GLASS ARTICLE CARRYING A TRANSPARENT PROTECTIVE LAYER WHICH IS RESISTANT TO ABRASION AND CAN BE LABELLED AND PROCESS FOR OBTAINING IT

DESCRIPTION

The invention relates to glass articles, in particular of hollow glass, carrying a coating which, while giving them good resistance to abrasion, has a good appearance (homogeneous, transparent and invisible coating) and enables labels to adhere.

Glass articles, in particular hollow glass, when being handled, filled, packaged and possibly washed before being reused, can bump into each other, producing abrasion, in particular scratches, which reduces their mechanical strength.

The surface of glass articles has already been treated in order to improve their abrasion resistance, regardless of whether these glass articles are dry or wet, for example as a result of being washed.

Thus document US 3 438 801 describes the treatment of glass bottles to improve their dry abrasion resistance by deposition, in a first stage, at 150°C, of an aqueous solution of a diaminosilane (3-(2-aminoethyl)aminopropyltrimethoxysilane, here called DAMO) and, in a second stage at 140°C, of an aqueous emulsion of polyethylene used in combination with potassium oleate.

These glass bottles are generally intended to be labelled and, consequently, the abrasion-resistant layer applied to the surface of the glass must also allow good adhesiveness of a label by means of conventional adhesives like casein and dextrin. To obtain this good adhesiveness, as well as an appropriate abrasion resistance, US Patent 3 873 352 describes treating the surface of the glass with an aqueous composition containing polyethyleneiminepropyl-trimethoxysilane which has a molecular mass of approximately 1400 (or a mixture of this silane with a diaminosilane, DAMO) and polyethylene used in combination with potassium oleate.

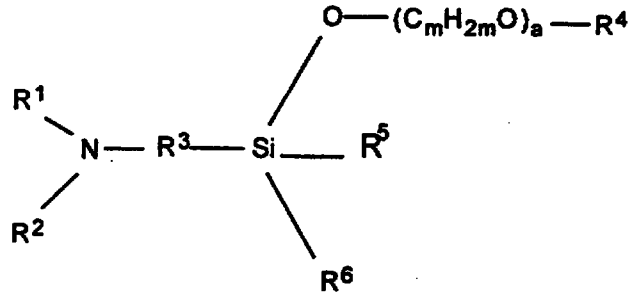
It has been noted, however, that these layers have a cloudy appearance which makes the glass article unusable and that the resistance to abrasion in the wet state is not sufficient. In addition, some of these layers do not enable labels to adhere well.

Attempts have therefore been made to form, on glass surfaces, coatings which have a good appearance and to which labels adhere well, while giving properties of resistance to abrasion when dry and in the wet state.

There has also been a search for a simple process for producing them, which can be exploited industrially, both on the production line for these glass articles and when they are recycled, for example,

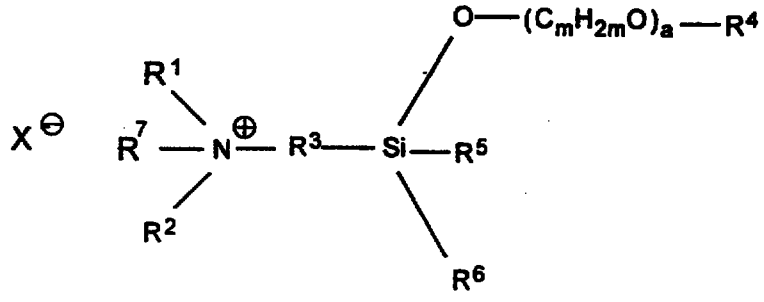
in order to be refilled.

The glass articles according to the invention which have these desired properties carry a coating resulting from the application, onto the glass surface, of at least one monoaminosilane and of at least one lubricating substance, the monoaminosilane(s) corresponding to the general formula:



I

or its quaternized form:



II

in which :

- each of R^1 and R^2, which are identical or different, denotes a hydrogen atom or an alkyl group containing from 1 to 4 carbon atoms,

- R^3 is a linear or branched alkylene group containing 2 to 11 carbon atoms, in particular 3 to 5 carbon atoms, or an oxyalkylene or polyoxyalkylene

group containing from 2 to 4 carbon atoms in the alkylene chain, this oxyalkylene or polyoxyalkylene group being bonded to the silicon via a carbon atom,

- R^4 denotes an alkyl group containing 1 to 4 carbon atoms,

- each of R^5 and R^6, which are identical or different, denotes an alkyl group containing 1 to 4 carbon atoms or else a group $-O-(C_nH_{2n}O)_b-R^4$ in which R^4 has the above meaning,

- each of m and n, which are identical or different, denotes the integer 2, 3 or 4,

- each of a and b, which are identical or different, denotes the integer 0, 1 or 2,

- R^7 denotes a hydrogen atom or an alkyl group containing from 1 to 4 carbon atoms, and

- $X^\ominus$ is an anion such as chloride, bromide, sulphate or methylsulphate.

