

COMMONWEALTH OF AUSTRALIA PATENTS ACT, 1952-1973
DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention Application No. made

(a) Here Insert (In full)
Name of Company.

by ^(a) Ferro Corporation

(hereinafter referred to as "Applicant") for a patent for an invention entitled:

(b) Here Insert Title of
Invention.

^(b) LEAD-FREE U.V. ABSORBING GLASS

(c) and (d) Here Insert
Full Name and Address
of Company Official
authorised to make
declaration.

^(c) I, ^(c) Walter C. Danison
Corporate Patent Counsel

^(d) of Ferro Corporation,
1000 Lakeside Avenue, Cleveland, Ohio 44114, U.S.A.

do solemnly and sincerely declare as follows:

1. I am authorised by Applicant to make this declaration on its behalf.

2. The basic Application(s) as defined by section 141 of the Act was/were made

(e) Here Insert Basic
Country or Countries
followed by date or dates
of Basic Application(s).

in ^(e) U.S.A. on the 17th day of December 1987 ..
..... on the day of 19 ..

(f) Here Insert Full
Name(s) of Applicant(s)
in Basic Country.

by ^(f) ROBERTS, Gordon J.

(g) Here Insert (In full)
Name and Address of
actual Inventor or
Inventors.

3. ^(g) ROBERTS, Gordon J.

of 5539 Hilltop Oval, Parma, Ohio 44129, U.S.A.

..... is/are
the actual Inventor(s) of the invention and the facts upon which Applicant is entitled to
make the Application are as follows:

Applicant is the Assignee of the said Inventor(s).

4. The basic Application(s) referred to in paragraph 2 of this Declaration was/were
the first Application(s) made in a Convention country in respect of the invention, the
subject of the Application.

DECLARED at ... Cleveland, Ohio U.S.A.
this 28th day of July 19 89

For and on behalf of

Ferro Corporation

^(h) *Walter C. Danison*
Walter C. Danison
(Signature of Declarant)

(h) Personal Signature
of Declarant (c) (no seal,
witness or legalisation).

To THE COMMISSIONER OF PATENTS.

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AU 248836 61805/60 19.6

(57) Claim

1. A U.V. absorbing glass composition comprising from 75 to 98 parts by weight of a lead oxide-free base glass and from 2 to 25 parts by weight of a U.V. additive selected from cerium oxide, manganese oxide, iron oxide, cobalt oxide, copper oxide, vanadium oxide, molybdenum oxide, and mixtures of two or more of said oxides, wherein said base glass contains, in parts by weight based on 100 parts by weight of the base glass, from 19 to 45 parts SiO₂, from 20 to 33 parts B₂O₃, from 8 to 15 parts alkali metal oxide, from 0 to 35 parts zinc oxide, from 0 to 10 parts zirconium dioxide, from 0 to 6 parts aluminium oxide, from

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0 to 3 parts barium oxide, from 0 to 8 parts P_2O_5 ,
from 0 to 6 parts La_2O_3 , and from 2 to 10 parts of
added fluorine.

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(54) Title: LEAD-FREE U.V. ABSORBING GLASS

(57) Abstract

The present invention relates to an improved U.V. absorbing glass composition comprising from about 75 to about 98 parts by weight of a lead oxide free base glass having dissolved therein from about 2 to about 25 parts by weight of a U.V. additive selected from the group consisting of cerium oxide, manganese oxide, iron oxide, cobalt oxide, copper oxide, vanadium oxide, molybdenum oxide, and mixtures of two or more of said oxides; and to an ink composition comprising from about 15 to about 25 % by weight vehicle, from about 8 to about 16 % by weight a ceramic pigment, and from about 59 to about 77 % by weight of said U.V. absorbing glass composition.

LEAD-FREE U.V. ABSORBING GLASS

BACKGROUND OF INVENTION

The present invention relates to glass compositions, and more particularly provides novel lead-free U.V. absorbing glass compositions. While the compositions of the present invention have particular utility in the compounding of inks such as silk screen inks to provide a U.V. absorbing glaze or enamel, they have utility in any application requiring a U.V. absorbing glass, including protective eyewear and the like.

There are a wide variety of applications in which a thin glaze or enamel of U.V. absorbing glass is deposited on part or all of a base glass substrate to prevent the transmission of ultraviolet light (in general the term "glaze" being understood to mean a transparent glass, while an "enamel" will be understood to mean a glass containing pigment or other particles in suspension). For example, in the fabrication of motor vehicles, particularly in the sealing of glass windshields and the like, materials are employed which tend to be very sensitive to ultraviolet light. In order to protect these sealant materials it is common practice to deposit a thin narrow strip of ultraviolet light absorbing enamel at the peripheral edges of such automotive glass to prevent transmission of potentially harmful U.V. radiation to the sealant.

While the discussion which follows will refer to "windshields" and/or "windshield glass", it will be understood that unless otherwise clear from the context, these terms will be understood to refer to any automotive glass member, i.e. windshield, rear window, side windows, etc.

At the present time, these enamels are typically compounded from a lead oxide containing glass composition, which is suspended, together with a black pigment, in a suitable vehicle to provide an ink which can be silk screened onto the edges of the automotive windshield. In



this way, during final shaping of the windshield member, the enamel or glaze can be fired, fusing it with the windshield to provide a thin layer of glass, typically about .25 to 2 inches wide and about 1 mil in thickness.

The glass compositions presently employed in such application typically do not have sufficient U.V. absorption characteristics to be employed as a glaze, and therefore are normally used in conjunction with a black pigment to provide an enamel having substantially better U.V. absorbing characteristics than the glass alone.

