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(57) Abrégé/Abstract:
An infrared and ultraviolet absorbing soda-lime-silica glass of a neutral tint containing 0.3 % to 0.7 % by weight total iron expressed as Fe_2O_3, together with amounts of Se, Co_3O_4 and a ferrous iron content to provide a ratio of ferrous iron to total iron in the range of 21 to 34. NiO and TiO_2 may be added to the glass. The resultant glass, in a nominal 4 mm thickness, has a visible light transmission of at least 70 % and a direct solar heat transmission at least 12 percentage points below the visible light transmission. The iron in the glass is preferably provided by the inclusion of the mineral wuestite in the glass batch formulation.

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(54) Title: GLASS COMPOSITIONS

(57) Abstract

An infrared and ultraviolet absorbing soda-lime-silica glass of a neutral tint containing 0.3 % to 0.7 % by weight total iron expressed as Fe_2O_3, together with amounts of Se, Co_3O_4 and a ferrous iron content to provide a ratio of ferrous iron to total iron in the range of 21 to 34. NiO and TiO_2 may be added to the glass. The resultant glass, in a nominal 4 mm thickness, has a visible light transmission of at least 70 % and a direct solar heat transmission at least 12 percentage points below the visible light transmission. The iron in the glass is preferably provided by the inclusion of the mineral wuestite in the glass batch formulation.

GLASS COMPOSITIONS

BACKGROUND OF THE INVENTION

The present invention relates to infrared (IR) and ultraviolet (UV) absorbing soda-lime-silica glass compositions for use in glazing. More particularly, the present invention relates to windows of a neutral tint made from such glasses primarily, but not exclusively, for vehicles such as automobiles.

Special glasses have been developed for use in vehicles which have low levels of direct solar heat transmission (DSHT) and ultraviolet transmission (UVT). These glasses aim to reduce the problems caused by excessive heating within the vehicle on sunny days, and to protect the interior furnishings of the car from the degradation caused by ultraviolet radiation. Glasses having good infrared absorption properties are usually produced by reducing iron present in the glass to the ferrous state or by adding copper. Such materials give glasses a blue color. The materials added to achieve good ultraviolet radiation absorption are Fe^{3+}, Ce, Ti or V. The quantities of such materials which are added to provide the desired level of absorption tend to color the glass yellow. Accordingly, if both good UV and good IR absorption are required in the same glass, the color of such glass is, almost inevitably, either green or blue. When the color of the glasses is defined by the CIELAB system, such commercial glasses, in 4 mm thickness and having greater than 60% light transmission, are found to be either very green (-a*>8) or very blue (-b*>7), neither of which are currently desirable from an aesthetic viewpoint.

Attempts have been made to produce grey or bronze-colored vehicle glazing having good protection against both IR and UV radiation, but such glasses still tend to have a greenish yellow tinge.

We have identified a requirement for a range of glasses having a neutral tint and a visible light transmittance (Illuminant A) of at least 70 percent such that, in the CIELAB system, the glasses have color co-ordinates lying in the ranges a* from -7 to +1, b* from -5 to +7.5. The term "neutral tint" is hereinafter used to describe glasses having such color co-ordinates.

We have further identified a requirement for glasses having a neutral tint which have visible light transmissions of at least 70 percent (at a thickness of 4 mm), but which also have a direct solar heat transmission which is at least twelve percentage points (preferably fifteen percentage points and most preferably twenty percentage points) less than the visible light transmission. Basically, glasses are known which do have a low direct solar heat transmission but nearly all of these have a low visible light transmission which tend to make such glasses of limited use in vehicles. Glasses satisfying the above-identified requirements should, we anticipated, be of more general use in vehicles due to the higher light transmission but the lower direct solar heat transmission should keep the interior of the car cool despite the higher light transmission.

Furthermore, we believed that it would be desirable if the glasses had an ultraviolet transmission less than 55% and ideally less than 50% because we felt that such a low transmission would minimize the adverse effects of ultraviolet radiation on plastics material and fabrics, particularly in automotive vehicles.

The field of tinted glasses is one in which relatively small changes can produce major changes in tint. Wide ranges disclosed in prior patents can encompass many possibilities, and it is only the teaching of the specific examples that can be relied on as identifying how particular tints associates with particular ranges of absorption of infrared and ultraviolet radiation can be obtained.

Our invention is based on the surprising discovery that the incorporation of relatively small amounts of certain coloring agents compensates for the green color arising from the presence of infrared and ultraviolet radiation absorbing components.