In particular, in the coating, the dry quantity of monoaminosilane(s) deposited onto the utilized surface of glass is between 10^{-4} mg/cm^2 and 5×10^{-2} mg/cm^2 and preferably 6×10^{-3} mg/cm^2 and 5×10^{-2} mg/cm^2 and the dry quantity of lubricating substance(s) deposited onto the utilized surface of glass is between 5×10^{-4} mg/cm^2 and 5×10^{-2} mg/cm^2 and, preferably, between 2×10^{-3} mg/cm^2 and 10^{-2} mg/cm^2.

Utilized surface is intended to mean the surface of the glass article which is usually subjected to abrasion and which must, consequently, receive a

protective coating.

In the above formulae of the monoaminosilanes, R^1 and R^2, which are identical or different, preferably denote a hydrogen atom or a methyl group, R^3 is, for example, a propylene, butylene, isopropylene and, preferably, propylene group, an oxyethylene, oxypropylene oxybutylene or polyoxyethylene, polyoxypropylene or polyoxybutylene group or a polyoxyalkylene group containing a number of different oxyalkylene units, R^4 preferably denotes a methyl or ethyl group, each of R^5 and R^6, which are identical or different, preferably denotes a methyl or ethyl group or else the group $-O-(C_nH_{2n}O)_b-R^4$, m and n preferably denote the integer 2 or 3, a and b preferably denote the number 0, 1 or 2, R^7 is preferably a hydrogen atom or a methyl group and $X^\ominus$ is the chloride, bromide, sulphate or methylsulphate anion.

Monoaminosilanes which are particularly useful in the invention are, for example, 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 4-aminobutyltrimethoxysilane, N-methyl-3-aminopropyltrimethoxysilane and 3-aminopropyltris(2-methoxyethoxyethoxy)silane.

The lubricating substance, useful in the invention, may be advantageously oleic acid, sodium stearate, ammonium stearate, an alkylamine acetate with a long chain (number of carbon atoms greater than or equal to 8) like tallow or coco, polyethylene glycol, a

polyolefin or a mixture of these products. In particular it is an optionally oxidized or partially oxidized polyolefin.

The oxidized or partially oxidized polyolefin may be advantageously polyethylene, polypropylene or polyisobutylene. It is preferably polyethylene.

Oxidized or partially oxidized polyethylene which has a relatively low weight-average molecular mass, for example between 1000 and 15 000 is advantageously employed.

A process for manufacturing this glass article consists in depositing onto the glass surface the silane(s) and the lubricating substance(s) and in heat-treating them simultaneously or subsequently.

The heat treatment preferably takes place at a temperature of between 60°C and 160°C and more particularly between 80°C and 150°C. At temperatures that are higher than 160°C the layers obtained do not allow the labels to adhere well and the optical quality of the deposit is insufficient.

In particular, to obtain the coating which has the properties sought after, it suffices to heat at least the glass surface to a temperature in the range shown, that is to say to a temperature of between 60°C and 160°C and advantageously between 80°C and 150°C, before or after the deposition of the components silane(s) and lubricating substance(s). The surface temperature can be controlled by any appropriate means,

for example by employing an infrared pyrometer.

The process of deposition onto the glass surface, described above, can be carried out in a single stage, the silane(s) and the lubricating substance(s) being in the same composition. It is also possible to deposit the silane(s) in a first stage and then the lubricating substance(s) in a second stage.

The coating formed on the surface of the glass is obtained, for example, from aqueous compositions of monoaminosilane(s) and of lubricating substance(s).

In particular, whether the deposition is carried out in a single stage or in two stages, the aqueous compositions employed for these depositions may contain from 0.005 % to 2 % by weight, preferably from 0.01 % to 1.5 % by weight, of monoaminosilane(s) and from 0.10 % to 2 % by weight, preferably from 0.15 % to 1.5 % by weight, of lubricating substance(s).

As indicated above, the lubricating substance is advantageously an optionally oxidized or partially oxidized polyolefin. It is generally in the form of a nonionic or ionic aqueous emulsion.

The deposition may be carried out on the glass surface by any appropriate process, for example by brushing or spraying, particularly when the surface to be treated is at high temperature, or by spraying or dipping in an aqueous solution when the surface to be treated is at low temperature.

The composition(s) may be sprayed onto the glass surface by any appropriate means and, in particular, by employing a pneumatic spraying device; an ultrasonics-assisted spraying device may also be employed.

