

PATENT SPECIFICATION

(11) 1 428 880

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- (21) Application No. 38313/74 (22) Filed 2 Sept. 1974
 (31) Convention Application No. 2 404 752
 (32) Filed 1 Feb. 1974 in
 (33) Germany (DT)
 (44) Complete Specification published 17 March 1976
 (51) INT CL² C03C 3/26, 3/16; C09K 9/00
 (52) Index at acceptance

CIM 11B5B 11C10 11C1 11C4 11C7 11C9 11F15 11F1
 11F23 11F29 11F34 11F8 11H 11J2 11K2 11K4
 11K8 13E 13J 13N 13S2A
 C4S 43Y 670 708 70Y 711 712 713 714 715 717 719 720
 722 729 72Y 735 738 73Y 740 747 756 757 75Y
 76Y 782 78Y



(54) IMPROVEMENTS IN OR RELATING TO PHOTOTROPIC GLASS

(71) We, CARL-ZEISS-STIFTUNG, a Foundation established under the laws of Germany, of Heidenheim a.d. Brenz, Württemberg, Germany, trading as JENAER GLASWERK SCHOTT & GEN., do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a phototropic glass which is free from fluorine and boric oxide and preferably also free from magnesium oxide.

Various phototropic glasses are known. Similarly, phosphate glasses having very different compositions but also phototropic glasses have been known for a relatively long time. Thus, Sakka and MacKenzie (U.S. Patent Specification 3,615,761 or J. Amer. Ceram. Soc. 55 (1972), 553) describe, *inter alia* phosphate glasses with phototropic properties and containing silver and halogen. A description of phototropic phosphate glasses which is comprehensive as regards the scope of the possibilities of composition is to be found in German Offenlegungsschrift 2,234,283. In these cases, silver halide crystals which are dispersed in the glass cause phototropy. Con-

sequently, they are distinguished for example, from glasses which are based on silicate and borate, which likewise contain silver halide crystals as carrier of the phototropy and are described for example in German Patent Specification 1,421,838 or German Patent Specification 1,596,847 only as regards the basic glass composition. German Patent Specification 1,596,847 corresponds to U.K. Specifications 1,213,798 and 1,213,799.

Glasses of one or more oxides are built up from lattices of the main components. The main components are combined to form the lattice as coordination polyhedrons, attached *via* the corners. These structural units (main components) are SiO₄ tetrahedrons, for example in silicate glasses; similar structural units exist in borate and phosphate glasses. These structural units are bonded to one another with different degrees of strength in different glasses. The stronger the central cations of these structural units polarise the surrounding oxygens, the smaller is the bonding strength with adjoining structural units (e.g. with the adjacent tetrahedron). The polarisation of the oxygen atoms by the central cations is set out as follows according to Dietzel (Z. Elektrochem 48 (1942) 9):

TABLE I

Central cation	Valency in the glass Z	Distance <i>a</i> in Angstroms between cation and oxygens	Field Strength Z/a^2
Si	4	1.60	1.56
B	3	1.36	1.62
P	5	1.55	2.08

The greater the field strength of the central cation of such a structural unit, the more strongly does the enclosing oxygen sheath become polarised and the smaller is the bonding force of this structural unit (consisting of central cation and enclosing oxygen sheath) outwardly to the adjoining structural units.

Consequently, the bonding strength between the main components decreases, i.e. the entire glass structure is loosened, when changing from silicate to borate or even to phosphate glasses.

Phototropic glasses of which the phototropic properties are established by silver halide crystals and possibly small amounts of metallic silver are claimed in German Patent Specification 1,596,847, and these glasses are characterised in that they consist of one or more glass-forming oxides as main components, of which the bonding with one another in the glass is weaker than the bonds in a silicate basic glass with SiO_2 as glass-forming component.

German Patent Specification 1,596,847

claims more particularly borate glasses which have better phototropic properties than the silicate glasses known at the time, because of the weaker bonding of the main components to one another.

It is apparent from the foregoing considerations which are generally available to the technical experts that also the phosphate glasses must likewise be suitable for providing phototropic glass with favourable properties as regards variation in optical density under the influence of an exciting luminous flux.

If the main component B_2O_3 is replaced by P_2O_5 in accordance with the teaching of German Patent Specification 1,596,847 then the bonding of the main components with one another in the glass which is then formed becomes weaker. There are then produced from the examples of the said German Patent Specification the following compositions which do indeed have phototropic properties but of which the phototropy is of relatively poor quality. To facilitate comparisons compositions are given in parts by weight.

TABLE 2

	1	2	3	4	5	6
P_2O_5	14.9	81.4	47.8	71.0	67.5	73.6
PbO	69.4	—	35.6	—	—	—
MgO	—	—	—	15.4	13.5	—
BaO	—	—	—	—	15.4	—
ZnO	9.90	10.2	—	—	—	9.20
Al_2O_3	1.98	—	12.5	9.60	—	—
Na_2O	0.10	—	—	—	—	—
K_2O	—	5.08	—	—	—	7.40
KCl	—	—	—	0.48	—	0.92
KBr	1.49	1.53	1.44	1.44	1.45	1.38
KI	1.49	1.53	1.44	1.44	1.45	1.38
LiF	0.50	—	0.96	0.29	0.29	0.28
Ag_2O	0.19	0.30	0.29	0.38	0.38	0.37
CuO	0.005	—	0.01	—	0.02	0.02
$\text{K}_2\text{Cr}_2\text{O}_7$	—	—	—	0.01	0.005	0.01
ZrO_2	—	—	—	—	—	5.52

As already described in the said German Patent Specification 1,596,847 a contribution to stabilisation can be made by using SiO_2 in small quantities. As a result thereof, the

structure of the glass again becomes stronger. According to German Patent Specification 1,596,847, and bearing in mind the foregoing considerations, glasses are thus possible such

as those which are set out by way of example in Table 3. These glasses are listed in parts by weight to facilitate comprehension.

