroja cercana (menor a 14 %), y en un mayor grado la transmisión de radiación ultravioleta (menor a 12 %), que comprende los siguientes componentes en porcentaje en peso: Fe₂O₃ de 1.20 a 2.0 %, FeO de 18 a 28 % (porcentaje de reducción), Co₃O₄ de 0.020 a 0.030 %, selenio de 0.0025 a 0.010 %, CuO de 0.0050 a 0.050 %. Este vidrio evita el uso de los compuestos colorantes tales como el níquel, cromo y manganeso.</p>		

LOW LIGHT TRANSMISSION NEUTRAL GRAY GLASS

BACKGROUND OF THE INVENTION.

A. FIELD OF THE INVENTION.

This invention refers to a composition and to a method for the commercial production of a privacy glass, of neutral gray color, having a low light transmission (less than 20%), and low solar energy transmission showing a low infrared radiation transmission (less than 14%), and especially a low ultraviolet transmission (less than 12%), for use in the construction industry and mainly in the automotive industry.

B. DESCRIPTION OF THE RELATED ART.

Several patents have been developed for obtaining gray glass, for "privacy" purposes, having low light transmission and low infrared and ultraviolet radiation transmission.

The glasses disclosed in almost all the prior patents referring to a type of neutral gray glass for privacy purposes, are based on three basic components: iron oxide, cobalt oxide and selenium, using different proportions and, together with the typical formulation of a soda-lime-silica glass, constitute the basic composition of the glass.

That it is the case of the glasses of the U. S. Patents No. 4,873,206 of James Jones, issued October 10 of 1989, the Patent No. 5,393,593 of Gulotta et al, issued February 28 of 1995, and the Patent No. 5,278,108 of Cheng et al, issued January 11 of 1994, in which these components are used without any additional component.

Some other glasses disclosed in other patents, such as those mentioned in the following paragraphs, use, besides the three mentioned components,

different metallic elements conferring the characteristics to the final product, that allow them to be classified as privacy glasses, in order to be used in the construction and automotive industries.

The U. S. Patent No. 5,308,805 of Baker et al, issued May 4 of 1994,
5 describes a neutral gray glass having a low transmission, in which one of the claimed components is the nickel oxide in proportions of 100 to 500 ppm.

In the past, the heat absorbing gray glasses containing nickel in their structure, frequently presented inclusions of nickel in the form of sulfide which, during the melting of the glass, were formed until appearing as small invisible
10 particles which were impossible to distinguish in viewing an already formed glass. The problem that presented these inclusions of nickel sulfide, is due to their high coefficient of thermal expansion that can cause thermal stresses sufficient to fracture a glass plate. This is a singular problem when the glass pieces are subjected to a thermal treatment as the tempering, in which the
15 presence of the nickel sulfide causes an excessive percentage of breakdown pieces during or as a consequence of the tempering process.

An additional disadvantage of the glasses containing nickel, is the change of color that they undergo after the thermal process, such as for example, after tempering.

20 U.S. Patent No. 5,023,210 of Krumwide et al, issued June 11 of 1991, discloses a low transmission neutral gray glass composition that does not include nickel. In order to achieve similar characteristics to that of a neutral gray glass, Krumwide uses chromium oxide in amounts of 220 to 500 ppm as Cr_2O_3 , in its composition which, in these proportions, produces a gray tone and
25 adjusts the levels of selenium and cobalt oxide in order to make it a neutral

tone. However, in previous references it is mentioned a preference to avoid the use of these compounds because of the problems presented by the difficulty of melting the chromium compounds (U.S. Patent No. 4,837,206), and additionally because these have difficulties for discarding the solid materials containing said compounds. Also, in the U. S. Patent No. 5,308,805 there is mentioned the inconvenience of the chromium oxide used as coloring agent, since it requires the use of additional operations and apparatuses to the conventional ones into the melting furnaces in order to reach the necessary conditions to produce the desired glasses.