When the deposition is done by brushing, a brush may be employed which is impregnated with the composition or else with a precipitate obtained by precipitation of the components in acidic medium.

According to one embodiment of the invention an aqueous composition of monoaminosilane(s) and of lubricating substance(s) is deposited in a single stage. This composition may be deposited directly onto the glass surface at a temperature which is in the range indicated above, that is to say at a temperature of between 60°C and 160°C and, advantageously, between 80°C and 150°C. The heat treatment is then simultaneous.

It is also possible to deposit the composition of monoaminosilane(s) and of lubricating substance(s) onto the glass surface which is at a temperature lower than 60°C, for example at the ambient temperature or at a lower temperature. This is particularly the case when the glass articles, like bottles, are to be recycled. After the deposition onto the glass surface, the components are heat-treated by heating at least the glass surface to a temperature within the range indicated above.

Another embodiment of the invention consists in depositing onto the glass surface, in a first stage, an aqueous solution of monoaminosilane(s) and, in a second stage, an aqueous composition of lubricating substance(s). The aqueous solution of silane(s) may be deposited directly onto the glass surface at a temperature of between 60°C and 160°C and the aqueous composition of lubricating substance(s) is next deposited still at a temperature of between 60°C and 160°C. Between the two depositions it may be necessary to heat the glass article to be treated in order that at least the glass surface should be at the temperature necessary for the deposition of the aqueous composition of lubricating substance(s), that is to say at a temperature within the above range.

Another process consists in depositing, first, the aqueous solution of silane(s) onto the surface of the glass which is at a temperature lower than 60°C, for example at the ambient temperature, and then in heating at least the glass surface to a temperature of between 60°C and 160°C, preferably between 80°C and 150°C, and, next, in depositing the aqueous composition of lubricating substance(s). To produce this second deposit according to the invention, at least the glass surface must be heated, if necessary, to a temperature of between 60°C and 160°C before or after the deposition of this aqueous composition of lubricating substance(s).

According to another embodiment of the invention the aqueous solution of silane(s) and the aqueous composition of lubricating substance(s) are deposited successively at a temperature lower than 60°C and then the deposit is heat-treated by heating at least the glass surface to a temperature of between 60°C and 160°C.

The heat treatment may be performed by any appropriate means. In particular, it may take place at the exit from the annealing lehr, during the manufacture of the glass articles. It may also be carried out in an oven, with a hot air blast, with infrared radiation or microwaves.

When the deposition of the components silane(s) and lubricating substance(s) takes place on the surface of the glass at a temperature higher than 60°C or, preferably, higher than 80°C, the rise in temperature for the heat treatment is not necessary; in this case the deposition and the heat treatment are done simultaneously.

The deposition of the components onto the surface of the glass articles at low temperature may offer an advantage, in particular in the case of recycling with a view to the articles being reused. This deposition may take place, for example, after the washing of these articles.

In the nonlimiting examples which illustrate the invention the glass articles (bottles) are placed

in a rotary device rotating at a speed of 75 to 130 rev/min and the deposition is done by spraying.

The treated bottles are next tested to determine their resistance to abrasion in the dry and wet state, the appearance of the layer and the adhesiveness of a label. The tests are the following:

1. Abrasion resistance

The test consists in placing two bottles which have undergone the same treatment, in a horizontal position, one on the other, their generatrix forming an angle of 30° and in pressing them one against the other while making them slide one over the other. When the pressure is increased the abrasion is produced at the moment when the force applied must be increased to make the bottles continue to slide one over the other. The force of application is limited to 450 N because a higher force would result in the breakage of one or both bottles.

The acceptable value of the resistance to abrasion depends on the requirements made necessary by the use of the glass articles. Abrasion values of 200 N when dry and of 100 N in the wet state may be considered to be minimum values. It is generally considered that a good abrasion is obtained with values greater than 300 N when dry and greater than 200 N in the wet state.

By way of information, with untreated bottles an abrasion appears starting at approximately 20 N.

2. Adhesiveness of a label

A paper label is applied with the aid of a conventional adhesive such as a casein-based aqueous adhesive. It is left to dry for 3 to 4 hours at ambient temperature or alternatively 20 minutes at 60°C.

To determine the adhesiveness of the label an attempt is made to tear the latter away and the surface of the label remaining on the glass is inspected:

100 % of the label	:	excellent adhesiveness
80 % of the label	:	acceptable adhesiveness
< 80 % of the label	:	adhesiveness not acceptable

3. Appearance of the layer

The layer must be homogeneous, transparent and invisible.

