

# ALIEN PROPERTY CUSTODIAN

## METHOD OF CHANGING THE PHYSICAL AND CHEMICAL PROPERTIES OF THE SURFACE OF OBJECTS OF SILICIOUS MATERIAL

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It is a well known fact that the behaviour of the surface of a glass object can be quite different from that of the glass beneath, as is proved, for instance, in the case of fresh fractures. This difference very often obtains when the surface is not coated with a layer of glass of another composition or origin, or with varnish, resins or other suitable material. After a short time, the action of water on a surface of fracture has gone far to remove the alkali of the glass and to thus create a very thin hydrolized surface layer which is poor in alkali and retards further attacks by water. To increase the effect of this retardation, the suggestion has been made to submit glass objects to prolonged boiling in water or to treat them with acid solutions, hot acid, for instance sulphuric acid, or with acid vapours. Experience has proved, however, that permanent protective layers cannot be obtained in this manner, to say nothing of the fact that acid solutions strongly attack many glasses, lay open polishing scratches and entail roughness and other irregularities of the surface. The produced hydrolized, i. e. gelatinous, surface layer, which is richer in silica, obviously remains pervious to water. It is more vulnerable mechanically, ultimately changes and, especially when heated to over 100° centigrades, becomes chinky and porous, thus preparing the way for further attacks.

It is also known that the permanence of the resistance of glass surfaces can be further improved by the influence of acid gases for instance at the softening temperature of the glass in question, obviously because of a fusing of the gelatinous surface layer, which is richer in silica. The use of this proceeding is restricted, however, since the necessary heating to near softening temperature entails in the glass surface and the glass deformations and other changes which, to say the least, render their use for instance for optical lenses or prisms more difficult. This proceeding is also precarious on account of the alkali showing near the said softening temperature a tendency to travel and, accordingly, to penetrate into the surface layer and to thus reduce the achieved improvement more or less.

According to the invention, an effective and permanent improvement of the surfaces of glass and of those of other silicic, i. e. ceramic, objects as well as other important technical changes as to physical and chemical properties can be arrived at also at temperatures considerably below that required for softening (as a rule below 400 centigrades) by adopting the following three measures. The surface of the object to be treated is coated with a lixiviated layer; substances containing hydrophobe groups are introduced into this layer; and the structure of the surface is made to close and solidify by interior changes. The new method can be carried into effect es-

pecially by causing the object to be treated to react at a temperature below its melting point in consequence of exposure to acids and substances containing hydrophobe groups.

Providing a lixiviated layer on the surface to be treated is effected either by lixiviating this surface or coating it with a gelatinous layer of, for instance, water-glass. A lixiviation of the surface does not require the object to consist of components which are easily soluble and components that can be less easily dissolved. Prolonged watering can produce, for instance also on quartz, a similar surface, which can be proved by the absorption effect with respect to, for instance, certain pigments. The entire body need not naturally consist uniformly of the material to be treated in the above-described manner; it may be for instance of a non-silicious material coated with silicious material. On the other hand, the object can be at the outset entirely of a material which, in the sense of the invention, is to be considered as lixiviated. For instance the narrow free edge of the water-glass layer by means of which two glass objects are cemented to each other can be rendered more resistant by introducing substances that contain hydrophobe groups and solidifying this edge.

By substances containing hydrophobe groups are to be understood materials that dissolve in water either not at all or only to a very slight extent, as for instance grease, oil and other hydrophobe carbohydrates, sebacic acid etc.

The aforesaid three measures can be taken simultaneously or subsequently to each other. The lixiviation can take place at the same time as the treatment with substances containing hydrophobe groups. It is also possible, however, to begin with producing the lixiviated layer, to expose the object to substances containing hydrophobe groups and, finally, to effect the solidification.

In general, a lixiviation of glass objects by acids (excepting fluorhydric acid) is to be preferred to that by means of water, since acids attack also the bivalent oxides and thus produce such a structure of the surface as is looser and more receptive of the hydrophobe substances. By a milder or a protracted lixiviation, a suitable surface layer is obtained even when the objects to be treated contain only as small a percentage of silica as 0.1%.

Paraffins, stearic acid, oleic acid and other hydrophobe substances with a high boiling point have proved to be very suitable. If polished or non-prepared glass objects are heated in these substances, in the presence of acids, water adheres to these objects either only with difficulty or not at all, even subsequently to cleaning, prolonged boiling in grease-dissolving substances, or

after treatment with other kinds of otherwise dissolving substances. This condition cannot obtain when the objects are merely smeared over with such materials and then cleaned. The process taking place is probably as follows. Similarly to the action of watery acid solutions, that of acids produces a surface layer which is rich in silicic acid and perhaps gelatinous, whereupon this layer is penetrated by the hydrophobe substance, modifies at the temperature required by the treatment and solidifies, thus preventing the hydrophobe substance from being dissolved.

