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METHOD FOR PRODUCING OPTICAL GLASSES

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In ordinary optical crown and flint glasses the relation between the refractive index n_d and the mean dispersion $n_F - n_C$ is such that the relation $n_d \geqq 13.815\ (n_F - n_C + 0.1)$ applies for glasses having a refractive index smaller than 1.65 and the relation $n_d \geqq 11.7\ (n_F - n_C + 0.1216$ for glasses having a refractive index greater than 1.65. While up to the present it has been possible already to produce glasses which relative to the mean dispersion showed a considerably higher refractive index than the minimum value indicated by the aforementioned relations, it did not appear possible but for some special type of fluorous alumoborosilicate glasses having a mean dispersion below 0.0073, also to inversely attain a noticeably lower refractive index.

According to the invention however, optical glasses having a mean dispersion below 0.0073 can be produced with a considerably lowered refractive index than heretofore while such optical glasses having a mean dispersion greater than 0.0073 can be produced to a large extent with a lowered refractive index if their content of fluorides as well as of aluminium oxide and titanium oxide is kept as large as possible, but their content of earth alkaline oxides and of boric acid anhydride as small as possible, admitting further large quantities only of alkalies, or lead oxide, if desired, or antimony oxide and arsenic oxide.

Of those substances which according to the invention are desirable to be introduced in largest possible quantities, fluorides, as alkali-fluoride, silico-fluoride, alumo-fluoride and others, have the highest reducing effect upon the refractive index relative to the dispersion. There is one difficulty when introducing fluorides, in that they evaporate differently depending upon the composition of the glass and upon the melting temperature. The behavior of highly alkaline glasses and of glasses with an abundancy of boric acid is a relatively favorable one, which presumably is in first place attributable to their low melting temperature. Also in these glasses, however, not much more than 70% at the most of the introduced fluor remain in solution. It being practically immaterial in what linked form the fluor is introduced, it will be advisable in calculating the batch to elect a preliminary batch free from fluorides to begin with and then in part replace the oxides contained therein by corresponding fluorides. In the following the equivalent replacement of x parts by weight oxygen by fluor is symbolically indicated by x% O/F. An example of a glass batch would accordingly read:

$$40\%\ SiO_2 + 20\%\ B_2O_3 + 10\%\ Al_2O_3 + 10\%\ Na_2O + 10\%\ K_2O + 10\%\ CaO\ (=100\%) + 1\%\ O/F$$

According to the atomic weights 116.2 weight parts K_2F_2 would correspond, for example, to a quantity of 94.2 weight parts K_2O, of which 16 weight parts oxygen are equivalently replaced by 38 weight parts of fluor. In other words, 1% O/F means the replacement of

5.89% K_2O by 7.26 KF (potassium fluoride)
3.88% Na_2O by 5.25 NaF (sodium fluoride)
3.5% CaO by 4.87 CaF_2 (fluor spar)
1.94% Na_2O + 1.06 Al_2O_3 by 4.38 Na_3AlF_6 (cryolite)
1.29% Na_2O + 1.26 SiO_2 by 3.93 Na_2SiF_6 (sodium silico-fluoride)

Thus when using potassium fluoride or sodium silicofluoride the following parts would have to be melted down:

SiO_2	40.0	38.74
B_2O_3	20.0	20.0
Al_2O_3	10.0	10.0
Na_2O	10.0	8.71
K_2O	4.11	10.0
CaO	10.0	10.0
KF	7.26	-----
Na_2SiF_6	-----	3.93
	101.37	101.38

One weight-part of oxygen being equivalently replaced by 2.375 weight-parts of fluor, an average would result of 1.375 weight-parts more than according to the preliminary batch. If the evaporation of the fluorides is thereby to be set out at, say, 30%, it will be necessary to introduce 1.43% O/F into the batch in order that the glass may contain 1% O/F.