The inspection is visual:

Layer not visible, good appearance	= value 0
Layer, as a whole, not visible with, however, very small visible points, acceptable appearance	= value 1
Visible layer, appearance not acceptable	= value 2
Cloudy appearance, not acceptable	= value 3

In these examples there are employed:

- as silane, 3-aminopropyltrimethoxysilane: APTMO

  3-aminopropyltriethoxysilane: APTEO

  [3-(2-aminoethyl)amino-

propyl]trimethoxysilane: DAMO

or N-methyl-3-amino-propyltrimethoxysilane: MAPTMO

- as polyolefin, oxidized or partially oxidized polyethylene is employed:

- the product Glasskote® SC100 from the company Elf Lubricants North America, which is in the form of aqueous emulsion with a solids content of 25 %;
- the product OG®25 from the company Trüb Emulsion, which is in the form of an aqueous emulsion with a solids content of 25 %;
- the product AC®629 from the company Allied Signal, which is in the form of an aqueous emulsion with a solids content of 25 %.

EXAMPLE 1

a) Preparation of the aqueous composition

0.60 g of an aqueous polyethylene emulsion SC100 and 20 g of water were introduced into a 250-ml bottle provided with a bar magnet.

After having stirred for 1 minute 0.5 g of APTEO are added. Stirring is applied for 1 minute, then the composition is made up to 100 g with water and stirred again for 1 minute.

The composition thus prepared, containing 0.15 % of polyethylene and 0.5 % of silane (APTEO), is ready for use.

b) Deposition process

The glass bottles to be treated are heated in an oven at 140°C-150°C for one hour. The hot bottles are secured onto a rotary device.

While the rotary device is being rotated at a rate of 120 rev/min, the composition is sprayed, for 5 seconds, with the aid of a pneumatic spraying device (2 bar pressure).

The bottles are left to cool to ambient temperature. The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 2.5×10^{-3} mg/cm^2.

A label is bonded on with the aid of an aqueous adhesive of the casein type; the bottles are then subjected to the abovementioned tests. The results are shown in Table 1.

EXAMPLE 2

The procedure is as in Example 1; the components (silane and polymer), their percentages and the test results are shown in Table 1. The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 8.2×10^{-3} mg/cm^2.

EXAMPLE 3

The procedure is as in Example 1, but an aqueous emulsion is employed, with a solids content of 25 % of partially oxidized polyethylene (OG®25 from the company Trüb Emulsion). The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 4.1×10^{-3} mg/cm^2.

The results are given in Table 1.

EXAMPLE 4

The procedure is as in Example 1, but N-methyl-3-aminopropyltrimethoxysilane (MAPTMO) is employed as monoaminosilane. The components (silane and polymer), their percentage and the test results are shown in Table 1. The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 4.1×10^{-3} mg/cm^2.

EXAMPLES 5 TO 8

The procedure is as in Example 1. The components (silane and polymer), their percentage and the test results are shown in Table 1. The dry quantities of products are the following:

	Silane	Polymer
Ex. 5	4.1×10^{-3} mg/cm^2	2.1×10^{-3} mg/cm^2
Ex. 6	4.9×10^{-3} mg/cm^2	2.5×10^{-3} mg/cm^2
Ex. 7	4.1×10^{-3} mg/cm^2	4.1×10^{-3} mg/cm^2
Ex. 8	2.5×10^{-3} mg/cm^2	4.1×10^{-3} mg/cm^2

EXAMPLE 9 (comparative)

The tests shown above are carried out on glass bottles carrying no deposit.

The results are given in Table 1.

EXAMPLE 10 (comparative)

The procedure is as in Example 1 but [3-(2-aminoethyl)aminopropyl]trimethoxysilane (DMAO) is employed as silane. The dry quantities of products are

the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 2.5×10^{-3} mg/cm^2.

The results are given in Table 1.

EXAMPLE 11 (comparative)

As in Example 1, a coating is formed on glass bottles starting with an aqueous composition containing 0.5 % of DAMO as silane and 1 % of product AC®629 (partially oxidized polyethylene). The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 1.6×10^{-2} mg/cm^2.

As can be noted from the results given in Table 1, the coatings obtained from a composition containing an ethylene diaminopropyltrimethoxysilane (DAMO) have an insufficient resistance to abrasion in the wet state and the appearance of the coating is unacceptable.