TABLE 3:

	7	8	9	10	11
SiO ₂	4.49	3.10	2.99	8.55	7.46
B ₂ O ₃	6.00	5.05	4.00	7.05	7.56
P ₂ O ₅	39.33	33.75	32.73	30.19	34.62
PbO	—	5.79	27.35	—	1.99
MgO	6.99	11.57	1.54	3.16	—
BaO	10.93	12.78	4.61	6.52	5.17
ZnO	0.44	—	—	—	—
CaO	—	—	—	6.92	4.87
ZrO ₂	1.75	—	—	—	1.99
TiO ₂	—	—	—	0.49	0.99
Al ₂ O ₃	17.48	12.05	9.60	21.51	18.90
Na ₂ O	4.81	12.15	6.45	5.93	5.97
K ₂ O	6.12	1.93	4.07	6.92	8.46
KCl	0.70	0.39	2.31	0.99	0.90
KBr	0.35	1.16	1.38	0.99	0.40
KI	0.09	—	—	—	—
LiF	0.36	—	0.77	—	0.50
Ag ₂ O	0.17	0.29	0.19	0.18	0.18
CuO	0.02	—	—	0.02	0.04
KHF ₂	—	—	—	0.59	—

10 Examples 7 to 11 also show that a certain quantity of B₂O₃ can be incorporated into such phototropic phosphate glasses.

15 Phosphate glasses are generally known for their particularly poor chemical stability. It is true that this can be counteracted by a high content of Al₂O₃, but this again results in a deleterious effect on the *per se* already bad crystallisation strength.

20 A glass which is to be used as spectacle glass (distant portion glass) must satisfy conditions as regards profitability at the time of production. This to say, the yield in normal production assemblies must be combined with

a sufficient output and a lowest possible number of complaints or claims.

Using the glass manufacturing apparatus 25 which is in general use at the present time, it is possible to process glasses which ensure a throughput of more than 60 kg/h. For this purpose, it is necessary that this glass with a viscosity between 10³ and 10^{4.5} poises is portioned 30 by cutting with shears, in order thereafter to be pressed. With this viscosity, which is relatively high for liquid glass, however, many glasses not containing silicate already crystallise with such high crystallisation speeds 35 that a profitable production becomes im-

possible. In order to obviate this defect, it is possible to fall back upon a lowering in viscosity and special production (because the portioning by cutting with shears is no longer possible at low viscosities) or to accept a decrease in the output by temporarily interrupting the production and flushing away the disturbing crystals formed during the production time by a brief raising of the temperature.

All glasses disclosed in German Offenlegungsschrift 2,234,283 were remelted from this point of view and tested for their crystallisation properties. After carrying out 60 melting operations, it was shown that these compositions did not fulfil the qualification for a technical production.

As qualification for the possibility of using any glass as spectacle glasses, there are applicable the following specifications which are generally acknowledged by the experts to be desirable:

- refractive index n_d of 1.5225 to 1.5238;
- no crystallisation between 10^4 and 10^5 poises;
- sufficient chemical stability (characterised by the hydrolytic stability according to DIN (German Industrial Standard) 12,111 and by the resistance to the welding test);
- sufficient capacity for chemical hardening in the standard bath for normal spectacle crown glass (this condition is normally set in those cases where increase in strength is legally prescribed for all spectacle glasses).

The object of the present invention is an improved phototropic glass suitable for spectacles and which avoids or minimises one or more of the above-mentioned defects.

According to the present invention there is provided a phototropic glass which is free from fluorine and boric oxide and comprises the following constituents expressed in percentages by weight:

SiO ₂	12.1	to	13.9
P ₂ O ₅	30.4	to	33.9
Al ₂ O ₃	22.5	to	25.7
ZrO ₂	1.0	to	2.6
Na ₂ O	3.0	to	7.5
K ₂ O	5.3	to	10.5
CaO	3.1	to	5.0
BaO	3.1	to	7.0
SrO	0	to	0.5
PbO	0.4	to	2.5

TiO ₂	0.1	to	0.6
La ₂ O ₃	0.05	to	2.0
Ag ₂ O	0.05	to	1.0
CuO	0	to	0.1
Cl and/or Br	0.20	to	10.0

the balance, if any, being one or more compatible constituents. Preferably the lower limits of the Na₂O, K₂O and BaO contents are 4.7, 6.5 and 5.5 respectively. The preferred lower limit of Ag₂O is 0.1. The preferred upper limit of Cl and/or Br is 6.0 but, if desired, it may be as low as 1.0.

