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(54) Title: METHOD AND MATERIAL FOR PROTECTING GLASS SURFACES

(57) Abstract

A method and material is disclosed for protecting glass surfaces in a stack of glass sheets by applying an interleaving material comprised of a high molecular weight polymer having a number average molecular weight of at least 100,000 to one or both major surfaces of the glass sheets. The glass sheets are then stacked in face-to-face relation for shipment or storage.

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TITLE

METHOD AND MATERIAL FOR PROTECTING GLASS SURFACES

FIELD OF THE INVENTION

The present invention relates generally to a method and material for separating glass sheets and protecting them from marring during storage and shipment, particularly when stacked in a conventional manner. In particular, the present invention relates to the application of a mechanical interleaving material to pyrolytically coated glass sheets, e.g., sheets having a pyrolytically deposited metal oxide and/or silicon-containing coating thereon, prior to stacking. References in this specification to "stacked glass sheets" are to be understood as referring to an assembly of glass sheets whose major surfaces are in adjacent face-to-face relationship.

BACKGROUND OF THE INVENTION

During the storage and transit of stacked glass sheets, a common problem is the deterioration in the quality of the surfaces of the glass sheets. In particular, relative movement between adjacent sheets is liable to cause marring of the adjacent glass surfaces. Marring is a particular problem when stacking glass sheets having pyrolytically deposited coatings thereon.

It is generally known in the art to separate adjacent glass surfaces by interposing sheets of paper between the sheets of glass to protect the glass surfaces. However,

techniques that utilize paper interleaving are time consuming and costly. Less expensive methods suggested for separating glass sheets involve the use of particulate interleaving materials, which may include natural products such as wood flour and ground corncobs, or synthetic products such as polyethylene, polystyrene or polyacrylate beads, to name a few. Poly(methyl methacrylate) is currently the predominant material used by the glass industry as an interleaving material.

While the synthetic particulate interleaving materials provide a measure of mar protection at relatively low cost, they are sometimes not sufficient to prevent marring on particular glass products, especially pyrolytically coated glass. Pyrolytic coatings of tin oxide, particularly relatively thick ones, are very susceptible to marring, due to their relatively rough surface topography. Such pyrolytic coatings are commonly utilized, for example, in multiple sheet or insulating glass products, and are described further in United States Patent Nos. 4,146,657 and 4,187,336 to Gordon. It would therefore be desirable to provide a method and material for separating stacked glass sheets coated with this material which prevents marring and which is compatible with normal production practices in the glass industry.

As noted above, polyethylene has previously been suggested as a possible interleaving material. For example, U.S. Patent No. 4,011,359 to Simpkin et al discloses an interleaving material for separating glass

sheets and protecting them from scratching and staining. The material comprises a porous, finely divided support material, impregnated with a weakly acidic material, and fine particles of a chemically inert plastic material. The inert plastic separator material may be polyethylene, polystyrene, polytetrafluoroethylene or a methacrylate polyester, and preferably has a larger particle size than the acid-impregnated support material. The interleaving material may be applied to the glass by conventional powder applicators.

U.S. Patent No. 4,447,496 to Franz et al discloses a method of protecting glass surfaces by the treatment of the glass surfaces with an organotin compound prior to the application of a particulate interleaving material. While various interleaving materials, such as polyethylene, polystyrene, polytetrafluoroethylene and polyacrylate are suggested, Franz et al indicate that porous cellulose materials such as wood flour are preferred.

U.S. Patent No. 2,995,533 to Parmer et al discloses a protective coating for glassware which is subjected to abrasive contact with other glassware during handling or shipment. An aqueous emulsion of polyethylene is applied to the glassware. It is noted that the molecular weight of the polyethylene can be as high as 2,000.

While the above materials do provide a measure of protection to normal clear glass, they fail to provide protection to pyrolytic coatings of tin oxide, particularly coatings that are relatively thick, e.g., so

called Low-E coatings. It would therefore be desirable to supply a method and material for interleaving both uncoated and pyrolytically coated glass sheets which provides superior resistance to marring during storage or transportation of the glass sheets. In addition, it is desirable for the method and material to prevent the development of low pressures, or even a vacuum, between the stacked glass sheets which may inhibit unloading of the stacked glass sheets.

It must be noted that the prior art referred to hereinabove has been collected and examined only in light of the present invention as a guide. It is not to be inferred that such diverse art would otherwise be assembled absent the motivation provided by the present invention.