TABLE 1

One-stage process

EX.	SILANE	POLYMER	ABRASION RESISTANCE		APPEARANCE	ADHESIVENESS OF A LABEL
			dry	wet		
1	APTEO 0.5 %	SC100 0.15 %	350	250	1	100 %
2	APTMO 0.5 %	SC100 0.5 %	300	250	1	100 %
3	APTEO 0.5 %	OG25 0.25 %	400	400	0	100 %
4	MAPTMO 0.5 %	OG25 0.25 %	400	350	1	100 %

5	APTEO 0.25 %	OG25 0.125 %	400	300	0	100 %
6	APTEO 0.3 %	OG25 0.15 %	400	350	0	100 %
7	APTEO 0.25 %	OG25 0.25 %	400	350	1	100 %
8	APTEO 0.15 %	0G25 0.25 %	400	350	1	100 %
9 comparative			20	20	0	100 %
10 comparative	DAMO 0.5 %	SC100 0.15 %	300	100	2	100 %
11 comparative	DAMO 0.5 %	AC629 1 %	400	100	3	100 %

EXAMPLE 12

The procedure uses the same conditions as Example 1, but the glass bottles are heated in an oven at 80-90°C. The components (silane and polymer), their percentage and the test results are shown in Table 2. The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 3.1×10^{-3} mg/cm^2.

EXAMPLE 13

The procedure is as in Example 1, but the glass bottles are heated in an oven to 120-130°C. The components (silane and polymer), their percentage and the test results are shown in Table 2. The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 3.1×10^{-3} mg/cm^2.

EXAMPLE 14

In this example the aqueous composition of

silane and polymer is deposited onto glass bottles at ambient temperature:

a) preparation of the aqueous composition:

The procedure is as shown in Example 1, the components and the percentages given in Table 2 being employed.

b) the deposition process:

The bottles, which are at ambient temperature, are secured to a rotary device. While the device is rotated at a speed of 120 rev/min, the composition is sprayed for 5 seconds with the aid of a pneumatic spraying device (2 bar pressure).

The temperature of the surface of the bottles is then brought to 80°C with the aid of an infrared oven with a power output of 18 kW.

The bottles are allowed to cool to ambient temperature. The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 4.1×10^{-3} mg/cm^2. A label is bonded with the aid of an aqueous adhesive of the casein type, and the bottles are then subjected to the tests mentioned above. The results are shown in Table 2.

TABLE 2

Single-stage process

EX.	SILANE	POLYMER	ABRASION RESISTANCE		APPEARANCE	ADHESIVENESS OF A LABEL
			dry	wet		
12	APTEO 0.5 %	OG25 0.19 %	400	400	1	100 %
13	APTEO 0.5 %	OG25 0.19 %	400	400	1	100 %
14	APTEO 0.5 %	OG25 0.25 %	400	400	0	100 %

EXAMPLE 15 (two stages)

The two components (silane and polyethylene) are deposited in two stages.

The silane employed is APTEO in aqueous solution at a concentration of 0.5 %.

An aqueous emulsion containing 0.15 % of Glasskote®SC100 is employed to form the polyethylene deposit.

The glass bottles, heated in an oven to 140°C-150°C for one hour are secured to a rotary device. While the rotary device is rotated at a speed of 120 rev/min, the aqueous solution of silane is sprayed for 5 seconds with the aid of a pneumatic spraying device (2 bar pressure) and the polyethylene composition is then sprayed for 5 seconds. The bottles are allowed to cool and subjected to the tests mentioned above. The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer:

2.5×10^{-3} mg/cm^2.

The results are given in Table 3.

EXAMPLE 16 (two stages)

The procedure is as in Example 15. The components (silane and polymer), their percentage and the results of the tests are shown in Table 3. The dry quantities of products are the following: silane: 1.6×10^{-3} mg/cm^2, polymer: 4.1×10^{-3} mg/cm^2.

EXAMPLE 17 (two stages)

In this example the aqueous silane composition is deposited onto the glass surface at low temperature (1°C).

The procedure is as in Example 15 with components (silane and polymer) and percentages shown in Table 3.

The bottles, which are at 1°C, are secured to a rotary device.

While the device is rotated at a speed of 120 rev/min the composition containing the silane is sprayed for 5 seconds with the aid of a pneumatic spraying device (2 bar pressure).

The temperature of the surface of the bottles is then brought to 80°C with the aid of an infrared oven with a power output of 18 kW.

The bottles are allowed to cool to a temperature lower than 50°C and the aqueous composition containing the polymer is then applied by the same method. The temperature of the surface of the bottles

is next brought to 80°C with the aid of an infrared oven of a power output of 18 kW.

The bottles are allowed to cool to the ambient temperature. The dry quantities of products are the following: silane: 1.6×10^{-3} mg/cm^2, polymer: 2.1×10^{-3} mg/cm^2.

A label is bonded with the aid of an aqueous adhesive of the casein type; the bottles are then subjected to the tests mentioned above.

The results are shown in Table 3.