In his work entitled "Coloured Glasses" (Society of Glass Technology, 1951 Reprint 1967, pages 212-213 and 232-234) Weyl discusses the use of metal oxide mixtures to color glass. In the course of his discussion, Weyl notes that mixtures of TiO_2 with Fe_2O_3 or CeO_2 can promote a shift in the iron or cerium valence, thereby shifting the light wave length absorbed by the glass. He specifically suggests that cerium oxide may impart U.V. light absorbing characteristics to lead glasses.

It will, of course, be understood that it is highly desirable to provide a glass having improved ultraviolet light absorbing characteristics. It will be equally apparent that it would be particularly advantageous to obtain such improved U.V. properties in a glass which was lead free, so as to provide greater safety by elimination of lead from both the work place in which the glass compositions are prepared and used as well as the final glass compositions itself.

The present invention provides a U.V. absorbing glass composition comprising from 75 to 98 parts by weight of a lead oxide-free base glass and from 2 to 25 parts by weight of a U.V. additive selected from cerium oxide, manganese oxide, iron oxide, cobalt oxide, copper oxide, vanadium oxide, molybdenum oxide, and mixtures of two or more of said oxides, wherein said base glass contains, in parts by weight based on 100 parts by weight of the base glass, from 19 to 45 parts SiO_2 , from 20 to 33 parts



B_2O_3 , from 8 to 15 parts alkali metal oxide, from 0 to 35 parts zinc oxide, from 0 to 10 parts zirconium dioxide, from 0 to 6 parts aluminium oxide, from 0 to 3 parts barium oxide, from 0 to 8 parts P_2O_5 , from 0 to 6 parts La_2O_3 , and from 2 to 10 parts of added fluorine.

The invention also provides a method of improving U.V. absorbing properties of a glass composition, which comprises mixing said ingredients.

10 The novel U.V. absorbing glass composition of the present invention preferably contains about 77% to about 98% by weight of a base glass composition having dissolved therein from about 2% to about 23% by weight of a U.V. absorbing oxide portion as defined above. In general, the base glass should have compatible expansion characteristics and fusion temperatures to suit the substrate soda-lime glass.

20 Where the glass is to be employed in conjunction with automotive applications, slightly different properties may be required according to the particular glass member involved. For use in conjunction with the substantially flat side windows and the curved rear window which are tempered, an enamel containing the glass of the present invention must mature and be compatible with a fast fire, to approximately 1150 to 1250°F (glass temperature) for a relatively brief period, i.e. one to five minutes or so. On the other hand, the curved front is sagged or pressed into shape necessitating a slower fire, generally approximately 1100 to 1150°F with a longer hold, i.e. 4 to 30 minutes. In both such applications a coefficient of expansion of $80 \times 10^{-7}/^{\circ}C$ or less is desirable so as to yield some compression in the enamel layer. Unless otherwise clear from the context, temperatures referred to herein are glass temperatures, that is to say the temperature of the glass itself, which may be somewhat lower than oven temperature, particularly in commercial applications.



Since one of the most immediate utilities of the glass compositions of the present invention is in the area of enamels for automotive applications, a substantial portion of the discussion herein will be directed to such applications, and the specific properties desired for such applications. It will, however, be understood that this merely represents one particular end use for which the glass compositions of the present invention are particularly suited, and that the glass compositions of the present invention are not limited to automotive applications, nor to any particular set of physical properties or characteristics which such end uses might dictate.

The glasses of the foregoing type can be melted in sintered fused silica crucibles at 1200°C with little attack on the crucible, though melting time must be controlled somewhat closely because of fluorine loss and will vary according to the size of the batch, i.e. optimum time for a 500 gm batch may be 25 to 30 minutes while the optimum time for a 1 kg batch of the same compositions might be 55 to 65 minutes. The melt may be handled by any suitable means though typically it is quenched by steel rolls into flake or frit, using techniques well known to those skilled in the art.

Where the glass is to be employed in silk screen ink enamels for automotive type applications the quenched frit is generally milled in alcohol, dried, mixed with a suitable quantity of black ceramic pigment then dispersed in a suitable vehicle with other well known additives to form the screening ink which can be applied to the preshaped glass members by silk screening and then fired to provide the ultimate U.V. absorbing enamel layer.

PREFERRED EMBODIMENT

The preferred U.V. absorbing additive of the present invention comprises a mixture of molybdenum oxide, iron oxide, cobalt oxide, cerium oxide and manganese oxide and the mixture is present in from about 6 to about 15 parts



by weight based on the overall weight of the entire glass formulation.

A particularly preferred range of metal oxides for the glass compositions of the present invention would be SiO_2 25-38%, B_2O_3 22-30%, ZrO_2 0-8%, Al_2O_3 0-5%, R_2O total ($\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{Li}_2\text{O}$) 9-14%, ZnO 8-21%, BaO 0-3%, MoO_3 2-4%, Fe_2O_3 1-5%, CoO 1-4%, CuO 0-4%, CeO_2 1-5%, MnO_2 0-4%, V_2O_5 0-2%, P_2O_5 0-4%, TiO_2 0-3%, CaO 0-4%, La_2O_3 0-5%, F_2 2-10%.

10 It will, of course, be apparent that some of the metal oxides which are employed in the U.V. absorbing component of the compositions of the present invention may tend to impart a color to the glass which may for aesthetic reasons limit the quantity of such metal oxide that can be employed, even in the preparation of black pigment containing enamels. For example, manganese oxide, while very effective in absorbing U.V. light, tends to impart an overpowering reddish tinge which can be aesthetically objectionable in certain applications.