SUMMARY OF THE INVENTION

The present invention provides a method and material for protecting a glass surface from marring during shipment or storage of stacked glass sheets. An interleaving material comprised of a high molecular weight polymer or mixtures of such polymers having a number average molecular weight of at least 100,000 is applied to one or both major surfaces of the glass sheets. As examples of such polymers may be mentioned utra-high molecular weight polyethylene and poly(methyl methacrylate). The glass sheets are then stacked in face-to-face relation for shipment or storage.

The interleaving material in accordance with the present invention provides superior resistance to marring compared to prior art particulate interleaving materials, along with the dimensional stability and impact resistance required to prevent the development of a vacuum between the stacked glass sheets.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In accordance with the invention, glass sheets are provided with a high molecular weight polymer interleaving material, for example ultra-high molecular weight polyethylene, prior to stacking in a face-to-face relation. It has been determined, however, that a polyethylene having a number average molecular weight less than 100,000 still resulted in significant marring of a pyrolytically coated, specifically tin-oxide coated, glass sheet. In addition, these relatively low molecular weight polyethylenes were found to transfer material to the coated glass surface under the high loads experienced by an interleaving material in a typical arrangement of stacked glass sheets.

Accordingly, the interleaving material of the present invention is comprised of a high molecular weight polymer having a number average molecular weight of at least 100,000. Preferably, the number average molecular weight of the interleaving material is at least 1,000,000. In a most preferred embodiment, the number average molecular weight of the interleaving material is in the range of

about 3 million to 6 million. The interleaving material of the invention exhibits excellent toughness, abrasion resistance, resistance to stress cracking and low moisture absorption, while retaining the low coefficient of friction typical of all polyethylenes.

These properties have been found to be critical in an interleaving material, especially when used with pyrolytically coated glass sheets. This is because the marring of tin-oxide coated glass sheets by, for example, a poly(methyl methacrylate) interleaving material of less than the desired high molecular weight is believed to be caused by a thin deposit of the poly(methyl methacrylate) on the tin-oxide coated surface, the marring sites having been identified by secondary ion mass spectrometry as poly(methyl methacrylate). In addition, electron microscopy of tin-oxide coated surfaces previously marred by a poly(methyl methacrylate) interleaving material fails to reveal any scratching of the surface.

The interleaving material in accordance with the invention may be a continuous film or sheet but preferably is formed of particles having an average size of between about 20 to 300 microns, preferably about 100 to 300 microns, and the particles may be of any suitable shape. The interleaving material may be formed of powder ground to the required size. From the standpoint of dimensional stability, it is preferable to form the interleaving material of generally spherical beads, although there may be production difficulties in forming polyethylene in

these molecular weight ranges into generally spherical beads. The particle size should be large enough to provide sufficient separation between the stacked glass sheets to maintain the glass sheets in spaced-apart relationship and prevent the development of a vacuum between adjacent sheets, and small enough such that the tendency to settle to the bottom of a vertically disposed stack of glass sheets is reduced. A size range of 20 microns to 300 microns satisfy these requirements.

Further, polyethylenes, even those having number average molecular weights greater than 1,000,000, will undergo plastic deformation under static loads over time. Where the stacked glass sheets will remain in that arrangement for a relatively long time, the load on the polyethylene particles may cause some deformation, reducing the separation between adjacent glass sheets to the extent that a vacuum will develop. Thus, in a most preferred embodiment, the average particle size is between about 150 microns and 300 microns, to allow for some deformation during long periods of storage and shipment.

The high molecular weight interleaving materials used in accordance with the invention, while providing improved resistance to marring, will not protect against the staining which may occur with pyrolytically coated stacked glass sheets. Therefore, the glass sheets are still treated with a conventional stain inhibitor, preferably an acid material. One preferred acid is adipic acid. The

quantity of acid applied need only be enough to provide adequate stain protection to the glass surface.

A preferable method for the application of the acid material is by spraying an aqueous solution onto the surface of a glass ribbon during a float glass manufacturing process. For pyrolytically coated glass, the stain inhibitor is preferably applied to the coated surface.

The particulate high molecular weight interleaving material may be applied to either major surface of the glass sheets in any suitable manner, either before or after the application of the stain inhibitor. Preferably, the interleaving material is electrostatically charged and dispersed on the surface of a glass ribbon during a float glass manufacturing process at a point where the glass ribbon is at or near ambient temperature. For pyrolytically coated glass, the interleaving material is also preferably applied to the coated surface.

The invention is more easily comprehended by reference to specific embodiments which are representative of the invention. It must be understood, however, that the specific embodiments are provided only for the purpose of illustration, and that the invention may be practiced otherwise than as specifically illustrated without departing from its spirit and scope.

