



FIRE-RETARDING GLASSES FORMED FROM GLASS PANES AND GEL
LAYERS IN A SANDWICH-LIKE STRUCTURE

The invention relates to fire-retarding glasses formed from glass panes and gel layers in a sandwich-like structure, wherein the gel layers are reaction products of gel formers, which comprise aqueous solutions of amine salts and acidic metal phosphates or of amine salts, acidic metal phosphates and boric acid, are introduced into the spaces between the glass panes of a composite structure of panes and are gelled by the effect of heat.

Fire-retarding glasses in this sandwich-like structure, using such gel formers, are known from DE 42 36 936 A1. These known fire-retarding glasses loosen fire-retarding glasses which do not employ genuine gel layers, but which utilise solutions having very high-viscous layers, such as are described in DE 37 29 867 A1. The production of fire-retarding glasses becomes easier to accomplish with these gel formers, which act on a new basis, but they still have, in practical usage, processing and stabilising properties which render application more difficult, despite their having a good fire-retarding effect.

In addition, this also applies to fire-retarding glasses, such as are described in EP 0 732 388 B1, EP 0 582 168 B1 and EP 0 596 324 B1, and they still depend on the basis of the initially mentioned gel formers with water as the aqueous medium.

These fire-retarding glasses, based on aluminium phosphate amine salts are difficult to handle in the production process. More especially, the high viscosity necessitates a long initial treatment of the gel former for degassing purposes and renders difficult the filling of the sandwich-like structure. In addition, the long, varying gel times incur considerable expenditure for a production sequence which is constantly checked for quality



and can be planned. Whilst there is basically good stability from the effect of UV and temperatures, material faults (gel cracks) may occur because of faults in the subsequent treatment.

Other known fire-retarding glasses, which are on the market, are based on water-glass gels which are modified with organic additions. These fire-retarding glasses have a good fire-retarding effect, but they also exhibit disadvantageous stability properties. In addition, because of the continuous effect of UV and temperatures, fire-retarding glasses which contain water-glass form gas bubbles which substantially impair the visual properties of the composite structure after some time. More especially in the field of façades, therefore, additional measures are required, e.g. UV protective films, to protect the fire-retarding glasses, provided with the gel layers, from these effects.

Fire-retarding glasses are also known which employ hydrogels as the fire-retarding composition. Because of the great thickness used for the gel layers, these fire-retarding glasses have a considerable weight per unit area and, in addition, can only be produced in fixed batches. Moreover, because of this great weight, they are not universally usable and are only usable for specific applications.

A binding and coating agent is known from DE 44 01 636 C2 and comprises a mixture of aluminium phosphate amine salts and silica sol. Although said agent has intumescence properties, these mixtures are not employed for fire-retarding glazing purposes, because of their lack of transparency. Such a use necessitates great layer thicknesses, and the entire system needs to have a very good permeability to light without any diffusion.

An object of the invention is to provide fire-retarding glasses of the initially mentioned type, which remain permanently clear under normal

conditions and have a high level of stability to UV and temperatures and, accordingly, they are easier to handle in the production process.

This object is achieved, according to the invention, in that the mixtures of the gel former are introduced into aqueous sols of colloidal silica and gelled.

In the case of this aqueous medium, the gel former specifically gels in a substantially shorter time and thus permits the fire-retarding glasses to be manufactured economically. With a substantially reduced initial viscosity, a hard gel is surprisingly obtained, which permits the entire system to be accomplished in a distinctly improved manner. The minimal shrinkage during the gelling process substantially simplifies production. A high level of transparency for the gel layers is surprisingly achieved, and this permits the use of the above-mentioned mixture in fire-retarding glasses for the first time.

Commercially available silica sols may be employed as the silica sols. Said sols are usually produced by the exchanger treatment of dilute alkali silicate solutions. According to one embodiment, the silica sols employed have particle surfaces between 50 and 500 m²/g. The solids content of the silica sols is between 10 and 50 % by wt., and the pH value is between 7 and 8.

Mixtures of acidic metal phosphates with amine salts of boric acid are preferably employed as the gel formers. The acidic metal phosphates are preferably obtained by reacting aluminium hydroxide with orthophosphoric acid, but the reaction products of mixtures of phosphates and phosphoric acid, as well as other metal compounds, may also be used. A highly suitable mixture may be obtained, for example, by reacting 1 mol aluminium hydroxide with a multiple equivalent of orthophosphoric acid, preferably with 3 to 5 mol orthophosphoric acid. Amine salts of boric acid are obtained by reacting water-soluble, preferably aliphatic, amines with boric acid. In such case, a

ratio of boric acid to the aliphatic amine of between 1 to 2 and 1 to 4 is preferred. Primary, secondary or tertiary amines or mixtures thereof may be employed as the amine, the employment of primary amines, e.g. monoethanol amine, being preferred.

The aluminium phosphate amine salt solution, at temperatures between 10 and 75° C, preferably 20 and 60° C, is given for the mixture formation. The pH value in the given solution may be set with basic solutions to pH values between 5.8 and 6.5 or 8 to 10. Aqueous solutions of sodium or potassium hydroxide are particularly highly suitable. Water-soluble amines may be added, more especially for pH values in the range of 5.8 to 6.5. The silica sol is introduced with intensive agitation. The mixture ratio may be between 1 to 0.005 and 1 to 0.25. The resultant solution is almost clear.

After one treatment for degassing purposes, the solution is introduced into a multiple-layered composite structure of panes and subsequently gelled in a drying cabinet at temperatures between 50 and 120° C. Gelling may be effected with one step or in a plurality of steps. The gels, thus obtained, are transparent and clear.