10 The U. S. Patent No. 5,346,867 of Jones et al, issued September 13 of 1994, discloses a heat absorbing glass composition having a neutral gray color, which uses manganese and titanium oxide in order to increase the retention of the selenium (that is a high cost component), during the production process. Although from previous references (U. S. Patent No. 4,873,206), it was known that the use of the manganese has a tendency to form a yellowish-brown coloration when it is exposed to the ultraviolet radiation, for example, to the received solar radiation, making difficult to maintain the uniformity of the product, and the use of the titanium causes a yellowish coloration when the glass enters into contact with the liquid tin of the float process. This is what makes undesirable these two aspects during the production of the glass because it makes critical the control of color in order to obtain the desired tone during the manufacture. Jones et al mentioned in their Patent '867, that the process of solarization is a phenomenon associated with the change of Fe^{3+} to Fe^{2+} which cause an undesirable change in the color, mentioning that they found that this does not occurs in the disclosed glass, and additionally the use

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of the titanium oxide is incorporated into the glass in order to obtain the desired range of dominant wave length, as well as to reduce the transmission of ultraviolet radiation.

On the other hand, it is well known by the persons skilled in the art, that
5 the addition or substitution of one or more colorants for other or others colorants, or the change in the relative proportional amount in the glass composition, affects not only the color of the product, as for example the dominant wave length of the color or the excitation purity, but also the luminous transmission, the heat absorption and additional properties such as
10 the transmission of ultraviolet and infrared radiation.

Since old times the copper has played an important role in the production of colored glass, ceramics and pigments. It has been recognized, for example, the coloration of the Persian ceramic for their tonality conferred by the copper. Of special interest for the ceramic artists, are the turquoise blue
15 and especially the Egyptian and Persian blue dark (Woldemar A. Weil; Colored Glasses, Society of Glass Technology, Great Britain, p. 154-167, 1976).

Copper has been used in the glass compositions, not only in those of soda-lime-silica type, but also in others such as those containing, for example, borosilicate. Therefore, the developed color depends on the base of the glass,
20 on its concentration and on its oxidation state.

For the case of the mentioned glass as a base, the copper in the form of the oxide imparts a blue coloration of a greenish tone, specifically turquoise, however, in the glass, the copper can be in its monovalent state, which does not impart color. So, the blue greenish coloration depends not only on the
25 amount of copper present, but on the ionic balance between the cuprous and

cupric states. The maximum absorption of the copper oxide is in a band centered at 780 nm and a maximum weak secondary peak is present at the 450 nm, which disappears at the high soda content (around 40% weight)(C. R. Bamford, Colour Generation and Control in Glass, Glass Science and Technology, Elsevier Scientific Publishing Company, p. 48-50, Amsterdam, 1977).

In the production of red ruby glass, a mixture containing copper oxide together with any reducer agent (SnO is commonly used), is melted in reduced conditions. The initial mixture shows the blue characteristic color of the copper II, but as soon as the melting begins, changes the color to a pale straw yellow which takes place during this stage. Due to a thermal treatment to a temperature between the annealing point and the softening point, the ruby red color is developed. If, during the melt, the reduction state is carried out beyond a critical stage, the color changes to brown and appears opaque or "turned off". On the other hand, if the copper is insufficiently reduced, some traces of blue color are kept and the ruby red color is not developed (Amal Paul, Chemistry of Glasses, Chapman and Hall, p. 264-270, London, 1982).

U.S. Patent No. 2,922,720 of Parks et al, issued June 20, 1957, discloses the use of the copper in the glass as: ". . . The copper has been used as coloring agent for glass upon developing a coloration ruby red, but in order to obtain the color in a open melt furnace, it has been necessary the use of cyanogens as reducer agent . . . ", additionally mentions the effect of the copper in the coloration of the glass, as due to the colloidal suspension of particles of metallic copper in the glass, and by analogy it is believed that a particle size

produces the ruby red colors, depending on the intensity of the color of the copper concentration. For smaller particle sizes, the effect of color is null.