The phototropic glass of this invention will generally realise the following phototropic properties: a transmission decrease of at least 50% upon exposure to light, and a regeneration of the transmission after terminating the exposure to light of at least 20% after 10 minutes, based on a glass thickness of 2mm. Desirably the phototropic glass will contain silver-rich and halogen-rich (wherein halogen means Cl and/or Br), non-crystalline phase separations with a diameter between 40 and 350 Å, will show no crystallization in a viscosity range between 10^4 and 10^5 poises; will have a refractive index, n_d , from 1.5225 to 1.5238 will be strengthenable chemically by ion-exchange in a medium containing potassium ions at a temperature below that at which the viscosity is $10^{4.5}$ poises, whereupon alkali metal ions smaller than potassium will diffuse out of the glass; will have a linear thermal expansion coefficient (between 20 and 300°C.) from 99 to 105×10^{-7} per °C.; and will have a chemical stability characterised by a titration value, in accordance with DIN (German Industrial Standard) 12,111, of less than 0.2 ml HCl.

According to another aspect of this invention we provide a process for producing a phototropic glass of the invention, wherein a melt corresponding to the glass composition required is cast, cooled for solidification and heat treated at 560°—640° C. for 1—3 hours.

Furthermore, according to the invention, the proportion of the Al₂O₃ is appreciably higher than the amounts customarily used for photographic glasses.

The usual phototropic glasses which contain silver and halogen only show good phototrophy when they contain B₂O₃; phototropic glasses of conventional type which are free from B₂O₃ have by contrast either no phototrophy or only an inferior phototrophy. Glasses with and without B₂O₃ and also their phototropic properties are set out in Table 4. In order to increase the understanding thereof, this Table shows parts by weight.

TABLE 4

	12	13	14	15	16	17	18	19
SiO ₂	61.5	61.5	7.5	7.5	9.1	9.1	50.0	53.0
B ₂ O ₃	—	16.6	—	4.0	—	5.0	—	18.0
P ₂ O ₅	—	—	36.5	36.5	35.0	35.0	2.0	2.0
Al ₂ O ₃	10.7	10.7	22.0	22.0	25.0	25.0	8.0	8.0
ZrO ₂	—	—	—	—	—	—	1.0	1.0
Na ₂ O	10.7	10.7	6.5	6.5	6.5	6.5	4.0	4.0
K ₂ O	—	—	6.5	6.5	8.0	8.0	1.0	1.0
MgO	—	—	4.4	4.4	3.4	3.4	2.0	2.0
CaO	—	—	9.0	9.0	6.9	9.0	—	—
BaO	—	—	6.7	6.7	6.7	6.7	4.0	4.0
PbO	—	—	—	—	—	—	6.0	6.0
TiO ₂	—	—	1.0	1.0	0.5	0.5	—	—
Ag ₂ O	0.6	0.6	0.14	0.14	0.18	0.18	0.42	0.42
CuO	0.01	0.01	0.02	0.02	0.01	0.01	—	—
Cl	—	—	0.6	0.6	0.6	0.6	1.0	1.0
Br	0.8	0.8	0.3	0.3	0.3	0.3	0.5	0.5
F	2.5	2.5	0.1	0.1	0.3	0.3	—	—
Temperature treatment	1 h 610°	1 h 610°	2 h 580°	2 h 580°	1 h 620°	1 h 620°	1 h 640°	1 h 640°
Saturation transmission after exposure to light	no blackening	40%	6%	53%	12%	68%	no blackening	44%
Regeneration after 10 min.	—	20%	2%	24%	4%	27%	—	17%

5 It is apparent from Table 4 that the omission of the component B₂O₃ impairs the phototrophy. One is consequently obliged
 10 always to incorporate a minimum amount of B₂O₃ into the glass, so that the precipitation of the silver halide crystals (microcrystals, such as described for example in German Patent Specification 1,421,838 or German Patent Specification 1,596,847) proceeds favourably and is not disturbed by other phase separations.

15 It has now been found in a completely surprising manner that, even in the complete absence of B₂O₃, glasses having photo-

tropic properties can be obtained which are at least equally as good as those of the glasses with which the phototrophy is produced by silver halide crystals (German Patent Specification 1,421,838 and 1,596,847 and German Offenlegungsschrift 2,234,283). The glasses according to the invention can even provide phototrophy which is superior to that of the known glasses as regards the depth of density and regeneration speed.

20 It was even more surprisingly found that the phototrophy with the glasses according to the invention is not caused by silver halide crystals, but by non-crystalline segregation
 25

phases which are rich in silver halide.

In order to produce particularly suitable precipitation conditions for the non-crystalline segregation phases rich in silver and halogen, there must be maintained the P_2O_5 range specified by this invention.

Moreover, so as to avoid the crystallisation of the segregation phases rich in silver and halogen, it is necessary to subject the halogens to a particular selection. Fluorine must not be used as halogen; it seems to promote the crystallisation of the segregation phases when already present in low concentrations.

Furthermore, it was found that, for a profitable production, it is desirable to have a viscosity which is relatively high for phosphate glasses, but that with a range of SiO_2 as specified by this invention, it is at the same time necessary to keep the content of MgO absent or as low as possible. Since MgO has a great influence on the crystallisation of the basic glass (this basic glass crystallisation is to be distinguished from the crystallisation of the silver halide crystals or the non-crystalline segregations with a high silver halide content and serving as carriers of the phototropy).