Means for changing the structure of gelatinous layers by interior modifications in such a manner that this structure closes and solidifies are known. The most simple means is heat. It is also possible, however, to use in the new method other proceedings of any, for instance electric, kind which effect interior modifications of the gelatinous part and the solidification thereof.

The most simple manner of carrying the new method into practice consists in immersing the object to be treated into a bath which contains acid and hydrophobe groups and has a temperature below that at which the object begins to soften. As the possibilities of chemical attacks on the object are very different, depending as they do on the composition of the object, and as the resulting surface layer is prone to modify and solidify more or less easily, according to its content of gelatine-forming agents, the most suitable composition of the bath, the height of the temperature and the duration of the exposure are very different. In general, the lixiviation will have to be the stronger and the temperature the higher, the more silica or other gelatine-forming agents are contained in the glass. Good results can be obtained in most glasses for instance with paraffin substances containing oleic, stearic or other acids and at temperature above 100 centigrades. Half an hour of exposure at approximately 200 centigrades may do eventually. A treatment with hydrophobe substances which are completely acid-free, for instance with specially purified paraffin, is not, however, effective. Many of the substances containing hydrophobe groups do not, however, require a special addition of acid, since they are acids at the outset, or because acid is produced in them at the temperature of the treatment.

The lixiviated layer can be produced before the treatment with the substances containing the hydrophobe groups, this lixiviation being effected by water and watery solutions, for instance by aqueous acid solutions. In this case, it is easier to obtain comparatively thick layers. The effect aqueous acid solutions produce on polished glass objects or the simultaneous presence in the bath of water and acids soluble in water very often entails, however, that polishing scratches are rendered visible. In general, a slight content of water in the bath permits to accelerate the formation of the desired surface layer. Avoiding mineral acids in the water permits the prevention of scratches.

If the hydrophobe substances have been introduced into the surface layer at a low temperature, or if the treatment in the bath has been too short to cause a solidification of the structure of the surface layer obtained, the solidification can be accelerated and completed in air by subsequent heating to higher temperatures. It will be convenient, as a rule, to cause the hydrophobe substance to act above a temperature of 100°

or to heat the object ultimately to above 100 centigrades.

It has been proved further that also other substances absorbable on the lixiviated surface layer, for instance organic dyeing substances, can be lastingly introduced into the surface when they are caused to act during or after the lixiviated layer having been produced, but before solidification. This possibility to introduce such substances can be used for instance also for causing glass surfaces to have special catalytic or fluorescence properties or, generally speaking, to obtain such properties which are not peculiar to the material to be treated.

The objects treated by the described method have in addition to their opposition against adhesion of water, which can be turned to account practically for instance for inactivating and immunizing containers or for influencing condensations on surfaces, a capacity of resistance against attacks by steam or water, acids and weak lyes which is in most cases very pronounced and higher than twice the ordinary resistance. This fact is to be appreciated especially when glasses poor in silica are concerned, which are easily stained, and which are often used for optical purposes on account of their special properties. The new method permits the practical use of glasses that are even poorer in silica than those employed so far, which may not have an  $\text{SiO}_2$  content lower than 30%. Exactly these easily stained glasses give a clear idea as to the difference existing between the effect of a mere coating with hydrophobe substances and that of introducing these substances into the surface. Simply coating the glass does not protect from the action of water and acid solutions, in spite of an immunity of the surface against adhesion being ostensibly produced, but merely entails a retardation of this action, in contradistinction where to glasses treated according to the new method remain unchanged even in the long run.

Hot concentrated lyes and fluorhydric acid, however, noticeably attack even the glasses submitted to treatment, so that the glass substance is not made entirely inaccessible by the protection treatment. It is surely due to this fact that thin glass layers submitted to the method and used for instance in glass electrodes permit the passage of electric current very well in spite of the slight adhesiveness of water. However, the method concerned by the invention permits, on the other hand, to use for the said purposes glasses which are rich in alkali (and may contain even more than 20% thereof) and which are, accordingly, highly conductive electrically and would, if devoid of a protective layer, be attacked very strongly by the solutions to be tested.

The thicknesses the layers are to have in order to afford good protection are very slight in general and in most cases hardly measurable. Thicknesses of few  $m\mu$  will do. Greater thicknesses influence the reflection capacity, the magnitude of which is determined first of all by the refractive index of the object to be treated. When noticeably thick, the surface layers, which the method has caused to be richer in silica, and which have therefore a lower refractive index, reduce the reflection capacity by interference, it being possible without detriment to largely reduce this reflection capacity at thicknesses of the layer of 100  $m\mu$ .

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