EXAMPLE 18, comparative (two stages)

In this example [3-(2-aminoethyl)amino-propyl]trimethoxysilane (DAMO) in the form of aqueous solution at a concentration of 0.5 % is employed as silane and the product AC629, in the form of aqueous solution at a concentration of 0.15 % as polyethylene, in accordance with the teaching of US Patent 3,438,801. The deposition conditions are those of Example 15. The dry quantities of products are the following: silane: 8.2×10^{-3} mg/cm^2, polymer: 2.5×10^{-3} mg/cm^2.

The results are given in Table 3.

TABLE 3

Two-stage process

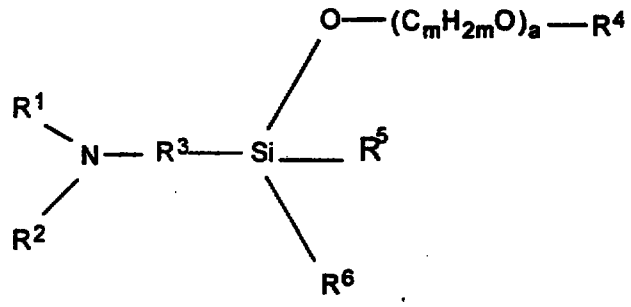
EX.	STAGE 1 SILANE	STAGE 2 POLYMER	ABRASION RESISTANCE		APPEARANCE	ADHESIVENESS OF A LABEL
			dry	wet		
15	APTEO 0.5 %	SC100 0.15 %	400	400	1	100 %
16	APTEO 0.1 %	OG25 0.25 %	400	400	1	100 %
17	APTEO 0.1 %	OG25 0.125 %	400	350	0	100 %
18 com-parative	DAMO 0.5 %	AC629 0.15 %	250	250	2	no <80 %

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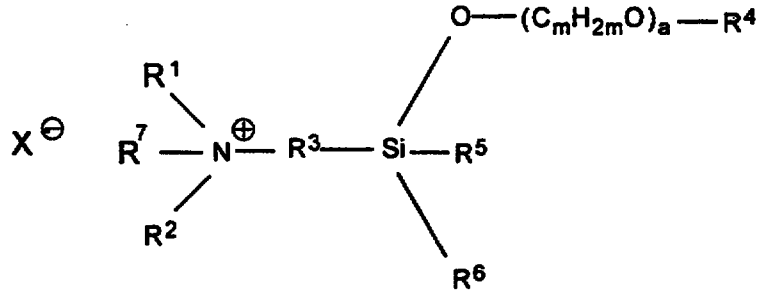
CLAIMS

1. Glass article carrying a coating which is practically transparent, capable of being labelled and resistant to abrasion, this coating resulting from the application, onto the glass surface, of at least one monoaminosilane and of at least one lubricating substance, the monoaminosilane(s) corresponding to the general formula:



I

or in its quaternized form:



II

in which :

- each of R^1 and R^2, which are identical or different, denotes a hydrogen atom or an alkyl group containing from 1 to 4 carbon atoms,

- R^3 is a linear or branched alkylene group containing 2 to 11 carbon atoms, in particular 3 to 5 carbon atoms, an oxyalkylene or polyoxyalkylene group

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containing from 2 to 4 carbon atoms in the alkylene chain, this oxyalkylene or polyoxyalkylene group being bonded to the silicon via a carbon atom,

- R^4 denotes an alkyl group containing 1 to 4 carbon atoms,

- each of R^5 and R^6, which are identical or different, denotes an alkyl group containing 1 to 4 carbon atoms or else a group $-O-(C_nH_{2n}O)_b-R^4$ in which R^4 has the above meaning,

- each of m and n, which are identical or different, denotes the integer 2, 3 or 4,

- each of a and b, which are identical or different, denotes the integer 0, 1 or 2,

- R^7 denotes a hydrogen atom or an alkyl group containing from 1 to 4 carbon atoms, and

- $X^\ominus$ is an anion.

2. Article in accordance with Claim 1, in which the monoaminosilane(s) correspond to the formulae I or II in which R^1 and R^2, which are identical or different, denote a hydrogen atom or a methyl group, R^3 is a propylene, butylene or isopropylene group, R^4 denotes a methyl or ethyl group, each of R^5 and R^6, which are identical or different, denotes a methyl or ethyl group or else the group $-O-(C_nH_{2n}O)_b-R^4$, m and n denote the integer 2 or 3, a and b denote the number 0, 1 or 2, R^7 is a hydrogen atom or a methyl group and $X^\ominus$ is the chloride, bromide, sulphate or methylsulphate anion.

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3. Article according to Claim 2, in which the monoaminosilane(s) are chosen from the group made up of 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 4-aminobutyltrimethoxysilane, N-methyl-3-aminopropyltrimethoxysilane and 3-aminopropyltris(2-methoxyethoxyethoxy)silane.