The crystallisation behaviour is further influenced by other components. Thus, it was found that the concentrations of TiO_2 and ZrO_2 must be limited in accordance with the invention although both components are known as nucleus formers for promoting the crystallisation. For optical reasons, the upper limit for ZrO_2 is as specified by the invention, since otherwise the refractive index of the glass would rise to above the desired values, which are generally from 1.5225 to 1.5238. Similar conditions apply for the upper limit of La_2O_3 as specified by the invention. Both components have an additional significance for the production of a sufficient chemical stability of the glass. ZrO_2 and La_2O_3 also produce an influence on the precipitation of the non-crystalline segregation phases rich in silver halide.

The contents of alkali metal oxides and alkaline earth metal oxides not only influences the segregation kinetics of the non-crystalline segregation phases rich in silver halide, but also influences the other properties of the glass. It was found that the sum of the alkali metal oxides should advantageously be between 11.2 and 16.2% by weight, and this is of some importance more particularly as regards the possibility of solidifying the glass chemically by ion-exchange below $10^{4.5}$ poises in a medium which contains potassium ions e.g. in a KNO_3 melt, smaller alkali metal ions diffusing out of the glass. It was found in this connection that, contrary to expectation, the Li_2O should be contained in a smallest possible concentration and advantageously not at all in the initial glass prior to the ion-exchange although Li_2O plays an important

part as regards the crystallisation of the silver halide crystals in the prior known phototropic glasses.

As well as influencing the phase separation behaviour, alkaline earth metal oxides also have a strong influence on the linear thermal expansion coefficient. It was found that a content of at least 8.6% by weight, but at most 12.5% by weight, is particularly favourable.

BaO and CaO can be used with good results, but the CaO must not be above the upper limit specified by this invention, since otherwise the precipitation of the non-crystalline segregations rich in silver halide is deleteriously affected. Small amounts of SrO have a stabilising action. Lead oxide (PbO) in the range specified by the invention can serve for correcting the refractive index, in the same way as TiO_2 .

The content of Ag_2O and the content of halogen in the batch or mixture calculated by synthesis is dependent on the melting procedure and the remainder of the composition of the batch. (The amount of Ag_2O and halogen is for this purpose calculated from the analytically determined content of silver and halogen ions in which they are present in the glass. A proportion of metallic silver is improbable, but possible. Silver ions and halogen ions do not have to be in a stoichiometric ratio to one another, since also other components are included in the non-crystalline segregations which are rich in silver halide).

The range of silver oxide and halogens specified by the invention take into account vaporisation losses during the melting. The distribution of bromine and chlorine in the batch can be varied from a weight ratio of bromine to chlorine of 0.5 to 3.4, preferably 0.55 to 2.74. Copper oxide (CuO) can be added in the range specified by the invention for sensitisation purposes. The evaporation of the halides depends on the melting unit for the glass preparation and therefore much higher amounts of halides can also be used with the same result of halide concentration in the glass with other preparative methods. Consequently a more effective method of determination is given by analyzing the produced glass with RFA (hereinafter mentioned). Especially the desirable content of chlorine and bromine is between 0.2 and 1.0 wt.% in total, preferably between 0.35 and 0.87 wt.% with a preferred weight ratio of bromine to chlorine of 1.8 to 4.0 (concerning the weight %).

The phototropic glass of this invention has been defined. The following ranges are the preferred ranges of the various constituents expressed as parts by weight:

SiO_2	13.0	to	13.9
P_2O_5	31.2	to	33.9
Al_2O_3	22.5	to	25.7
ZrO_2	1.2	to	1.6

	Na ₂ O	4.7	to	7.5
	K ₂ O	6.5	to	10.5
	CaO	3.1	to	4.5
5	BaO	5.5	to	7.0
	SrO	0	to	0.3
	PbO	0.4	to	2.5
	TiO ₂	0.1	to	0.6
	La ₂ O ₃	0.05	to	2.0
10	Ag ₂ O	0.1	to	1.0
	CuO	0	to	0.05
	Cl+Br	0.20	to	6.0

The examples of compositions which are given in the following Table 5 show the limits of the invention with inclusion of many compositions which do not come within the scope of the invention; the property values which are reproduced in Tables 6 and 7 make it possible to recognise how narrowly defined is the composition range specified by the invention.