On account of the fluorides segregating more or less easily during the annealing process, either in the form of crystals or in the form of milky liquid drops depending upon the composition of the glass, the fluorides cannot be introduced into the glass in any arbitrary quantities. Optical glass requiring a very slow annealing process, this segregating tendency is a particularly marked one in optical glasses. To counter this segregating tendency the initial batch which serves for melting the new glasses is expediently made to contain from 5% to 30% of alkali oxide, at least half consisting of potassium oxide, owing to sodium oxide and lithium oxide having but little effect on the diminution of the refractive index relative to the dispersion. The introduction also of boric acid anhydride and aluminium oxide is adapted to counteract said segregating tendency. The introduction of titanium oxide is of the same effect although practically, there is a limit for the content of titanium oxide near approximately 30%, as otherwise a brown tint detrimental to optical glass becomes markedly noticeable in addition to crystallization and turbidity. For this reason it is expedient that the initial batch contain boric acid anhydride, aluminium oxide and titanium oxide to an extent of altogether at least 5%, but not more than 45%, whereby the sum total of boric acid anhydride and aluminium oxide should not exceed 40%. The brown tint becoming particularly noticeable when there is a large content of aluminium oxide the latter must not exceed that of boric acid anhydride more especially so the higher the content of titanium oxide may be. In the same manner also the content of antimony oxide and arsenic oxide must be kept low when the content of titanium oxide is high as they likewise promote brown tinting to a considerable extent. In the event of the content of titanium oxide amounting to 10% or more, provisions should suitably be made for the content of antimony oxide and arsenic oxide to amount together to not more than 10% at the most.

Also, in the presence of titanium oxide in fluorous melts, earth alkaline oxides lead to the formation of turbidities. Their content should for this reason be as low as possible and by no means exceed 5% of the initial batch. Also bivalent metal oxides should be avoided, if possible, as they promote the tendency of segregation and are antagonistical to the lowering of the refractive index. Of these oxides, the behaviour of lead oxide may yet be considered as the most favorable in both respects. In fact, if glasses are to be produced having a high mean dispersion and a lowered refractive index relative to the dispersion the introduction of lead oxide besides antimony and arsenic oxides is even recommended in order to avoid the occurrence of a brown tint despite the glasses containing great quantities of titanium oxide. The rise occasioned thereby in the refractive index can be partly counteracted by diminishing the content of boric acid.

The general rules governing the production according to the invention of optical glasses having a lowered refractive index relative to the dispersion are applicable in various ways depending upon the region in which the optical glasses lie. The first region is that where the mean dispersion is lower than 0.0073; the second, where the mean dispersion amounts to at least 0.0073 and where the refractive index is maximally 1.65; the third region being, where the refractive index is higher than 1.65.

The following applies within the first region: Pure alkali-silicate-fluoride glasses segregate crystals when the content of fluor is low and turbidities when the content of fluor is high, the extent of both defects increasing the lower the alkali content may be. Potassium glasses react more favorable in this respect than sodium or lithium glasses. By introducing boric acid anhydride and aluminium oxide the segregating tendency can be sufficiently suppressed, as pointed out before, so that substantial quantities of oxygen can be replaced by flour without thereby impairing the production of glasses which are free from crystals and turbidities. The known type of fluor-alumo-borosilicate glasses composed in accordance with the above correspond to a preliminary batch containing 5% to 25% alkali oxide and 15% to 35% boric acid anhydride and aluminium oxide in total, whereby the content of boric acid anhydride is always greater than that of aluminium oxide, the replacement of the oxygen being about 4% O/F. They have a mean dispersion under 0.0073 and a diminution of the refractive index by maximally 0.017 under the magnitude 13.815 $(n_F-n_C+0.1)$. However, the investigations on which the invention bases have shown that boric acid anhydride weakens the refraction-diminishing effect of the fluorides to a greater or lesser extent, whilst aluminium oxide increases that effect, thus leading to greater diminutions of the refractive index. It must be noted however that the effect of the boric acid anhydride, and also but to a lesser extent that of the aluminium oxide, is not additive, but is dependent upon the introduced quantity. In the case of the content being low the boric acid anhydride substantially weakens the refraction-diminishing effect of the fluorides, while in the case of greater contents of from say, about 10% on the initial batch, the effect for the same increases. However, if the amount of aluminium oxide exceeds that of boric acid anhydride the same increase in boric acid anhydride is capable even to enhance the said effect. In addition to that the quantity of fluoride may then be increased up to and above 4% O/F, thus making it possible to raise the diminution of the refractive index to more than 0.018 if the content taken of aluminium oxide is the same at least as that of the boric acid anhydride and the sum of both of them is made to amount from 10% to 45%. The desired diminution of the refractive index can be achieved and the tendency towards segregation and crystallization, also with high contents of fluoride, avoided if the initial batch of silicon dioxide, boric acid anhydride, aluminium oxide, and alkali oxides is made to amount to at least 95% in total, i. e. if the content of the other substances is kept at a low level.