SUMMARY OF THE INVENTION

According to the present invention, there is provided an IR and UV absorbing soda lime silica glass of a neutral tint (as herein defined) having, in a 4mm thickness, a visible light transmission of at least 70%, a direct solar heat transmission at least 12 percentage points below the visible light transmission, a UV transmission not greater than 55%, a dominant wavelength less than 560 nm and a color purity not greater than 6, preferably not more than 5 and most preferably no more than 3. Most, preferably the direct solar heat transmission is at least 20 percentage points lower than the visible light transmission. The composition comprises a soda-lime-silica base glass and a total iron content, expressed as Fe_2O_3, in the range of from 0.3 to 0.7% by weight. The glass is tinted to a neutral color by the inclusion of 0.5 to 10 parts by million (ppm) of Se, from about 3 to 25 ppm of Co_3O_4, and a ferrous iron content to provide a ratio of ferrous iron to total iron in the range of 21 to 34, preferably 25 to 31 (i.e., percent of total iron as ferrous iron (Fe^{2+}) of 21% to 34%, preferably 25% to 31%*). NiO and TiO_2 may be added to the glass, in ranges of 0 to 50 ppm NiO and 0 to 1.5 weight percent TiO_2. Thus, it has been determined that amounts of NiO and TiO_2, in the above ranges can produce beneficial affects on color purity and UV absorption, respectively, without deleteriously influencing the unique and highly advantageous properties of our novel glass.

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* As is well known, the iron content in glasses is usually present in both the Fe_2O_3 (ferric) and FeO (ferrous) forms. As is conventional, the total amount of iron present in a glass is expressed herein as Fe_2O_3, regardless of the form actually present.

In accordance with one aspect of the present invention, there is provided a neutral gray colored glass composition having a base glass portion comprising:

SiO_2	65 to 80 percent by weight
Na_2O	10 to 20 percent by weight
CaO	5 to 15 percent by weight
MgO	0 to 10 percent by weight
Al_2O_3	0 to 5 percent by weight
K_2O	0 to 5 percent by weight

and a colorant portion consisting essentially of:

Fe_2O_3 (total iron)	0.30 to 0.70 percent by weight
FeO	0.08 to 0.16 percent by weight
Co_3O_4	3 to 25 ppm
Se	0.5 to 10 ppm

wherein the color of the glass as made on a conventional float glass tank, is characterized by a dominant wavelength less than 560 nanometers, a color purity of no higher than 6 percent, an ultraviolet light transmission less than 55%, a visible light transmission of 70 percent or greater at a thickness of 4 millimeters, and a direct solar heat transmission at least 12% below the visible light transmission, and wherein the percent reduction of the total iron is between 21% and 34%.

For the purpose of the present specification and claims, references to visible light transmission are to light transmission (LT) measured using CIE Illuminant A; UVT or ultraviolet radiation transmission is an integrated term representing the area under the transmission versus wavelength curve for wavelengths between 300 and 400 nm; and references to direct solar heat transmission (DSHT) are references to solar heat transmission integrated over the wavelength range 350 to 2100 nm according to the relative solar spectral distribution Parry Moon for air mass 2.

Suitable batch materials for producing glasses according to the present invention, which materials are compounded by conventional glass batch ingredient mixing devices, include sand, limestone, dolomite, soda ash, salt cake or gypsum, niter, iron oxide, carbon, selenium and cobalt oxide (Co_3O_4). In the event TiO_2 and/or NiO are desired in the composition, a titanium compound such as titanium dioxide and a nickel compound such as nickel oxide may be included in the batch. In this connection, and in accordance with an important embodiment of this invention it has surprisingly been discovered that the use of wuestite as the source of iron is particularly advantageous, supplying at least a partial amount or preferably all of the Fe_2O_3 and substantially eliminating the need for carbon. Thus, carbon is a very deleterious element in neutral tint glasses, e.g., grey and bronze glasses, but is required to raise the ferrous values of the glasses where employing rouge as the batch iron source.

The use of wuestite as the iron source instead of rouge greatly increases the ferrous value of a glass. The use of a raw material with a higher natural ferrous value allows better control of higher ferrous values in glasses such as the neutral tint glasses of this invention.

The batch materials are conveniently melted together in a conventional glass making furnace, to form a neutral tinted infrared energy and ultraviolet radiation absorbing glass composition, which thereafter may be continuously cast onto the molten metal bath in a float glass process.

The composition of soda-lime-silica flat glasses suitable for use in accordance with the present invention typically have the following weight percentage constituents:

SiO_2	65-80%
Na_2O	10-20
CaO	5-15
MgO	0-10
Al_2O_3	0-5
K_2O	0-5
BaO	0-5
B_2O_3	0-5

Other minor ingredients, including melting and refining aids such as SO_3, may also appear in the glass composition. The coloring constituents of the present invention set forth above are added to this base glass. The glass is essentially free of colorants other than iron, cobalt, and selenium, and optionally nickel and titanium, other than any trace amounts of oxides that may be present as impurities. Accordingly, the glass of the present invention may be melted and refined in a conventional tank-type melting furnace and formed into flat glass sheets of varying thicknesses by the float method in which the molten glass is supported on a pool of molten metal, usually tin, as it assumes a ribbon shape and is cooled.