20 The glass preferably contains from about 8% to about 16% by weight of a ceramic pigment.

By way of illustration and not by way limitation, the following examples will describe specific glass compositions within the scope of the present invention and their preparation.

EXAMPLE I

30 A "base" glass composition was prepared containing 45 parts by weight SiO_2 , 25 parts by weight B_2O_3 , 6 parts by weight ZrO_2 , 9 parts by weight Na_2O , 7.5 parts by weight ZnO , 4 parts by weight K_2O , 0.5 parts by weight Li_2O and 6 parts by weight F_2 . 3 parts by weight of various candidate



metal oxides were then added to 97 parts by weight of base glass, and the percentage of transmission of U.V. light from a long wavelength ($365\text{m}\mu$) U.V. source, and from a short wavelength ($254\text{m}\mu$) U.V. source were measured. The results of these test for 10 specific candidate U.V. additives are set forth in Table I.

EXAMPLE 2A

A second base glass composition, similar to that of Example 1, was prepared containing 44 parts SiO_2 , 26 parts B_2O_3 , 6 parts ZrO_2 , 9 parts Na_2O , 4 parts K_2O , 4 parts ZnO with 6 parts by weight of F_2 added. The further series of samples marked 11 through 18 were prepared by adding 7 parts by weight of U.V. additive to 93 parts by weight of base glass. In sample 11, 4 parts CeO_2 , and 3 parts TiO_2 were added to the base glass; for sample 12, 4 parts Fe_2O_3 and 3 parts vanadium oxide were added to the base glass; for sample 13, 3 parts cerium oxide and 4 parts manganese oxide were added to the base glass; for sample 14, 4 parts manganese oxide and 3 parts copper oxide were added to the base glass; for sample 15, 3 parts cerium oxide and 4 parts copper oxide were added to the base glass; for sample 16, 6 parts manganese dioxide and 1 part copper oxide were added to the base glass; for sample 17, 3 parts copper oxide and 4 parts vanadium oxide were added to the base glass; and for sample 18, 3 parts iron oxide and 4 parts titanium oxide were added to the base glass. The foregoing samples were subjected to long and short wavelength U.V. radiation as described in Example 1 and the percent of transmission was measured and is set forth in Table II.

EXAMPLE 3

A base glass slightly different from that of Example 2 was prepared containing 44 parts SiO_2 , 25 parts B_2O_3 , 7 parts ZrO_2 , 9 parts Na_2O , 4 parts K_2O , plus 6 parts by weight F_2 as before to which 11 parts of the additive were added. This base glass was used to prepare 3 additional

TABLE I

U.V. TRANSMISSION OF GLAZES FIRED ON FLOAT GLASS AT 1250°F/4MINS

Sample No.	% Transmission at 365 m μ	% Transmission at 254 m μ	Remarks	% Absorbers	Absorbers Used
0	58.1	3.2	Base Glass	0	None
1	34.4	2.1		3	3% CeO ₂
2	20.4	1.0		3	3% MnO ₂
3	21.5	1.3		3	3% Fe ₂ O ₃
4	21.5	1.3		3	3% CoO
5	22.6	2.3		3	3% CuO
6	29.0	2.4		3	3% V ₂ O ₅
7	15.1	0.8	Partially crystallized	3	3% NiO
8			Didn't dissolve	3	3% Cr ₂ O ₃
9	22.6	1.4		3	3% MoO ₃
10	58.1	3.5		3	3% WO ₃

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samples designated 19, 20 and 21. Sample 19 contained 89 parts base glass and 4 parts cerium oxide, 6 parts manganese oxide and 1 part cobalt oxide. Sample 20 contained 89 parts base glass, 3 parts cerium oxide, 5 parts manganese oxide, 2 parts copper oxide, and 1 part cobalt oxide. Sample 21 contained 19 parts base glass, 3 parts cerium oxide, 3 parts manganese oxide, 2 parts copper oxide, 1% cobalt oxide and 2% titanium oxide. The results for the testing of samples 19 through 21 are also set forth in Table II which compares the transmission figures for samples 11 through 21 with a commercial lead glass presently employed in production of commercial U.V. absorbing enamel compositions.

EXAMPLE 4

Two further compositions containing a higher level of U.V. additive were prepared. Sample 22 contained 40 parts SiO_2 , 25 parts B_2O_3 , 6 parts ZrO_2 , 8 parts Na_2O , 4 parts K_2O and 6% F_2 as before, plus 1 part Cerium oxide, 8 parts manganese oxide, 3 parts copper oxide, 1 part cobalt oxide, 2 parts iron oxide and 2 parts titanium dioxide. Sample 23 contained 38 parts SiO_2 , 23 parts B_2O_3 , 4 parts ZrO_2 , 8 parts Na_2O , 4 parts K_2O plus 6% F_2 as before, and also 1 part cerium oxide, 10 parts manganese oxide, 6 parts copper oxide, 2 parts cobalt oxide, 2 parts iron oxide and 2 parts titanium dioxide. These two samples were also tested for transmission of long and short wavelength U.V. light and the results for these tests comparing these two samples with another sample of commercial lead glass as set forth in Table III.