If it is intended to arrive in the second of the aforementioned regions and for this purpose increase to more than 0.0073 the mean dispersion of the fluor glasses by introducing earth alkaline or bivalent metal oxides, small contents of such additions already suffice to bring about a turbidity-forming tendency. Though this tendency clearly falls off in the order BeO, MgO, CaO, SrO, BaO, ZnO, CdO, PbO, it is still strong enough, even at PbO, to call for a reduction in the content of fluor in order to obtain glasses free from turbidity, the reduction in question having to be carried to an extent which prevents the attainment of the desired diminution of the refractive index as a result of the refraction-diminishing effect of the fluorides being counteracted both, by the effect of the boric acid anhydride which weakens that property and also by the effect of the bivalent oxides themselves. However, according to the invention, the introduction of antimony oxide is adapted to increase the mean dispersion above 0.0073 and to produce glasses which, relative to the dispersion, have a lowered refractive index. Antimony itself, though acting in a somewhat opposite sense even if it be noticeably less so than boric acid anhydride or bivalent oxides, it does not by far to the same extent as the bivalent oxides lead to crystallization and turbidity in the presence of fluor. With the segregating tendency being equal, the fluorides and aluminium oxide can be incorporated to an appreciably higher extent even when substantial quantities of antimony oxide are present. In view of the fact however that, practically, the aforesaid modifications of fluoro-alumo-borosilicate glasses are bound to go at the expense of the content of silica, the glasses obtained in this manner will have a lower chemical resistivity, particularly a greater acid-solubility, and a greater swelling capacity if exposed to water. Micro-fissures easily occur when the polished surfaces of such glasses dry out. Another reason why greater contents of antimony oxide should be avoided is that they give rise to optically detrimental tints of yellow or brown color. The behaviour of arsenic oxide is similar to that of antimony oxide.

It has been shown however that by introducing quantities of at least 0.2% of titanium oxide jointly with or in place of antimony oxide these difficulties can be done away with to a great extent and that such an introduction is of a particular advantage in that titanium oxide, even if applied in small quantities, increases the mean dispersion to a considerable degree, while at the same time entailing a diminution in the refractive index relative to the dispersion and minimizing the acid-solubility and swelling capacity.

Also boric acid anhydride and aluminium oxide should expediently be contained in the glasses, whereby the quantity of aluminium oxide is to amount to at least as much as the boric acid anhydride. In doing so it will be of advantage to so choose the batch that the glasses contain in total at least just as much aluminium oxide, titanium oxide, antimony oxide and arsenic oxide, as their total content of boric acid anhydride and possible earth alkali oxides.

The effect of the fluor, as expressed in % O/F, upon the diminution of the refractive index corresponding on the average to about five times the opposite effect of boric acid, the weight-parts of oxygen equivalently replaced by fluor should amount to at least one fifth of the content of the total of boric acid anhydride and earth alkali oxides of the initial batch.