4. Article according to one of Claims 1 to 3, in which the lubricating substance is chosen from the group made up of oleic acid, sodium stearate, ammonium stearate, long-chain alkylamine acetate, polyethylene glycol, a polyolefin or a mixture of these substances.

5. Article according to one of Claims 1 to 4, in which the lubricating substance is an optionally oxidized or partially oxidized polyolefin.

6. Article in accordance with Claim 5, in which the oxidized or partially oxidized polyolefin is oxidized or partially oxidized polyethylene.

7. Article in accordance with Claim 6, in which the polyethylene has a weight-average molecular mass of between 1000 and 15 000.

8. Article in accordance with one of Claims 1 to 7, in which the dry quantity of monoaminosilane(s) on the utilized surface of glass is between 10^{-4} mg/cm^2 and 5×10^{-2} mg/cm^2 and preferably between 6×10^{-3} mg/cm^2 and 5×10^{-2} mg/cm^2 and in which the dry quantity of lubricating substance(s) on the utilized surface of glass is between 5×10^{-4} mg/cm^2 and 5×10^{-2} mg/cm^2 and

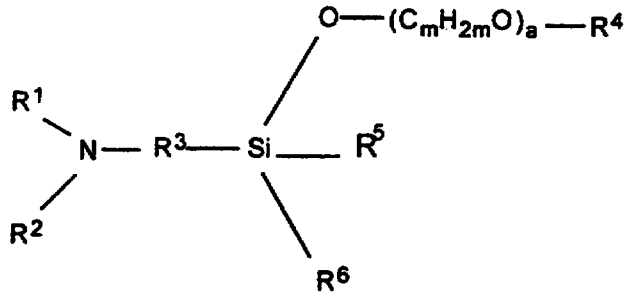
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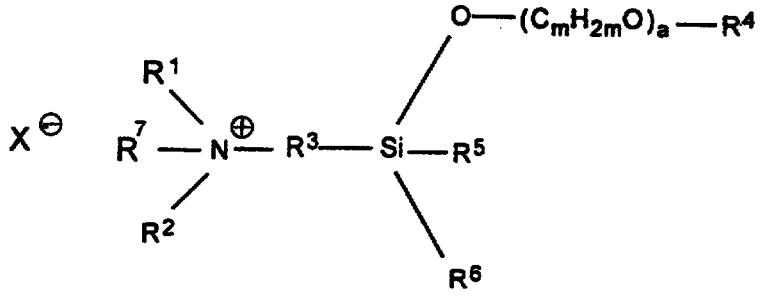
preferably between 2×10^{-3} mg/cm^2 and 10^{-2} mg/cm^2.

9. Process for the manufacture of an article in accordance with one of Claims 1 to 8, characterized in that it consists in depositing onto the glass surface and in heat-treating simultaneously or subsequently at least one monoaminosilane and at least one lubricating substance, the monoaminosilane(s) corresponding to the general formula:



I

or in its quaternized form:



II

in which:

- each of R^1 and R^2, which are identical or different, denotes a hydrogen atom or an alkyl group containing from 1 to 4 carbon atoms,

- R^3 is a linear or branched alkylene group containing 2 to 11 carbon atoms, in particular 3 to 5 carbon atoms, or else an oxyalkylene or polyoxyalkylene

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group containing from 2 to 4 carbon atoms in the alkylene chain, this oxyalkylene or polyoxyalkylene group being bonded to the silicon via a carbon atom,

- R^4 denotes an alkyl group containing 1 to 4 carbon atoms,

- each of R^5 and R^6, which are identical or different, denotes an alkyl group containing 1 to 4 carbon atoms or else a group $-O-(C_nH_{2n}O)_b-R^4$ in which R^4 has the above meaning,

- each of m and n, which are identical or different, denotes the integer 2, 3 or 4,

- each of a and b, which are identical or different, denotes the integer 0, 1 or 2,

- R^7 denotes a hydrogen atom or an alkyl group containing from 1 to 4 carbon atoms, and

- $X^\ominus$ is an anion.

10. Process in accordance with Claim 9, according to which the heat treatment is carried out at a temperature of between 60°C and 160°C and, more particularly, between 80°C and 150°C.

11. Process in accordance with Claim 10, according to which the heat treatment is carried out by heating at least the surface of the glass article to a temperature of between 60°C and 160°C and preferably between 80°C and 150°C.

12. Process in accordance with one of Claims 9 to 11, according to which an aqueous composition of monoaminosilane(s) and of lubricating substance(s) is

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deposited in one stage onto the glass surface.

13. Process in accordance with Claim 12, according to which the composition is deposited onto the glass surface which is at a temperature of between 60°C and 160°C, preferably between 80°C and 150°C.