EXAMPLE 5

A series of compositions particularly suited for fast fire applications were prepared in a manner similar to that set forth in the preceding examples. The metal oxide composition of these glasses is set forth in Table IV. The U.V. transmission data at different firing temperatures for

TABLE II

U.V. TRANSMISSION OF GLAZES FIRED ON FLOAT GLASS AT 1250°F/4MINS

Sample No.	% Transmission at 365 m μ	% Transmission at 254 m μ	Remarks	% Absorbers	Absorbers Additive Used
A-1	53.3	1.6	Commercial Lead-U.V. Glass	0	None
11	18.3	0.7		7	4% CeO ₂ 3% TiO ₂
12	34.4	1.6		7	4% Fe ₂ O ₃ 3% V ₂ O ₅
13	23.7	0.7		7	3% CoO ₂ 4% MnO ₂
14	10.8	0		7	4% MnO ₂ 3% CuO
15	14.0	0.9		7	3% CeO ₂ 4% CuO
16	29.0	0		7	6% MnO ₂ 1% CoO
17	22.6	1.5		7	3% CuO 4% V ₂ O ₅
18	5.2	0.8	Partially crystallized	7	3% Fe ₂ O ₃ 4% TiO ₂

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TABLE II (Cont.)

U.V. TRANSMISSION OF GLAZES FIRED ON FLOAT GLASS AT 1250°F/4MINS

Sample No.	% Transmission at 365 m μ	% Transmission at 254 m μ	Remarks	% Absorbers	Absorbers Additive Used
19	21.5	0.9		11	4% CeO ₂ 6% MnO ₂ 1% CoO
20	24.7	1.9		11	3% CeO ₂ 5% MnO ₂ 2% CuO 1% CoO
21	19.4	1.0		11	3% CoO ₂ 3% MnO ₂ 2% CuO 1% CoO 2% TiO ₂

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TABLE III

U.V. TRANSMISSION OF GLAZES FIRED ON FLOAT GLASS AT 1250°F/4MINS

Sample No.	% Transmission at 365 m μ	% Transmission at 254 m μ	Remarks	% Absorbers	Absorbers Additive Used
A-2	62.4	2.2	Commercial Lead-U.V. Glass	0	None
22	1.0	0		17	1% CeO ₂ 8% MnO ₂ 3% CuO 1% CoO 2% Fe ₂ O ₃ 2% TiO ₂
23	0	0		23	1% CeO ₂ 10% MnO ₂ 6% CuO 2% CoO 2% Fe ₂ O ₃ 2% TiO ₂

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TABLE IV
GLASS COMPOSITIONS

BASE GLASS	SAMPLE NO.												
	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO ₂	16.64	16	16	16	16	16	18	20	22	26	30	32	34
B ₂ O ₃	26.62	26	25	25	26	26	25	24	23	22	20	20	20
ZnO	34.23	34	32	30	31	30	27	26	25	22	20	17	15
Na ₂ O	10.03	9	9	9	9	9	6	6	6	6.71	6.71	6.71	6.71
K ₂ O							3	3	3	3.29	3.29	3.29	3.29
CaO	4.38	4	3	3	4	4	3	3	3	3	2	2	2
TiO ₂					3	4	4	4	4	3	2	3	3
ZrO ₂	2.10	3	3	3	3	3	3	3	3	3	5	5	5
F ₂	4	4	4	4	4	4	4	4	4	4	4	4	4
U.V. Additive													
MoO ₃	3	3	3	3	4	3	3	3	3	3	3	3	4
Fe ₂ O ₃	3	3	3	5	1	1	2	2	2	-	-	-	-
MnO ₂		2	2	2	1		1	1	1	-	-	-	-
CuO			3	3			1	1	1	2	2	2	-

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TABLE IV (Cont.)

GLASS COMPOSITIONS

BASE GLASS	SAMPLE NO.												
	1	2	3	4	5	6	7	8	9	10	11	12	13
CoO			1	1	3	2	2	2	2	3	3	3	4
CeO ₂						2	2	2	2	3	3	3	3
Fe ₂	4	4	4	4	4	4	4	4	4	4	4	4	4

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TABLE IV (Cont.)

GLASS COMPOSITIONS

BASE GLASS	SAMPLE NO.												
	14	15	16	17	18	19	20	21	22	23	24	25	26
SiO ₂	36	38	38	38	38	38	38	38	38	38	38	36	36
B ₂ O ₃	20	20	21	21	20	20	20	20	20	22	24	22	24
ZnO	13	13	12.5	12	10	13	10	8	10	10	8	12	10
Na ₂ O	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71	6.71
K ₂ O	3.29	3.29	3.79	4.29	3.29	3.29	3.29	3.29	3.29	3.29	3.29	3.29	3.29
CaO	3	-	2	2	2	2	2	3	2	-	-	-	-
TiO ₂	3	3	-	-	-	-	-	-	-	-	-	-	-
AMP*	-	-	-	-	2	-	2	4	2	2	2	2	2
ZrO ₂	5	5	5	5	6	6	6	6	6	6	6	6	6
F ₂	4	4	4	4	4	4	4	4	4	4	4	4	4
U.V. Additive													
MoO ₃	4	4	3	3	4	4	4	4	4	4	4	4	4
Fe ₂ O ₃	-	-	1	1	1	-	2	2	2	2	2	2	2
MnO ₂	-	-	-	-	-	-	-	-	-	-	-	-	-

*AMP is Aluminum Metaphosphate, Al(PO₃)₃.

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TABLE IV (Cont.)