15

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TABLE 5

No.	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37
SiO ₂	8.06	11.76	8.53	6.50	8.50	8.24	8.86	8.86	8.69	6.69	10.69	8.95	3.13	8.16	8.47	10.62	8.69	10.22
B ₂ O ₃	3.82	4.31	2.80	3.83	3.83	4.40	3.94	5.41	3.86	3.86	3.86	3.98	4.32	4.08	4.24	3.86	3.86	7.43
P ₂ O ₅	33.97	30.21	33.40	35.40	33.40	32.00	36.97	32.97	30.34	32.34	31.34	33.30	66.40	63.14	65.54	32.34	32.34	31.12
Al ₂ O ₃	23.40	23.87	23.91	23.91	23.91	23.93	19.62	23.62	25.17	25.17	22.17	23.86	8.74	8.10	8.58	23.17	23.17	22.30
ZrO ₂	1.81	1.40	2.90	1.90	1.90	1.90	—	—	—	—	—	—	—	—	—	—	—	0.93
Na ₂ O	6.08	6.08	6.10	6.10	6.10	6.11	4.91	5.91	6.79	5.79	5.79	10.93	7.12	6.73	6.35	5.79	5.79	5.57
K ₂ O	9.26	9.26	9.30	9.30	8.30	8.81	9.86	8.86	7.69	8.69	8.69	2.98	5.40	5.10	—	5.63	6.51	7.02
Li ₂ O	—	—	—	—	1.00	—	—	—	—	—	—	—	0.11	0.10	2.12	—	—	—
MgO	—	—	—	—	—	—	—	—	—	—	—	—	4.32	4.00	4.24	3.06	2.18	1.34
CaO	3.79	4.79	3.80	4.80	2.80	4.20	3.94	2.40	3.86	3.86	3.86	3.98	—	0.08	—	3.86	3.86	3.72
BaO	5.37	5.37	5.39	4.39	6.39	4.00	4.92	4.92	6.76	4.82	4.82	4.97	—	0.16	—	4.83	4.83	4.65
SrO	0.09	0.09	0.09	0.09	0.09	0.07	—	—	—	—	—	—	—	—	—	—	—	0.47
PbO	1.81	0.81	1.81	2.29	2.76	1.81	4.92	4.92	4.83	6.76	4.83	4.97	—	—	—	4.83	4.83	1.86
TiO ₂	0.92	0.92	0.93	0.40	—	0.93	—	0.30	—	—	—	—	—	—	—	—	—	0.47
La ₂ O ₃	0.50	—	—	0.05	—	—	0.98	0.68	0.97	0.97	0.97	1.00	—	—	—	0.97	2.90	1.86
Ag ₂ O	0.60	0.60	0.50	0.50	0.50	0.40	0.59	0.59	0.58	0.58	0.58	0.60	0.43	0.41	0.42	0.58	0.58	0.56
CuO	—	—	—	—	—	—	—	—	—	—	—	—	0.04	0.04	0.04	—	—	—
Cl	0.99	1.99	1.99	2.99	1.99	1.33	1.97	2.07	2.13	2.23	2.33	2.00	2.16	2.04	2.12	1.93	1.93	1.86
B	2.99	1.99	1.99	0.99	1.99	1.33	1.97	1.97	1.93	1.93	1.93	2.00	3.24	3.06	3.18	1.93	1.93	1.86
F	0.54	0.54	0.54	0.54	0.54	0.54	0.49	0.39	0.28	0.18	0.08	0.50	—	—	—	0.48	0.48	0.47

TABLE 5 (Continuation)

No.	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56
SiO ₂	9.94	12.65	—	15.50	19.57	10.13	5.07	5.08	6.74	4.74	4.92	8.81	4.89	5.03	4.94	8.82	13.17	11.50	14.06
B ₂ O ₃	9.94	—	12.26	6.99	7.83	12.36	17.43	18.51	3.35	18.61	16.72	6.85	11.75	8.04	7.91	6.86	—	—	—
P ₂ O ₅	30.28	32.39	32.39	22.49	24.17	22.49	22.49	22.57	38.30	22.50	30.48	32.78	32.78	33.68	37.56	32.85	32.42	34.21	36.10
Al ₂ O ₃	21.70	24.29	24.29	24.32	18.79	24.32	24.32	24.40	20.83	24.54	19.67	23.49	23.49	24.63	19.77	23.53	24.32	25.12	21.96
ZrO ₂	0.90	1.92	1.92	1.93	1.86	1.93	1.93	1.01	1.93	1.02	—	—	—	—	—	—	2.02	2.62	2.21
Na ₂ O	5.42	6.07	6.07	6.08	5.87	6.08	6.08	6.10	7.09	6.14	5.90	5.87	4.87	6.03	6.93	5.88	6.08	3.00	8.23
K ₂ O	8.14	9.11	9.11	9.12	8.81	9.12	9.12	9.15	8.14	9.20	8.85	8.81	9.81	9.05	7.89	8.82	9.12	10.91	5.32
Li ₂ O	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.37
MgO	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	0.23
CaO	4.12	4.05	4.05	5.05	3.96	4.05	4.05	5.47	3.06	4.09	0.98	0.98	—	1.01	0.99	0.98	4.06	5.21	0.82
BaO	5.52	6.18	5.06	4.37	5.19	5.27	5.37	5.39	5.38	5.42	4.92	4.89	4.89	6.03	5.93	4.92	6.23	3.12	0.91
SrO	0.45	0.10	0.10	1.10	0.10	0.20	0.10	0.10	0.10	0.10	0.05	0.05	0.05	0.05	0.05	0.05	0.05	—	1.05
PbO	0.31	1.82	2.12	0.82	1.76	1.82	1.82	0.43	2.83	1.84	4.92	4.89	4.89	6.03	5.93	4.92	1.42	—	1.20
TiO ₂	0.45	0.41	0.91	0.91	0.88	0.91	0.91	0.46	0.91	0.46	—	—	—	—	—	—	0.30	0.12	1.42
La ₂ O ₃	1.81	0.50	—	—	—	—	—	—	—	—	1.48	1.47	1.47	—	1.68	1.47	0.20	0.05	3.72
Ag ₂ O	0.54	0.61	0.61	0.61	0.59	0.61	0.61	0.61	0.61	0.61	0.59	0.62	0.59	0.40	0.40	0.39	0.56	0.35	0.27
CuO	—	—	—	—	—	—	—	—	—	—	0.04	0.01	0.04	0.03	0.03	0.04	0.04	—	—
Cl	1.81	2.02	2.02	2.02	1.96	2.02	2.02	2.03	2.03	2.05	1.96	1.96	1.96	1.30	1.28	1.27	2.23	0.97	1.23
Br	1.81	2.02	2.02	2.02	1.96	2.02	2.02	2.03	2.03	2.05	1.96	1.96	1.96	2.01	1.98	1.96	7.60	3.82	0.90
F	0.45	0.71	0.71	0.71	0.68	0.71	0.71	0.71	0.71	0.72	0.49	0.49	0.49	—	—	0.49	—	—	—