The glass compositions of the present invention are particularly suited for the production of infrared energy and ultraviolet radiation absorbing glass for automotive and architectural glazings. Thus, glass sheets of this composition may be heat strengthened or tempered, or alternately annealed and laminated together through an interposed transparent resinous layer, for example composed of polyvinyl butyral, and employed, for example, as a windshield. Generally, the glass sheets for windshield use are of a thickness in the range of from about 1.7 mm to about 2.5 mm, while those tempered and used as sidelights or backlights are in the range of about 3 mm to about 5 mm thick.

Unless otherwise noted, the term percent (%) as used herein and in the appended claims, means percent (%) by weight. Wavelength dispersive X-ray fluorescence was used to determine the weight percents of TiO_2 and total iron expressed as Fe_2O_3. Percent reduction of total iron was determined by first measuring the radiant transmission of a sample at a wavelength of 1060 nanometers, using a spectrophotometer. The 1060 nm transmission value was then used to calculate optical density, using the following formula:

$$\text{Optical density} = \text{Log}_{10}\frac{T_o}{T}$$

(T_o = 100 minus estimated loss from reflection=92; T = transmission at 1060 nm).

The optical density was then used to calculate the percent reduction:

$$\text{percent reduction} = \frac{(110)\text{x}(\text{optical density})}{(\text{Glass thickness in mm})\text{x}(\text{wt\% total } Fe_2O_3)}$$

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The concentrations of each of the three essential colorant constituents depend upon the optical properties desired for the glass and are interrelated to each other. Iron is added, typically as Fe_2O_3, and is partially reduced to FeO. The total amount of iron in the batch is critical, and must equal from 0.3 percent to about 0.7 percent by weight, expressed as Fe_2O_3. Likewise, the degree of reduction is critical and must equal between 21% and 34%. If the iron is more highly reduced than the critical amount, or if a higher total amount of iron is employed, the glass will become too dark and the Illuminant A visible light transmittance will drop below about 70 percent. Additionally, the glass batch melting process will become increasingly difficult as the increased amount of FeO prevents the penetration of heat to the interior of the melt. If the iron is less reduced than the critical amount, or if a lower total amount of iron is employed, then the direct solar heat transmittance for a desired thickness glass can rise to an unacceptable level, i.e., above about 58%.

From about 3 to about 25 ppm cobalt oxide is added, typically as Co_3O_4, along with about 0.5 to about 10 ppm selenium. The proper selenium and cobalt content provides an aesthetically pleasing, neutral tint, somewhat gray color to the glass. Preferred compositions, include a soda-lime-silica base glass and colorants consisting essentially of 0.45 to 0.65 total iron (as Fe_2O_3), with a ratio of ferrous iron to total iron of 25 to 31, 1 to 5 ppm Se, 8 to 20 ppm Co_3O_4, 0 to 35 ppm NiO and 0 to 1 weight percent TiO_2.

The following examples illustrate glass compositions in accordance with the invention that are readily formed into glass articles or glazings such as automobile windshields. The compositions absorb both infrared and ultraviolet rays and have an Illuminant A visible light transmission of at least about 70% and a direct solar heat transmission at least 12 percentage points less than the visible light transmission.

The examples, except examples 1 and 11 which are for comparison purposes only, illustrate but do not limit the invention. In the examples, all parts and percentages are by weight and:

(a) Fe_2O_3, FeO, and TiO_2 are expressed in percent; Se, Co_3O_4 and NiO are expressed in parts per million;

(b) total iron is expressed as if all iron present were present as ferric oxide; and

(c) the FeO content is calculated from the equation

$$\%FeO = \frac{\%Fe^{2+}}{100} \times Fe_2O_3 \times \frac{143.7}{159.7}$$

Fe_2O_3=percentage total iron, expressed as Fe_2O_3, in the glass (143.7 being the molecular weight of 2 x FeO and 159.7 being the molecular weight of Fe_2O_3).

The transmittance data in the Table below and throughout are based on a nominal glass thickness of 4mm.