GLASS COMPOSITIONS

BASE GLASS	SAMPLE NO.												
	14	15	16	17	18	19	20	21	22	23	24	25	26
CuO	-	-	1	1	-	-	-	-	-	-	-	-	-
CoO	4	4	4	4	4	4	2	2	2	2	2	2	2
CeO ₂	3	3	2	2	3	3	4	4	4	4	4	4	4
Fe ₂	4	4	4	4	4	4	4	4	6	4	4	4	4

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TABLE IV (Cont.)
GLASS COMPOSITIONS

BASE GLASS	SAMPLE NO.		
	27	28	29
SiO ₂	36	34	36
B ₂ O ₃	24	24	24
ZnO	10	10	10
Na ₂ O	6.71	6.71	6.71
K ₂ O	3.29	3.29	3.29
CaO	2	4	-
ZrO ₂	6	6	6
Other			BaO 2
F ₂	4	4	4
U.V. Additive			
MoO ₃	4	4	4
Fe ₂ O ₃	2	2	2
CoO	2	2	2
CeO ₂	4	4	4
F ₂	4	4	4

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a particularly effective composition, Sample 29, is set forth in Table V. It should be noted that while Table V sets forth test data for sample 29, all of the samples were found to have substantially improved U.V. absorbing characteristics.

EXAMPLE 6

One kilogram batches of two glass compositions, one for regular fire application and one for fast fire application having the oxide compositions set forth in table VIA were prepared from the batch materials set forth in Table VIB.

The materials in both cases were blended together carefully and melted in a refractory crucible at 1250°C for 1 hour. The melt was then quenched by passing through water cooled steel rolls with a gap of about 1/32" to produce a glass frit.

EXAMPLE 7

A series of samples were prepared corresponding to the regular fire composition of Table VI A, with separate batches being melted for 45 minutes, 60 minutes, 75 minutes and 90 minutes. Samples from each of these melts were mixed on a 90/10 glass to pigment weight basis with V-710 black pigment. Separate samples of each mix were then fired at 1250°F for periods of 4, 5 and 6 minutes. The resulting enamel was subjected to long and short wavelength U.V. radiation using a 90/10 mixture of commercial lead glass and V-710 black pigment as a control. The results of these tests are set forth in Table VII.

Where the glass compositions of the present invention are to be employed in compositions such as silk screen ink compositions, they are prepared by conventional means well known to those skilled in the art. Generally, the ink composition will contain from about 59 to about 77% by weight glass frit, from about 8 to about 16% by weight pigment and from about 15 to about 25% by weight vehicle. Typically, the pigment used in the present U.V.

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TABLE V

<u>Sample</u>	<u>Firing</u>	<u>% Trans. at 365 m</u>	<u>% Trans. at 254 m</u>
No pigment	1200°F	38.0	4.4
No pigment	1150°F	35.0	4.2
With 12-1/2%	1200°F	2.0	0.6
V-710 pigment	1150°F	1.5	0.7
With 12-1/2%	1200°F	0	1.0
F-6340 pigment	1150°F	0	1.0

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TABLE VI A

	<u>FAST FIRE</u>	<u>REGULAR</u>
SiO ₂	36	28
B ₂ O ₃	24	28
ZrO ₂	6	-
Al ₂ O ₃	-	3
Na ₂ O	6.71	5.06
K ₂ O	3.29	4.94
Li ₂ O	-	1.0
ZnO	10	17.5
BaO	2	-
MoO ₃	4	4
Fe ₂ O ₃	2	2.5
CoO	2	1.5
CeO ₂	4	4
MnO ₂	-	0.5
F ₂	4	6
Tg (°C)	454	415
DSP (°C)	515	470
Exp. Coeff. (RT- 300°C) x 10 ⁻⁷ /°C	76.4	80.0

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TABLE VI B

<u>Batch Material</u>	<u>Regular</u>	<u>Fast Fire</u>
Powdered Quartz	248.4 grams	309.0 grams
Dehydrated Borax	163.4 "	217.9 "
High Purity Anhydrous Boric Acid	168.8 "	90.6 "
Alumina hydrate	45.8 "	0 "
Potassium Silicofluride	116.5 "	77.7 "
Zinc Oxide	175.0 "	100.0 "
Molybdenum trioxide	40.0 "	40.0 "
Cobalt Oxide	15.0 "	20.0 "
Red Iron Oxide	25.0 "	20.0 "
Cerium Dioxide	40.0 "	40.0 "
Manganese Dioxide	5.0 "	0 "
Lithium Carbonate	25.1 "	0 "
Milled Zircon	0 "	90.0 "
Barium Carbonate	0 "	26.0 "

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TABLE VII

REGULAR FIRE GLASS*

<u>Sample</u>	<u>% Transmission at 365 mμ</u>	<u>% Transmission at 254 mμ</u>	
PF-98 (Lead Glass)	8.1	0	
Sample 1 Melted 45 Mins.	0	0	Wired at
Sample 2 Melted 60 mins.	0	0	1250°F,
Sample 3 Melted 75 mins.	0	0	6 mins.
Sample 4 Melted 90 mins.	0	0	
PF-98	13.5	0	
Sample 5 Melted 45 mins.	0	0	Fired at
Sample 6 Melted 60 mins.	0	0	1250°F,
Sample 7 Melted 75 mins.	0	0	5 mins.
Sample 8 Melted 90 mins.	0	0	
PF-98	13.5	0	
Sample 9 Melted 45 mins.	0	0	Fired at
Sample 10 Melted 60 mins.	0	0	1250°F,
Sample 11 Melted 75 mins.	0	0	4 mins.
Sample 12 Melted 90 mins.	0	0	