14. Process in accordance with Claim 12, according to which the composition is deposited onto the glass surface at a temperature lower than 60°C and a heat treatment is then applied by heating at least the glass surface to a temperature of between 60°C and 160°C, preferably between 80°C and 150°C.

15. Process in accordance with one of Claims 9 to 11, according to which an aqueous solution of monoaminosilane(s) is deposited in a first stage and an aqueous composition of lubricating substance(s) in a second stage.

16. Process in accordance with Claim 15, according to which the aqueous solution of monoaminosilane(s) is deposited onto the surface of the glass, which is at a temperature of between 60°C and 160°C, preferably between 80°C and 150°C, and then the aqueous composition of lubricating substance(s) is deposited at a temperature of between 60°C and 160°C, preferably between 80°C and 150°C.

17. Process in accordance with Claim 15, according to which:

a) first, the aqueous solution of monoaminosilane(s) is deposited onto the surface of the

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glass at a temperature lower than 60°C,

b) at least the surface of the glass is next heated to a temperature of between 60°C and 160°C, preferably between 80°C and 150°C, and

c) the aqueous composition of lubricating substance(s) is deposited, at least the glass surface being heated to a temperature of between 60°C and 160°C, preferably between 80°C and 150°C, before or after the deposition of the aqueous composition of lubricating substance(s).

18. Process in accordance with Claim 15, according to which the aqueous solution of monoaminosilane(s) and the aqueous composition of lubricating substance(s) are deposited successively at a temperature lower than 60°C and heat treatment is then applied by heating at least the glass surface to a temperature of between 60°C and 160°C, preferably between 80°C and 150°C.

19. Process in accordance with one of Claims 9 to 18, according to which the heat treatment is carried out with the aid of an oven, with a hot air blast, infrared radiation or microwaves.

20. Process in accordance with one of Claims 9 to 13, 15 and 16, in which the heat treatment takes place at the exit from the annealing lehr.

21. Process in accordance with one of Claims 9 to 20, according to which at least one monoaminosilane is employed corresponding to the

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formulae I or II, in which R^1 and R^2, which are identical or different, denote a hydrogen atom or a methyl group, R^3 is a propylene, butylene or isopropylene group, R^4 denotes a methyl or ethyl group, each of R^5 and R^6, which are identical or different, denotes a methyl or ethyl group or else the group $-O-(C_nH_{2n}O)_b-R^4$, m and n denote the integer 2 or 3, a and b denote the number 0, 1 or 2, R^7 is a hydrogen atom or a methyl group and $X^\ominus$ is the chloride, bromide, sulphate or methylsulphate anion.

22. Process in accordance with Claim 21, according to which the monoaminosilane is chosen from the group made up of 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 4-aminobutyltrimethoxysilane, N-methyl-3-aminopropyltrimethoxysilane and 3-aminopropyltris(2-methoxyethoxyethoxy)silane.

23. Process in accordance with one of Claims 9 to 22, according to which the components monoaminosilane(s) and lubricating substance(s) are deposited in aqueous composition(s) containing from 0.005 % to 2 % by weight, preferably from 0.01 % to 1.5 % by weight, of monoaminosilane(s) and from 0.10 % to 2 % by weight, preferably from 0.15 % to 1.5 % by weight, of lubricating substance(s).

24. Process in accordance with one of Claims 9 to 23, according to which the lubricating substance is chosen from the group made up of oleic acid, sodium stearate, ammonium stearate, long-chain alkylamine

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acetate, polyethylene glycol,. a polyolefin or a mixture of these substances.

25. Process in accordance with one of Claims 9 to 24, according to which the lubricating substance is an optionally oxidized or partially oxidized polyolefin.

26. Process in accordance with Claim 25, according to which oxidized or partially oxidized polyethylene is employed as polyolefin.

27. Process in accordance with Claim 26, in which the polyethylene has a weight-average molecular mass of between 1000 and 15 000.

28. Process in accordance with one of Claims 25 to 27, according to which the polyolefin is in the form of ionic or nonionic aqueous emulsion.

29. Process in accordance with one of Claims 9 to 28, according to which the dry quantity of monoaminosilane(s) deposited onto the utilized surface of glass is between 10^{-4} mg/cm^2 and 5×10^{-2} mg/cm^2 and preferably between 6×10^{-3} mg/cm^2 and 5×10^{-2} mg/cm^2 and the dry quantity of lubricating substance(s) deposited onto the utilized surface of glass is between 5×10^{-4} mg/cm^2 and 5×10^{-2} mg/cm^2 and preferably between 2×10^{-3} mg/cm^2 and 10^{-2} mg/cm^2.

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