The composite structure of panes may comprise sodium silicate glasses and/or boron silicate glasses. Partial systems may be manufactured, which are employed as protection against UV or temperatures in conjunction with UV-sensitive internal components.

After the gelling process, the fire-retarding glass strips may be cut to the desired dimensions. The edges of the composite structure entities are broken and sealed.

The fire-retarding composition is introduced, for example, into a standard composite structure of panes with sodium silicate panes measuring 4 x 3 mm and with spaces measuring 3 x 1.5 mm. In such case, the

composite structure of panes is sealed against hydrostatic pressure and subsequently heated in a drying cabinet to 90° C. After 2 to 8 h, the fire-retarding composition has gelled to form a hard gel. No more hydrostatic pressure then occurs. Once the desired composite structure entities have been cut, said structure is laterally packed and sealed.

The composite structure of panes, thus produced, constitutes a fire-retarding glass of high optimum quality and mechanical robustness and, in addition, has a high level of climate stability. The composite structure of panes is combinable with functional glasses.

The production of a gel former, which can be employed for the fire-retarding glasses according to the invention, is described with reference to one embodiment.

In a first preliminary stage, 100 g $\text{Al}(\text{OH})_3$ are dissolved in 445 g 65 % phosphoric acid, the solution being agitated for 1 h at 90° C.

In a second preliminary stage, 125 g H_3BO_3 are dissolved in 260 g 98 % $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2\text{OH}$ and heated to 90° C for 1 h.

The aqueous solutions, obtained in the two preliminary stages, are combined and set with 50 % NaOH to a pH value of 6.5. Subsequently, the solution thus set is added to 10 g 30 % silica sol (220 m²/g) at 65 ° C.

The fire-retarding composition (= gel former), thus obtained, is degassed before it is introduced into the composite structure of panes. The gel former is pretreated at a temperature of 20 to 60° C prior to being introduced into the composite structure of panes.

The gelling process occurs at a temperature of 50° C to 120° C in one or more stages, that is to say over a period of 1 to 24 h.

The quantities of the mixture proportions, given above as one embodiment, specify the ratio to one another. Multiples of these quantities are mixed together according to the required quantity of gel formers.

The composite structure of panes may include n glass panes and $(n-1)$ gel layers, n being > 2 , e.g. $n = 4$.

CLAIMS

1. Fire-retarding glasses formed from glass panes and gel layers in a sandwich-like structure, wherein the gel layers are reaction products of gel formers, which comprise aqueous solutions of amine salts and acidic metal phosphates or of amine salts, acidic metal phosphates and boric acid, are introduced into the spaces between the glass panes of a composite structure of panes and are gelled by the effect of heat, characterised in that the mixtures of the gel former are introduced into aqueous sols of colloidal silica and gelled.
2. Fire-retarding glasses as claimed in claim 1, wherein the gel former contains silica with particles of a specific surface of 50 to 500 m²/g, measured according to the BET method.
3. Fire-retarding glasses as claimed in claim 1 or 2, wherein the silica has a solids content of 10 to 55 % by wt., the gel former contains 25 to 85 % by wt. of an aqueous solution of amine salts and metal phosphates or of amine salts, metal phosphates and boric acid, and the gel former mixture has a solids content of 30 to 75 % by wt.
4. Fire-retarding glasses as claimed in one of claims 1 to 3, wherein the pH value of the gel former is set to between 5.8 and 6.5 or to between 8 and 10.
5. Fire-retarding glasses as claimed in claim 4, wherein the pH value is set by the addition of an aqueous solution of sodium or potassium hydroxide or of water-soluble amines.
6. Fire-retarding glasses as claimed in one of claims 1 to 5, wherein the mixture of the aqueous solution of amine salts and metal phosphates or of

amine salts, metal phosphates and boric acid relative to the proportion of silica sol is in the ratio of between 1 to 0.005 and 1 to 0.25.

7. Fire-retarding glasses as claimed in one of claims 1 to 6, wherein additives, such as anti-oxidants, bonding agents, reducing agents, UV stabilisers and pore formers, are added to the mixture of aqueous solutions of amine salts and metal phosphates or of amine salts, metal phosphates and boric acid with the silica sol.

8. Method of producing fire-retarding glasses as claimed in one of claims 1 to 7, wherein the gel former is introduced into a composite structure of panes, which is hydrostatically sealed at its lateral edges, wherein the gel former is introduced into a composite structure of panes and caused to gel by the effect of heat, and wherein blanks of desired dimensions are separated from the strip of the composite structure of panes, thus produced, and are packed and sealed at their lateral edges, characterised in that, prior to the gel former being introduced into the composite structure of panes, a first aqueous solution of 100 g $\text{Al}(\text{OH})_3$ is produced in 445 g 65 % phosphoric acid with agitation for 1 h at 90° C, and a second aqueous solution of 125 g HBO_3 is produced in 250 g 98 % $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{OH}$ with heating for 1 h at 90° C, in that these two aqueous solutions are combined and set to a pH value of about 6.5 with 50 % NaOH, in that 10 g 30 % silica sol is added to this aqueous solution, thus produced, at 55° C, and in that the gel former in this prescribed ratio to the components is made available according to the necessary requirements and introduced into the composite structure of panes.

9. Method as claimed in claim 8, wherein, after a preliminary treatment at a temperature of 20 to 60° C, the gel former is introduced directly into the composite structure of panes.

10. Method as claimed in claim 8 or 9, wherein the gelling process is accomplished at a temperature of between 50 and 120° C over a period of 1 to 24 h directly or in a plurality of steps.

11. Method as claimed in one of claims 8 to 10, wherein the silica sol is introduced into the aqueous solution, which is set to the pH value, with intensive agitation, a mixture ratio between aqueous solution and silica sol of between 1 to 0.005 and 1 to 0.25 being selected.