*Composition of Table VI A

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~~applications is a black ceramic pigment such as a V-710 pigment or F-6340 pigment (both manufactured by Ferro Corporation) though any suitable ceramic pigment may be employed. A typical vehicle for use in compositions such as these would be about 77 to about 84% by weight pine oil, about 15 to about 20% by weight acrylic resin, and from about 1 to about 3% surfactant such as a polymerized dialkyl phosphate, and/or a mixture of surfactants of the type commercially available from a number of sources.~~

Because of the greater U.V. light absorbency of the glass compositions of the present invention and the absence of lead from these compositions two particular advantages are readily apparent. First, the glass composition per se will be considerably lighter than would be the case for a similar lead containing composition which means less weight is used per piece of automobile glass, which would reduce the cost per piece. In addition because of the phenomenal improvement in U.V. light absorption, it will be possible to substantially reduce the amount of pigment required to maintain a particular level of U.V. absorbency. Other advantage will of course be obvious to those skilled in the art with respect to the particular base glass and/or U.V. additive combinations selected.

The novel unpigmented (or very lightly pigmented) glaze compositions of the present invention can also be employed to produce so called "tinted windshields" where a portion of the windshield, usually the top, is tinted typically a bluish color. This tinting has heretofore frequently been accomplished by soaking the composite windshield member (typically two outer layers of glass with a plastic safety layer of polymer such as polyvinyl butyrate in the middle) in a liquid dye bath until sufficient dye is absorbed by the polymeric safety layer to provide the desired degree of tint. Many of the glazes of the present invention have a ~~slightly bluish tinge, and could be much more quickly and~~

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applications is a black ceramic pigment such as a V-710 pigment or F-6340 pigment (both manufactured by Ferro Corporation) though any suitable ceramic pigment may be employed. A typical vehicle for use in compositions such as these would be about 77 to about 84% by weight pine oil, about 15 to about 20% by weight acrylic resin, and from about 1 to 3% surfactant such as a polymerized dialkyl phosphate, and/or a mixture of surfactants of the type commercially available from a number of sources.

10 Because of the greater U.V. light absorbency of the glass compositions of the present invention and the absence of lead from these compositions two particular advantages are readily apparent. First, the glass composition per se will be considerably lighter than would be the case for a similar lead containing composition which means less weight is used per piece of automobile glass, which would reduce the cost per piece. In addition because of the phenomenal improvement in U.V. light absorption, it will be possible to substantially reduce the amount of pigment required to maintain a particular level of U.V. absorbency. Other advantages will of course be obvious to those skilled in the art with respect to the particular base glass and/or U.V. additive combinations selected.

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The novel unpigmented (or very lightly pigmented) glaze compositions of the present invention can also be employed to produce so called "tinted windshields" where a portion of the windshield, usually the top, is tinted



typically a bluish color. This tinting has heretofore frequently been accomplished by soaking the composite windshield member (typically two outer layers of glass with a plastic safety layer of polymer such as polyvinyl butyrate in the middle) in a liquid dye bath until sufficient dye is absorbed by the polymeric safety layer to provide the desired degree of tint. Many of the glazes of the present invention have a slightly bluish tinge, and could be much more quickly and expeditiously applied to provide the desired degree of tint without prolonged soaking of the windshield member in a dye vat.

Thus the invention further provides a composite automotive windshield member bonded to an automobile using a U.V. sensitive adhesive composition, and having a thin composite of U.V. protective enamel fired thereon to screen transmission of U.V. light to said adhesive composition, wherein there is employed as said enamel, a U.V. absorbing glass composition of the invention.

In other uses, such as protective eyewear, the glass compositions of the present invention could provide much more scratch resistant lenses than are now available, and could be inexpensively cut from sheets of flat glass. Alternatively, the compositions can be applied as a glaze over regular lens glass which can be ground to prescriptions in the conventional manner either before or after glazing.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A U.V. absorbing glass composition comprising from 75 to 98 parts by weight of a lead oxide-free base glass and from 2 to 25 parts by weight of a U.V. additive selected from cerium oxide, manganese oxide, iron oxide, cobalt oxide, copper oxide, vanadium oxide, molybdenum oxide, and mixtures of two or more of said oxides, wherein said base glass contains, in parts by weight based on 100 parts by weight of the base glass, from 19 to 45 parts SiO_2 , from 20 to 33 parts B_2O_3 , from 8 to 15 parts alkali metal oxide, from 0 to 35 parts zinc oxide, from 0 to 10 parts zirconium dioxide, from 0 to 6 parts aluminium oxide, from 0 to 3 parts barium oxide, from 0 to 8 parts P_2O_5 , from 0 to 6 parts La_2O_3 , and from 2 to 10 parts of added fluorine.

2. The U.V. absorbing glass composition of claim 1 wherein said glass contains, in parts by weight based on 100 parts by weight of base glass, from 25 to 38 parts SiO_2 , from 22 to 30 parts B_2O_3 , from 0 to 8 parts ZrO_2 , from 0 to 5 parts Al_2O_3 , from 9 to 14 parts alkali metal oxide, from 8 to 21 parts ZnO , from 0 to 3 parts BaO , from 2 to 4 parts MoO_3 , from 1 to 5 parts Fe_2O_3 , from 1 to 4 parts CoO , from 0 to 3 parts TiO_2 , from 0 to 4 parts CaO from 0 to 5 parts La_2O_3 and from 2 to 10 parts of added fluorine.