In order to produce glasses within the third of the aforementioned regions, i. e., glasses having a refractive index higher than 1.65, the sum of the numbers of the percentage of antimony oxide, arsenic oxide, lead oxide and other bivalent oxides augmented by double the number of the percentage of titanium oxide must amount to more than 50 in the initial batch of the glasses according to the invention. To lower the refractive index relative to the dispersion, it will be expedient to introduce titanium oxide in quantities of from 0.2% to 30%. Tetravalent oxides other than titanium oxides, as well as pentavalent and hexavalent metal oxides appear to diminish rather than like titanium oxide clearly augment the diminution of the refractive index relative to the dispersion. The content of aluminium oxide, titanium oxide and of those oxides of antimony and arsenic, which in total have no practical influence on the diminution of the refractive index, expediently should be at least equal to that of boric acid anhydride and earth alkalies together. Since high contents of titanium oxide give rise to brown tints and turbidities it will be advisable to produce highly refracting glasses by the introduction of lead oxide which, of all bivalent oxides, raises the refractive number relative to dispersion to the least extent. Owing to their content of lead oxide and other bivalent oxides and in spite of a low content of boric acid anhydride and of the introduction of fluor in quantities of more than 0.1% O/F, glasses of this kind show only small diminutions in the refractive index, though it is true that in this region even a slight diminution is practically of greatest significance for achieving novel optical designs.

In the annexed table glass compositions are listed for a number of glasses producable by the new method, including the optical data of said glasses. The components of the preliminary batch are given as oxides, though there is nothing in the way of introducing the corresponding quantities of raw materials in another form. Thus, it is possible, for instance, to take crystallized boric acid (B_3HO_3) in place of boric acid anhydride (B_2O_3) and calcined soda (N_2CO_3) in place of soda (Na_2O).

As can be gathered from the optical data the glasses 1 to 14 ($n_F-n_C<0.0073$) belong to the first of the aforementioned regions, the glasses 15 to 34 ($n_F-n_C\geqq 0.0073$; $n_d\leqq 1.65$) to the second region, and the glasses 35 to 41 ($n_d>1.65$) to the third region. The value a given in the last column is the amount by which the refractive number n_d has been lowered relative to the lowest refractive index occasioned in ordinary optical glasses of the same mean dispersion. As stated in the aforegoing, for a refractive index lower than 1.65, (i. e., for the first and second region) the lowest value is obtained by the formula $n_d=13.815\ (n_F-n_C+0.1)$ for ordinary optical glasses, while for a refractive index higher than 1.65 (i. e., for the third region) the lowest value results from the equation

$$n_d=11.7(n_F-n_C+0.1216).$$

In other words, if for the glass 1 the value a

is given as 0.0280, for the refractive index $n_d=1.4443$ the equation holds good

$$n_d=13.815(n_F-n_C+0.1)-0.0280.$$

For the glass 35 the value $a=0.039$ accordingly means that $n_d=11.7(n_F-n_C+0.1216)-0.039$.