TABLE 6

No.	20	21	22	23	24	25	26	27	28
UDL [°C] ⁽¹⁾	970	950	975	985	975	950	1020	900	>1035
LDL [°C] ⁽²⁾	700	725	730	725	738	720	700	710	710
KG max [°C] ⁽³⁾								845	
Speed μ /min ⁽⁴⁾	7.3		6.2			>25	>15	5.3	
Start of dense devitrification [°C] ⁽⁵⁾	935	935	940	925	925	910	990		all dense white
UDL [°C]	29	30	31	32	33	34	35	36	37
LDL [°C]	>1035	>1635	990		1035	>1075	>1075	>1075	>1075
KG max [°C]	<750	<700	<700	No	<700	<700	<700	<700	<700
Speed μ /min				devit-	910	1020			
Start of dense devitrification [°C]	all dense white	all dense white	all dense white	ation	2.2	3	1025	dense white	dense white

⁽¹⁾ Liquidus temperature⁽²⁾ Lower crystallization limit⁽³⁾ Maximum temperature of crystallization⁽⁴⁾ Growth rate of crystallization⁽⁵⁾ For test procedures, see hereinafter

TABLE 6 (Continuation)

No.	38	39	40	41	42	43	44	45	46
UDL [°C]	>1075		945	>1075	>1075	1075	1060	1065	980
LDL [°C]	<700	No	<750	<750	<750	<750	<750	<750	765
KG max [°C]		devit-							
Speed μ /min		rific-							6
Start of dense devitrification [°C]	dense white	ation	920	dense white	dense white	1075	1020	1065	970
UDL [°C]	1055	>1020	>1025	>1025	>1025	>1025	>1025	No	923
LDL [°C]	<750	<720	<720	<720	<720	<720	<720	devitri-	795
KG max [°C]								fication	815
Speed μ /min		>15							0.8
Start of dense devitrification [°C]	1030		all dense white	all dense white	all dense white	all dense white	all dense white		

TABLE 7

	22	24	28	32	33	34	39	44	45
$\alpha \times 10^7$	109.6			108.6	106.1	105.3	103.5	105.6	103.5
Tg [°C]	463			462				451	
Ew [°C]	629							615	
Va [°C]	882							858	
Hydrol. stab. titrated ml HCl	0.081		0.70	0.92	0.41				
chem. hardening layer thickness [μm]	45	17	42	58	55	32	65	50	22
Compress. stress [nm/cm]	3900	2500	6000	4500	5200	2100	3200	4600	3000
Saturation transmission %	35	42	43	irrever- sible blacken- ing.	irrever- sible blacken- ing.	47	28	39	38
Regeneration % after 10 min	17	12	10	ing.	ing.	10	20	18	14
n_d	1.5225					1.5232	1.5229	1.5311	1.5238

(1) 20–300°C.

(2) Softening temperature according to ASTM.

(3) Working temperature according to ASTM.

TABLE 7 (Continuation)

	46	47	48	49	51	53	54	55	56
$\alpha \times 10^7$		104.3		105.4		108.0	103.5		
Tg [°C]		438		435	440	441	513	510	
Ew [°C]				584		596	717		
Va [°C]				837	811	844	987		
Hydrolytic Determination titrated ml HCl				0.31	0.10	0.22	0.09	0.25	
Chem. case-hardening thickness [μ m]	76	55	70	36	30	42	80	72	
Compressive stress [nm/cm]	5800	5000	7500	3200	3000	3800	8900	7000	irre- versible blacken- ing
Saturation transmission %		25	23	18	18	34	22	30	
Regeneration % after 10 min.		20	17	10	12	17	28	29	
n_d		1.5181	1.5230	1.5133	1.5170	1.5231	1.5231	1.5237	

The phototropic properties of the following basis) in accordance with the invention were investigated:

basic glass composition (batch or synthesis)	investigated:
SiO ₂	13.17% by weight introduced as pure sand
P ₂ O ₅	32.42% " introduced as phosphorus pentoxide
Al ₂ O ₃	24.32% " introduced as aluminium hydroxide
ZrO ₂	2.03% " introduced as zirconium dioxide
Na ₂ O	6.08% " introduced as sodium carbonate, nitrate and chloride
K ₂ O	9.12% " introduced as potash and bromide
CaO	4.06% " introduced as carbonate
BaO	6.23% " introduced as carbonate and nitrate
SrO	0.05% " introduced as nitrate
PbO	1.42% " introduced as red lead
TiO ₂	0.30% " introduced as oxide
La ₂ O ₃	0.20% " introduced as oxide
CrO	0.04% " introduced as oxide.