3. The glass composition of claim 1 wherein said glass also contains from 8% to 16% by weight of a ceramic pigment.



4. The glass composition of claim 2 wherein said glass also contains from 8% to 16% by weight of a ceramic pigment.

5. The glass composition of claim 1 wherein said glass corresponds to the following composition:

<u>Oxide</u>	<u>Percent by Weight</u>
SiO ₂	36
B ₂ O ₃	24
ZrO ₂	6
Na ₂ O	6.71
K ₂ O	3.29
ZnO	10
BaO	2
MoO ₃	4
Fe ₂ O ₃	2
CoO	2
CeO ₂	4
F ₂	4

6. The glass composition of claim 1 wherein said glass corresponds to the following composition:

<u>Oxide</u>	<u>Percent by Weight</u>
SiO ₂	28
B ₂ O ₃	28
Al ₂ O ₃	3
Na ₂ O	5.06
K ₂ O	4.94
Li ₂ O	1.0



10	ZnO	17.5
	MoO ₃	4
	Fe ₂ O ₃	2.5
	CoO	1.5
	CeO ₂	4
	MnO ₂	0.5
	F ₂	6

7. The glass composition of claim 5 wherein said glass also contains from 8% to 16% by weight of a ceramic pigment.

8. The glass composition of claim 6 wherein said glass also contains from 8% to 16% by weight of a ceramic pigment.

9. An ink composition comprising from 15 to 25% by weight vehicle, from 8 to 16% by weight pigment, and from 59 to 77% by weight glass frit, said glass frit comprising from 75 to 98 parts by weight of a lead oxide-free base glass and from 2 to 25 parts by weight of a U.V. additive selected from cerium oxide, manganese oxide, iron oxide, cobalt oxide, copper oxide, vanadium oxide, molybdenum oxide, and mixtures of two or more of said oxides, wherein said base glass contains, in parts by weight based on 100 parts by weight of the base glass, from 19 to 45 parts SiO₂, from 20 to 33 parts B₂O₃, from 8 to 15 parts alkali metal oxide, from 0 to 35 parts zinc oxide, from 0 to 10 parts zirconium dioxide, from 0 to 6 parts aluminum oxide, from 0 to 3 parts barium oxide, from 0 to 8 parts P₂O₅, from 0 to 6 parts La₂O₃, and from 2 to 10



parts of added fluorine.

10. The ink composition of claim 9 wherein said glass contains, in parts by weight based on 100 parts by weight of base glass, from 25 to 38 parts SiO_2 , from 22 to 30 parts B_2O_3 , from 0 to 8 parts ZrO_2 , from 0 to 5 parts Al_2O_3 , from 9 to 14 parts alkali metal oxide, from 8 to 21 parts ZnO , from 0 to 3 parts BaO , from 2 to 4 parts MoO_3 , from 1 to 5 parts Fe_2O_3 , from 1 to 4 parts CoO , from 0 to 3 parts TiO_2 , from 0 to 4 parts CaO , from 0 to 5 parts La_2O_3 and from 2 to 10 parts of added fluorine.

11. The ink composition of claim 9 wherein said vehicle comprises based on the weight of said vehicle, from 77 to 84% by weight pine oil, from 15 to 20% by weight acrylic resin and from 1 to 3% by weight surfactant.

12. The ink composition of claim 9 wherein said base glass corresponds to the following composition:

<u>Oxide</u>	<u>Percent by Weight</u>
SiO_2	36
B_2O_3	24
ZrO_2	6
Na_2O	6.71
K_2O	3.29
ZnO	10
BaO	2
MoO_3	4
Fe_2O_3	2



CoO	2
CeO ₂	4
F ₂	4

13. The ink composition of claim 11 wherein said base glass corresponds to the following composition:

<u>Oxide</u>	<u>Percent by Weight</u>
SiO ₂	36
B ₂ O ₃	24
ZrO ₂	6
Na ₂ O	6.71
K ₂ O	3.29
ZnO	10
BaO	2
MoO ₃	4
Fe ₂ O ₃	2
CoO	2
CeO ₂	4
F ₂	4

14. The ink composition of claim 9 wherein said base glass corresponds to the following composition:

<u>Oxide</u>	<u>Percent by Weight</u>
SiO ₂	28
B ₂ O ₃	28
Al ₂ O ₃	3
Na ₂ O	5.06
K ₂ O	4.94
Li ₂ O	1.0
ZnO	17.5
MoO ₃	4



Fe_2O_3	2.5
CoO	1.5
CeO_2	4
MnO_2	0.5
F_2	6

15. The ink composition of claim 11 wherein said base glass corresponds to the following composition:

<u>Oxide</u>	<u>Percent by Weight</u>
SiO_2	28
B_2O_3	28
Al_2O_3	3
Na_2O	5.06
K_2O	4.94
Li_2O	1.0
ZnO	17.5
MoO_3	4
Fe_2O_3	2.5
CoO	1.5
CeO_2	4
MnO_2	0.5
F_2	6

16. A method of improving the U.V. absorbing properties of a glass composition, which comprises admixing with from 75 to 98 parts by weight of a lead oxide-free base glass and from 2 to 25 parts by weight of a U.V. additive selected from cerium oxide, manganese oxide, iron oxide, cobalt oxide, copper oxide, vanadium oxide, molybdenum oxide, and mixtures of two or more of said oxides, wherein said base glass contains, in parts by weight based on 100



parts by weight of the base glass, from 19 to 45 parts
10 SiO_2 , from 20 to 33 parts B_2O_3 , from 8 to 15 parts
alkali metal oxide, from 0 to 35 parts zinc oxide, from 0
to 10 parts zirconium dioxide, from 0 to 6 parts aluminum
oxide, from 0 to 3 parts barium oxide, from 0 to 8 parts
 P_2O_5 , from 0 to 6 parts La_2O_3 , and from 2 to 10
parts of added fluorine.