	SiO_2	B_2O_3	Al_2O_3	Na_2O	K_2O	PbO	Sb_2O_3	As_2O_3	TiO_2		O/F	n_d	ν	n_C-n_F	a
1	47,1	13,5	20,3		19,1						8,3	1,4443	07,6	0,00657	0,0280
2	41,7	18,0	20,0		20,0			0,3			8,0	1,4380	67,7	0647	329
3	46,2	13,5	21,0		19,0			0,3			8,0	1,4395	07,5	0651	319
4	37,5	20,0	20,0		20,0					2,5 BaO	8,0	1,4484	07,4	0665	250
5	37,5	20,0	20,0		20,0	2,5					8,0	1,4465	66,0	0676	284
6	37,5	20,0	20,0		20,0		2,5				8,0	1,4469	65,2	0685	292
7	35,0	20,0	20,0		20,0		5,0				8,0	1,4507	63,2	0713	293
8	45,0	10,0	20,0		20,0		5,0				8,0	1,4454	64,8	0687	310
9	37,5	20,0	20,0		20,0					2,5 GeO_2	8,0	1,4402	66,0	0661	326
10	37,5	20,0	20,0		20,0					2,5 P_2O_5	8,0	1,4483	67,6	0663	248
11	37,5	20,0	20,0		20,0					2,5 WO_3	8,0	1,4459	65,8	0678	293
12	41,7	15,0	20,0		20,0			0,3		3,0 Tl_2O_3	6,0	1,4470	67,0	0667	267
13	37,5	20,0	20,0		20,0			2,5			8,0	1,4454	65,8	0677	296
14	45,0	15,0	20,0	2,5	17,5						6,0	1,4515	66,1	0683	243
15	30,0	15,0	15,0		20,0		20,0				8,0	1,5000	52,9	0945	121
16	15,0	15,0	20,0		20,0		30,0				12,0	1,5037	46,4	1085	277
17	20,0	25,0	15,0		20,0		20,0				8,0	1,5032	51,4	0979	131
18	34,7	12,0	22,0	2,0	16,0		13,0	0,3			3,5	1,4939	54,8	0902	122
19	35,7	12,0	22,0		18,0		9,0	0,3		3,0 CdO	4,0	1,4837	57,3	0844	144
20	29,7	15,0	25,0		20,0		10,0	0,3			4,0	1,4991	56,8	0878	037
21	25,0	15,0	20,0		20,9		15,0	5,0			8,0	1,4772	56,5	0844	209
22	25,0	15,0	20,0		20,0		15,0	5,0			6,0	1,4902	54,1	0906	165
23	26,7	18,0	25,0		20,0		10,0	0,3			8,0	1,4583	61,3	0748	265
24	69,7				20,0			0,3	10,0		2,0	1,5287	48,0	1101	049
25	49,7	15,0	5,0		20,0			0,3	10,0		4,0	1,5253	47,4	1108	003
26	49,5	10,0	10,0		20,0			0,5	10,0		4,0	1,5214	45,5	1146	184
27	54,1	7,9	8,5		20,0	1,2		0,5	7,8		4,0	1,51281	50,5	1015	089
28	51,5	7,9	8,5		20,0	1,2		0,5	10,3		3,0	1,53358	46,0	1160	082
29	49,2	8,0	9,0		23,0			0,5	10,0		3,0	1,5269	48,1	1095	059
30	49,5		5,0		20,0			0,5	25,0		2,0	1,6142	32,9	1867	252
31	51,9	7,9	8,5		20,0	1,2		0,5	10,0		10,0	1,50794	46,1	1101	257
32	49,8	10,0	8,5		20,0	1,2		0,5	10,0		10,0	1,51348	45,7	1123	260
33	47,5	10,0	10,0	2,0	18,0		3,0	2,0	5,0	2,5 BaO	3,0	1,5106	54,1	0943	012
34	37,9				11,6	40,0		0,5	10,0		4,0	1,64176	32,6	1966	113
35	37,2		1,5	1,0	6,5	48,3		0,5	5,0		1,0	1,67756	31,2	2171	039
36	39,5		5,0		15,0	20,0		0,5	20,0		2,0	1,65378	30,9	2115	199
37	33,5		5,9		15,0	30,0	5,0	1,5	10,0		2,0	1,66375	31,2	2126	115
38	37,9				11,6	40,0		0,5	10,0		2,0	1,67770	30,5	2220	105
39	37,0			1,5	6,0	50,0		0,5	5,0		1,0	1,6942	28,9	2400	189
40	34,5		2,5	1,5	6,0	50,0		0,5	5,0		2,0	1,6686	31,3	2135	079
41	31,8		2,5	1,5	8,7	50,0		0,5	5,0		4,0	1,66950	31,6	2122	052

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