10

15

Different amounts of silver and halogen components, introduced as silver nitrate and common salt or potassium bromide, respectively, were added to this basic glass in various individual melts with constant preparation procedure to obtain appropriate RFA-values of the silver and halide concentration; occasionally, the sensitising content of CuO introduced as oxide was also varied. After mixing the batch, the components were jointly placed in a melting crucible at 1435° C., melted and refined. Thereafter, the melt was cooled to 1200° C., poured into steel moulds and cooled to room temperature at a speed of 22°/h. Specimens of each glass were then produced with the dimensions 40×40×5 mm; these specimens were heated at 50°/10 min to 615° C., kept for 115 minutes at this temperature and then cooled to 190°/h to 300° C. The further cooling to room temperature took place at 50°/h. The relative content of Ag, Cl and Br in these specimens was established by X-ray fluorescence analysis RFA values; the refractive index, the phototropy and the degree of crystallinity of the precipitations, which are the supports of the phototropy, and also their value, were also established. The results are shown in Table 8. An addition of only 0.10% by weight of F, for example, already caused crystallisation of the carriers of the phototropy.

The refractive index n_d is established by means of the normal commercial Abbé refractometers. The viscosity is measured in dependence on temperature by using normal commercial rotary viscosimeters. The chemical stability is characterised by the titrimetrically established values of the alkali discharge according to DIN (German Industrial Standard) 12,111. The ion-exchange is judged by the preparation of thin sections of ion-exchanged glass, the section being arranged perpendicular to the glass surface. The thickness of the ion-exchange layer and the compressive stress obtaining there are established by photoelastic measurements with polarised light. The crystallisation stability of a glass is carried out by a tempering lasting 60 minutes in an oven with temperature gradients. At this time, the glass is protected against surface vaporisation. Then, after the tempering, the upper devitrification limit (=liquidus temperature), the lower devitrification limit, the maximum of the crystallisation (K_{max}) and the speed of growth of the crystals is then determined under a microscope. The thermal expansion and the transformation temperature were established dilatometrically.

The blackening behaviour and the regeneration of phototropic glasses is measured as monochromatic transmission measurement at 545 nm as a function of time. The excitation is then produced with unfiltered Xenon light of an intensity of 2 cal cm⁻² min⁻¹. If there

is no other notation, the temperature at the time of measurement is 20° C. and the thickness of the measured glass is 2 mm. All glasses had more than 86% transmission; mostly more than 90% transmission. Difference of transmission was calculated as difference before and after excitation.

The investigations by an electron microscope are carried out on specimens which were thinned by the ion steel etching method. As compared with the other thinning methods, this method has the particular advantage that the preparations do not come into contact during the thinning process or subsequent thereto with liquids and solutions and thus there is no soiling of the preparations with flotation and reaction, because the preparation is already fixed on the object support of the electron microscope during the thinning process and is introduced with said support without any further after treatment into the electron microscope. In addition, hydration of the preparations is avoided by not using liquids and solutions. Hence, the structures which are visible in or on the preparation in transmitted light are clearly to be associated with the preparation itself. However, if methods are used with which the preparation comes into contact with liquids, then frequently crystalline reaction products are found, which can be attributed to reactions of the glass surface with the liquid. From the preparations diluted with ions, and with transmitted radiation with electrons, it is possible in the first place to draw conclusions from the contrast as to the presence and the distribution of substances with unequal mass absorption. Additional indications concerning the crystal structure in matrix and segregation regions of the investigated phototropic glasses can be obtained from electron diffraction or fine-range electron diffraction exposures.

The data is reported in Table 8 wherein the composition figures are parts by weight per 100 parts by weight of the basic glass batch. RFA means X-ray fluorescent analysis with the "Siemens" SRS 1 instrument and the analyzing crystals were LiF for Br and Ag and PET-crystals for Cl. Wet chemical analysed standards were used.

The RFA values given in Table 8 show the relative concentrations with reference to the standard examples. The wet chemical analysis showed that the relative concentration 1 (RFA value) for silver oxide corresponds to 0.22 weight % Ag₂O, for bromine to 0.26 weight % Br and for chlorine to 0.24 weight % Cl. The calculated weight % of silver, chlorine and bromine are added.

From this analytical evaluation and from the desired and achieved phototropic properties of the glass the limit of concentrations of Ag₂O and the halides chlorine and bromine

5 The linear thermal expansion coefficient of
phosphate glasses or glasses which contain
phosphate as main component, often is higher
than 105×10^{-7} per °C. between 20 and
300° C. The combination of the alkali metal
oxide, alkaline earth metal oxide and lead
oxide components normally brings an increase
of the expansion coefficient. The usual way
to lower the expansion coefficient is by using
boric oxide or fluorine. In the glass of the
invention avoiding such use of boric oxide
and fluorine, the lowering of the expansion
into an appropriate area from 99 to

105×10^{-7} per °C. for better technical pro-
perties is achieved by the special combination
of the components SiO_2 , P_2O_5 , Al_2O_3 , ZrO_2 ,
 Na_2O , K_2O , CaO , BaO , SrO , PbO , TiO_2 ,
 La_2O_3 , Ag_2O , CuO and the halides Cl and
Br. 15

More detailed studies of chemical harden-
ability were performed, for example on Com-
positions 22 and 25 and on Composition 54
of Table 5. Table 9 shows the results in re-
lation to the duration of the ion-exchange
and the temperature involved. The hardening
was performed in a KNO_3 molten salt bath. 20 25

TABLE 9

Temperature [°C]	Time [h]	Layer thickness [μm]	Compressive stress [nm/cm]
<u>Composition 22:</u>			
400	16	18	1870
450	16	23	1850
480	16	45	3900
<u>Composition 25:</u>			
390	16	25	3600
400	16	30	3300
410	16	35	3200
420	16	35	2340
430	16	38	2060
<u>Composition 54</u>			
400	16		stress free
410	4	24	2940
410	16	38	6000
430	2	25	1300
430	4	30	5400
430	16	59	6980
440	16	55	6720
450	2	28	3940
450	4	46	3340
450	16	75	7300
450	16	60	5800
470	2	18	2960
470	4	49	6400
470	16	75	8920
470	16	77	7480
490	2	45	6220
490	4	52	7180
490	16	87	7100
510	2	45	7200
510	4	59	6880

Of the several examples recited above most are comparative but Examples 54, 57, and 61-67 illustrate the present invention.