17. The method of claim 16 wherein said glass contains in
parts by weight based on 100 parts by weight of base glass
from 25 to 38 parts SiO_2 , from 22 to 30 parts B_2O_3 ,
from 0 to 8 parts ZrO_2 , from 0 to 5 parts Al_2O_3 ,
from 9 to 14 parts alkali metal oxide, from 8 to 21 parts
 ZnO , from 0 to 3 parts BaO , from 2 to 4 parts MoO_3 , from
1 to 5 parts Fe_2O_3 , from 1 to 4 parts CoO , from 0 to 3
parts TiO_2 , from 0 to 4 parts CaO , from 0 to 5 parts
 La_2O_3 and from 2 to 10 parts of added fluorine.

18. A composite automotive windshield member bonded to an
automobile using a U.V. sensitive adhesive composition,
and having a thin composite of U.V. protective enamel
fired thereon to screen transmission of U.V. light to said
adhesive composition, wherein there is employed as said
enamel, a U.V. absorbing glass composition comprising from
75 to 98 parts by weight of a lead oxide-free base glass
and from 2 to 25 parts by weight of a U.V. additive
selected from cerium oxide, manganese
10 oxide, iron oxide, cobalt oxide, copper oxide, vanadium
oxide, molybdenum oxide, and mixtures of two or more of



said oxides, wherein said base glass contains, in parts by weight based on 100 parts by weight of the base glass, from 19 to 45 parts SiO_2 , from 20 to 33 parts B_2O_3 , from 8 to 15 parts alkali metal oxide, from 0 to 35 parts zinc oxide, from 0 to 10 parts zirconium dioxide, from 0 to 6 parts aluminum oxide, from 0 to 3 parts barium oxide, from 0 to 8 parts P_2O_5 , from 0 to 6 parts La_2O_3 , and from 2 to 10 parts of added fluorine.

19. The windshield member of claim 18 wherein said glass contains, in parts by weight based on 100 parts by weight of base glass, from 25 to 38 parts SiO_2 , from 22 to 30 parts B_2O_3 , from 0 to 8 parts ZrO_2 , from 0 to 5 parts Al_2O_3 , from 9 to 14 parts alkali metal oxide, from 8 to 21 parts ZnO , from 0 to 3 parts BaO , from 2 to 4 parts MoO_3 , from 1 to 5 parts Fe_2O_3 , from 1 to 4 parts CoO , from 0 to 3 parts TiO_2 , from 0 to 4 parts CaO , from 0 to 5 parts La_2O_3 and from 2 to 10 parts of added fluorine.

20. The windshield member of claim 18 wherein said glass also contains from 8% to 16% by weight of a ceramic pigment.

21. The windshield member of claim 19 wherein said glass also contains from 8% to 16% by weight of a ceramic pigment.

22. The windshield member of claim 18 wherein said glass corresponds to the following composition:

<u>Oxide</u>	<u>Percent by Weight</u>
--------------	--------------------------



SiO ₂	36
B ₂ O ₃	24
ZrO ₂	6
Na ₂ O	6.71
K ₂ O	3.29
ZnO	10
BaO	2
MoO ₃	4
Fe ₂ O ₃	2
CoO	2
CeO ₂	4
F ₂	4

23. The windshield member of claim 18 wherein said glass corresponds to the following composition:

<u>Oxide</u>	<u>Percent by Weight</u>
SiO ₂	28
B ₂ O ₃	28
Al ₂ O ₃	3
Na ₂ O	5.06
K ₂ O	4.94
Li ₂ O	1.0
ZnO	17.5
MoO ₃	4
Fe ₂ O ₃	2.5
CoO	1.5
CeO ₂	4



MnO ₂	0.5
F ₂	6

24. The U.V. absorbing glass composition of claim 1,
substantially as described in any one of the Examples.

DATED this 11th day of FEBRUARY 1991

FERRO CORPORATION

Attorney: WILLIAM S. LLOYD

Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 88/04515

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁴ : C 03 C 4/08; C 03 C 8/14; C 03 C 3/064; C 03 C 3/089; C 03 C 3/093; C 03 C 3/066		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁴	C 03 C	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	DE, B, 2845916 (RIEDEL-DE HAEN) 4 October 1979 see claims; examples --	1-27
Y	US, A, 2409412 (W.H. ARMISTEAD) 15 October 1946 see columns 3,4 --	1-7,16-20
Y	Chemical Abstracts, volume 106, no. 6, February 1987, (Columbus, Ohio, US), see page 289, abstract 37474r, & JP, A, 61151037 (MATSUSHITA ELECTRIC WORKS, LTD) 9 July 1986 --	1-7,16-20
Y	FR, A, 2122481 (CORNING GLASS WORKS) 1 September 1972 see claims --	1-7,16-20, 27
Y	GB, A, 2072159 (CENTRAL GLASS CO.) 30 September 1981 see claims; example --	1,8-15,21- 27
	./.	
¹⁰ Special categories of cited documents: 10 "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
22nd March 1989	17. 04. 89	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 P.C.G. VAN DER PUTTEN	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	EP, A, 0174893 (SAINT-GOBAIN VITRAGE) 19 March 1986 see claims; page 1, lines 23-33; example 1	1,8-15,21-27
Y	EP, A, 0074314 (SAINT-GOBAIN VITRAGE) 16 March 1983 see page 1, lines 18-26	1,13

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8804515
SA 26171

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 10/04/89
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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