TABLE I

	Example 1	2	3	4	5
Total Iron as Fe_2O_3	0.5	0.55	0.55	0.31	0.61
FeO	0.11	0.14	0.13	0.08	0.14
% of Total Iron as Fe^{2+}	25	29	27	27.2	26
Se	2	7	9	3	2
Co_3O_4	10	10	19	20	12
TiO_2	1.6	0.33	0.34	-	-
NiO	–	–	15	-	-
LT	72	71	71	75	73
DSHT	53	50	51	63	51
UTV	36	45	47	59	51
a*	-5.1	-4.8	-5.2	-2.0	-4.7
b*	7.5	3.2	2.4	0.2	1.5
λD	565	546	529	499	512
Purity	6.9	2.4	1.7	0.8	1.3

TABLE I (Continued)
Example

	6	7	8	9	10	11
Total Iron as Fe_2O_3	0.56	0.56	0.54	0.57	0.51	0.53
FeO	.13	0.14	0.13	0.16	0.12	0.09
% of Total Iron as Fe^{2+}	25	27	27	31	27	19
Se	2	1	1	<1	2	5
Co_3O_4	5	13	24	10	12	13
TiO_2	–	–	–	–	1.0	–
NiO	23	–	31	–	–	–
LT	76	74	72	74	71	71
DSHT	54	52	53	50	52	57
UTV	51	51	53	53	40	46
a*	-4.9	-5.3	-5.0	-6.2	-5.2	-1.9
b*	1.9	0.3	-1.0	-0.8	5.5	4.1
\D	518	498	499	494	560	569
Purity	1.3	2.3	3.3	3.6	4.8	4.0

The base glass composition for example 7, which is essentially the same for all of the examples, was as follows:

Component	Weight Percent of Total Glass
SiO_2	73.91
Na_2O	14.04
CaO	7.86
MgO	3.47
SO_3	0.20
Al_2O_3	0.16
K_2O	0.039

The batch mixture for example 7, which is likewise similar for all of the examples except for the colorants, was:

Constituent	Parts by Weight
Sand	154
Soda Ash	50
Gypsum	1
Limestone	11
Dolomite	33
Wuestite	1.02
C_3O_3	0.0011
Selenium	0.0014
Carbon	0.027

It is an advantage of the present invention that the composition can be manufactured into flat glass products using commercial manufacturing processes, in particular the float process. A sheet of glass that has been formed by the float process is characterized by measurable amounts of tin oxide that migrated into surface portions of the glass on at least one side. Typically a piece of float-forming glass has an SnO_2

concentration of at least 0.05% by weight in the first few microns below the surface that was in contact with the tin. Glass made by the float process typically ranges from about 2 millimeters to 10 millimeters in thickness.

Another characteristic of most float glass is the presence of traces of melting and refining aids such as sulfur, analyzed in the glass as SO_3, or fluorine or chlorine. Small amounts of these melting and refining aids (usually less than 0.3% by weight) may be present in the glass compositions of the present invention without effect on the properties.

This description of the invention has been made with reference to specific examples, but it should be understood that variations and modifications as are known to those of skill in the art may be resorted to without departing from the scope of the invention as defined by the claims that follow.

Claims

1. In a process for producing a neutral gray colored soda-lime-silica glass having a base glass composition comprising:

SiO_2	65 to 80 percent by weight
Na_2O	10 to 20 percent by weight
CaO	5 to 15 percent by weight
MgO	0 to 10 percent by weight
Al_2O_3	0 to 5 percent by weight
K_2O	0 to 5 percent by weight

wherein the neutral gray colored glass is made in a conventional float glass tank and contains oxides of iron, the process including admixing, heating and melting a soda-lime-silica glass batch mixture, the improvement comprising including in said glass batch mixture, wuestite, as at least a partial source of the iron oxides in the resulting glass.

2. A glass batch mixture having a base glass composition comprising:

SiO_2	65 to 80 percent by weight
Na_2O	10 to 20 percent by weight
CaO	5 to 15 percent by weight
MgO	0 to 10 percent by weight
Al_2O_3	0 to 5 percent by weight
K_2O	0 to 5 percent by weight

wherein the glass batch mixture is processed in a conventional float glass tank, the glass batch mixture comprising: oxides of iron, a source of silicon, a source of sodium, a source of calcium, and wuestite.

3. In a process for producing a neutral gray colored soda-lime-silica glass having a base glass composition comprising:

SiO_2	65 to 80 percent by weight
Na_2O	10 to 20 percent by weight
CaO	5 to 15 percent by weight
MgO	0 to 10 percent by weight
Al_2O_3	0 to 5 percent by weight
K_2O	0 to 5 percent by weight

wherein the neutral gray colored glass is made in a conventional float glass tank, and contains oxides of iron, the process including admixing, heating and melting a soda-lime-silica glass batch mixture comprising: sand, soda ash, dolomite, limestone and a sulfate selected from the group consisting of salt cake and gypsum, the improvement comprising including in said batch, wuestite, as at least a partial source of the iron oxides in the resulting glass.