The glass of the present invention, avoids the use of some metals that the above mentioned patent disclose as very important, this is the case of the nickel, the chromium and the manganese.

In the glass of the present invention, the copper oxide (CuO) is used additionally to the use of iron oxide, cobalt oxide and selenium, as an alternative for obtaining a lightly greenish gray tonality in the region of neutral color frequently used in the automotive and construction industry, additionally providing a reduction in the ultraviolet radiation transmission and a reduction in the near infrared region for the bands of absorption around the 800 nanometers which help to reduce the infrared solar transmission.

So that, in the present invention, a gray neutral glass having a luminous transmission less than 20%, and preferably between 15 and 18% for a glass thickness between 3.9 and 4.1 mm., and a reduction on the solar energy transmission that is expressed as a transmission of infrared radiation less than 14%, and an ultraviolet radiation transmission less than 12%, is achieved.

SUMMARY OF THE INVENTION

It is therefore a main objective of the present invention, to provide a neutral gray glass composition, by using copper in form of an oxide, as an alternative for obtaining the typical gray greenish color in the privacy glasses used in the construction industry and, preferably, in the automotive industry.

It is also a main objective of the present invention, to provide a neutral gray glass composition, based on a typical soda-lime-silica glass composition including the compounds of cobalt oxide, iron oxide and selenium, as well as

copper oxide, by means of which the use of nickel, chromium and manganese, is avoided.

It is still a main objective of the present invention, to provide a neutral gray glass composition, of the above mentioned nature, by using copper in the form of an oxide, that shows an absorption in the near infrared region, mainly in the ultraviolet region, due to its combination with the iron oxide, cobalt oxide and selenium, in order to substitute to the nickel, chromium and manganese in the existent formulations, since these chemical elements show undesirable characteristic on the product or on the process, under certain circumstances.

It is a further main objective of the present invention, to provide a neutral gray glass having a luminous transmission less than 20% and preferably between 15 and 18% for a glass thickness between 3.9 and 4.1 mm., and a reduction in the solar energy transmission that is shown as an infrared radiation transmission less than 14%, and an ultraviolet radiation transmission less than 12%.

It is additionally a main objective of the present invention, to provide a neutral gray glass having a dominant wave length of 480 to 575 nm, preferable from 500 to 570 nm and a color excitation purity less than 10%, preferably less than 8%.

These and other objectives and advantages of the neutral gray privacy glass, of the present invention, will be evident to the experts in the field, from the following detailed description thereof.

DETAILED DESCRIPTION OF THE INVENTION

The typical composition of a soda-lime-silica glass used in the construction and automotive industry, and formed by the so called glass float

process, is characterized by the following formulation based on the weight percentage with regard to the total weight of the glass:

Components	% by weight
SiO ₂	68 to 75
5 Al ₂ O ₃	0 to 5
CaO	5 to 15
MgO	0 to 10
Na ₂ O	10 to 18
K ₂ O	0 to 5

10 The neutral gray glass composition of the present invention is based on the above disclosed composition, to which the following coloring compounds have been added:

Components	% by weight
Fe ₂ O ₃	1.200 to 2.000
15 Co ₃ O ₄	0.020 to 0.030
CuO	0.005 to 0.050
Se	0.0025 to 0.010
% of reduction	18.0 to 28.0

20 It is common in the glass industry to refer the total iron content in the glass composition or in the glass melting mixture, as the total iron expressed as Fe₂O₃.

25 When a batch of glass is melted, part of that amount of total iron is reduced to FeO, while the rest is maintained as Fe₂O₃. The balance between the ferric and ferrous oxidation states in the melted mixture are the result of an equilibrium of the final oxidation-reduction state, which is a mixture between

the use of oxidation or reducing agents in the feed mixture, and the combustion characteristics, for example the air-gas relationship used in the furnace, in order to melt the mixture. The reduction of the Fe_2O_3 produces not only FeO , but also oxygen, decreasing the combined weight of the two compounds of iron
5 in the resulting glass.