WHAT WE CLAIM IS:—

- 5 1. A phototropic glass which is free from fluorine and boric oxide and comprises the following constituents, expressed in percentages by weight:

	SiO ₂	12.1 to 13.9
10	P ₂ O ₅	30.4 to 33.9
	Al ₂ O ₃	22.5 to 25.7
	ZrO ₂	1.0 to 2.6
	Na ₂ O	3.0 to 7.5
15	K ₂ O	5.3 to 10.5
	CaO	3.1 to 5.0
	BaO	3.1 to 7.0
	SrO	0 to 0.5
	PbO	0.4 to 2.5
20	TiO ₂	0.1 to 0.6
	La ₂ O ₃	0.05 to 2.0
	Ag ₂ O	0.05 to 1.0
	CuO	0 to 0.1
	Cl and/or Br	0.20 to 10.0

- 25 the balance, if any, being one or more compatible constituents.

2. A phototropic glass according to claim 1 wherein the lower limit of the Na₂O content is 4.7.

- 30 3. A phototropic glass according to claim 1 or claim 2 wherein the lower limit of the K₂O content is 6.5.

4. A phototropic glass according to any preceding claim, wherein the lower limit of the barium oxide content is 5.5.

- 35 5. A phototropic glass according to any preceding claim, wherein the lower limit of the silver oxide content is 0.1.

6. A phototropic glass according to any preceding claim, wherein the upper limit of Cl and/or Br is 6.0.

- 40 7. A phototropic glass according to claim 6 wherein the upper limit of Cl and/or Br is 1.0.

8. A phototropic glass according to any

preceding claim, which has the following phototropic properties: a transmission decrease of at least 50% upon exposure to light, and a regeneration of the transmission after terminating the exposure to light of at least 20% after 10 minutes, based on a glass thickness of 2 mm.

9. A phototropic glass according to claim 1 which contains silver-rich and halogen-rich (wherein halogen means Cl and/or Br) non-crystalline phase separations with a diameter between 40 and 350 Å; shows no crystallization in a viscosity range between 10 and 10⁵ poises; has a refractive index n_d from 1.5225 to 1.5238; can be strengthened chemically by ion-exchange in a medium containing potassium ions at a temperature below that at which the viscosity is 10^{14.5} poises, whereupon the alkali metal ions smaller than potassium diffuse out of the glass; has a linear thermal expansion coefficient between 20 and 300° C. from 99 to 105 × 10⁻⁷ per °C.; and has a chemical stability characterised by a titration value, in accordance with DIN (German Industrial Standard) 12 111, of less than 0.2 ml HCl.

10. A phototropic glass according to any preceding claim, which is free from magnesium oxide.

11. A phototropic glass according to claim 1 substantially as herein described and exemplified in any one of Examples 54, 57, and 61 to 67.

12. A process for producing a phototropic glass as defined in claim 1 wherein a melt corresponding to the glass composition required is cast, cooled for solidification and heat treated at 560°-640° C. for 1 to 3 hours.

13. A process according to claim 12 substantially as herein described and exemplified.

14. A phototropic glass obtained by a process as claimed in claim 12 or claim 13.

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- | | | | | |
|----|--------------------------------|------|----|------|
| 10 | SiO ₂ | 12.1 | to | 13.9 |
| | P ₂ O ₅ | 30.4 | to | 33.9 |
| | Al ₂ O ₃ | 22.5 | to | 25.7 |
| | ZrO ₂ | 1.0 | to | 2.6 |
| | Na ₂ O | 3.0 | to | 7.5 |
| 15 | K ₂ O | 5.3 | to | 10.5 |
| | CaO | 3.1 | to | 5.0 |
| | BaO | 3.1 | to | 7.0 |
| | SrO | 0 | to | 0.5 |
| | PbO | 0.4 | to | 2.5 |
| | TiO ₂ | 0.1 | to | 0.6 |
| 20 | La ₂ O ₃ | 0.05 | to | 2.0 |
| | Ag ₂ O | 0.05 | to | 1.0 |
| | CuO | 0 | to | 0.1 |
| | Cl and/or Br | 0.20 | to | 10.0 |
- 25 the balance, if any, being one or more compatible constituents.
2. A phototropic glass according to claim 1 wherein the lower limit of the Na₂O content is 4.7.
- 30 3. A photographic glass according to claim 1 or claim 2 wherein the lower limit of the K₂O content is 6.5.
4. A phototropic glass according to any preceding claim, wherein the lower limit of the barium oxide content is 5.5.
- 35 5. A phototropic glass according to any preceding claim, wherein the lower limit of the silver oxide content is 0.1.
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- 40 7. A phototropic glass according to claim 6 wherein the upper limit of Cl and/or Br is 1.0.
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