Consequently the combined weight of the FeO and Fe_2O_3 contained in the resulting glass composition, will be minor, less than that fed during the mixture, or less than the total of the initial iron used expressed as Fe_2O_3 . For this reason, it is understood that the total iron is the iron expressed in the form
10 of Fe_2O_3 , as it is used in the description of this patent application, as meaning of the amount of iron fed in the mixture before its reduction. And it is to be understood that the reduction value of the ferrous state is defined as the weight of the ferrous oxide (FeO) expressed as Fe_2O_3 in the glass product, divided by the weight percentage of total iron expressed as Fe_2O_3 . This amount in the
15 glass industry is commonly expressed in the form of a reduction percentage.

The physical properties, such as the light transmission, correspond to calculated variables based on internationally accepted standards. So that the light transmission is evaluated using the illuminant "A" and standard Observer of 2° , also known as of 1931 [C.I.E Publication. 15.2, ASTM E-308 (1990)].
20 The wave length range used for these purposes is of 380 to 780 ηm , integrating values in numeric form with intervals of 10 ηm . The solar energy transmission represents the heat which the glass achieves in direct form, evaluating it from 300 up to 2150 ηm with intervals of 50 ηm , the numeric form of calculation uses, as recognized standard values, those reported by Parry

Moon in "Proposed Standard Solar Radiation Curves for Engineer Use", Franklin Institute, Vol. 230, p. 604, table II, 1940.

The calculation of the ultraviolet radiation transmission (UV), involves only the participation of the solar UV radiation, so that it is evaluated in the range of 300 to 400 ηm of wave length using intervals of 10 ηm . For the infrared radiation transmission (IR), it is only contemplated, besides the UV radiation, the range wherein the solar spectrum has influence, so that the range of the near Infrared region from 800 to 2150 ηm , with intervals of 50 ηm , is used. Both calculations use the above mentioned solar radiation values of Parry Moon.

The amount of solar heat which is transmitted through the glass, can also be calculated by means of the contribution of the thermal energy with which participates each of the regions in which the solar spectrum has influence, placed from the ultraviolet region (280 ηm), to the near infrared region (2150 ηm), and which is of 3% for UV, 44% for the visible and around 53% for the IR, however, the values of the direct solar energy transmission, in the present invention, are calculated on the basis of a numeric integration taking into account the whole range of the solar spectrum which is of 300 to 2150 ηm , with intervals of 50 ηm and using the values of solar radiation reported by P. Moon.

The specifications for the determination of color, such as the dominant wave length and the purity of excitement, have been derived from the Tristimulus values (X, Y, Z) which have been adopted by the International Commission of Illumination (C.I.E.), as a direct result of experiments involving many observers. These specifications could be determined by the calculation

of the three-chromatic coefficients x,y,z of the Tristimulus values that corresponding to the red, green and blue colors, respectively. The three-chromatic values are plotted in the chromatic diagram and compared with the coordinates of the illuminant "C" considered as illumination standard. The comparison provides the information in order to determine the color purity excitement and its dominant wave length. The dominant wave length defines the wave length of the color and its value is located in the visible range, of the 380 to 780 ηm , while for the purity of excitement, the less the value it is, the nearest tends to be a neutral color. A deeper understanding of these topics can be obtained form the "Handbook of Colorimetry" published by the "Massachussets Institute of Technology", of Arthur C. Hardy, issued in 1936.

CLAIMS:

1. A neutral gray soda-lime-silica glass having a thickness between 3.9 and 4.1 mm including, as colorant components, in weight percentage:

- 5 Fe_2O_3 from 1.20 to 2.0%;
 FeO from 18 to 28%, as reduction percentage;
 Co_3O_4 from 0.020 to 0.030%;
 Selenium from 0.0025 to 0.010%; and
 CuO from 0.0050 to 0.050%;

10 the glass having a light transmission of less than 20%, a near infrared transmission of less than 14%, an ultraviolet radiation transmission of less than 12%, and a dominant wave length of 480 to 575 nm and a purity of color excitement of less than 10%.

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