EXAMPLE I

Sheets of annealed soda-lime-silica glass were formed having a tin oxide coating deposited thereon and cut into 4" X 8" sheets. The tin oxide coated surface of the glass sheets was dusted with a ground powder of the various interleaving materials to be tested at a rate of about 140 mg/ft^2. Two sheets at a time were mounted to a table and an uncoated glass sheet was placed over the samples. A 125 lbs. load was placed on the uncoated glass sheet, which was then moved relative to the samples for 250 strokes each 3/16" in length. Each sample was then washed in a conventional commercial glass washing machine using a water and detergent wash and a water rinse.

Eight samples were tested for each interleaving material, and the number of samples showing any marring was recorded. In addition, the total number of marred sites for each interleaving material was recorded. These results are shown in the Table below.

MATERIAL	# OF SAMPLES	# OF SAMPLES WITH MARRING	TOTAL # OF MARRED SITES
HB 312 CM[1]	8	3	3
HOSTALLOY 731[2]	8	2	2
DOW HDPE TYPE 1V - 10062N[3]	8	4	11
LDPE NA814-000[4]	8	5	ENTIRE SAMPLES MOTTLED

1. Ultra-high molecular weight polyethylene, 3 million to 6 million, available from HIMONT Incorporated.

2. Ultra-high molecular weight polyethylene, 3 million to 6 million, available from Hoechst-Celanese.

3. High density polyethylene, number average molecular weight in the range of 150,000 to 350,000, available from Dow Plastics.

4. Low density polyethylene, number average molecular weight in the range of 70,000 to 90,000, available from Quantum Chemicals.

For comparison, identical glass samples were produced and dusted with poly(methyl methacrylate) of number average molecular weight less than 100,000 and tested in the same manner as above. Eight out of eight such samples exhibited heavy mottling over most of the sheet.

EXAMPLE II

Two sheets of annealed soda lime silicate glass were formed having a tin oxide coating deposited thereon and cut into 10" x 12" sheets. The sheets were mounted in face to face relation with the interleaving material in powder form being dispersed between the coated face of the top sheet and the uncoated face of the bottom sheet. A 20 Kg load was applied to the top sheet and the two sheets were then oscillated relative to each other for a period of 30 minutes. Each sheet was then washed with deionized water in a washing machine, visually assessed and then

given a rating out of 10. It has been found in practice that a rating of 4 is on the border of acceptability. The results are shown in the table below:

MATERIAL	VISUAL ASSESSMENT	RATING
HB320[1] + adipic acid	Fault free surface	10
TS1192/1[2] + adipic acid	Occasional light marking present	8
TS1647[3] + adipic acid	Surface rub marks fairly visible	6½
TS1692[4] + adipic acid	Surface smear patches visible	6
Standard PMMA[5] + fine adipic (60 mesh)	Light streaking visible with occasional heavy rub mark	4

1. HB320: high molecular weight polyethylene, 3-6 Million, available from HIMONT Incorporated.

2. TS1192/1: high molecular weight poly(methyl methacrylate), number average molecular weight of 667,415, available from Bonar Polymers, County Durham, England.

3. TS1647: high molecular weight poly(methyl methacrylate), number average molecular weight of 492,524, available from Bonar Polymers, County Durham, England.

4. TS1692: high molecular weight poly(methyl methacrylate), number average molecular weight greater than 200,000, available from Bonar Polymers, County Durham, England.

5. Standard PMMA: high molecular weight poly(methyl methacrylate) 198,000, available from Bonar Polymers, County Durham, England.

WHAT IS CLAIMED IS:

1. A method for protecting stacked glass sheets which comprises the steps of:

a) applying an interleaving material to a major surface of a first glass sheet, said interleaving material being comprised of a high molecular weight polymer or mixtures thereof having a number average molecular weight of at least 100,000; and

b) bringing a major surface of a second glass sheet into face-to-face relation with said major surface of the first glass sheet.

2. The method according to claim 1, wherein the interleaving material is ultra-high molecular weight polyethylene having a number average molecular weight of at least 1,000,000.

3. The method according to claim 2, wherein the polyethylene interleaving material has a number average molecular weight of between about 3,000,000 and 6,000,000.

4. The method according to claim 1, wherein the interleaving material is poly(methyl methacrylate) having a number average molecular weight of at least 1,000,000.

5. A method according to any of claims 1 to 4, wherein the interleaving material is a particulate having an average particle size sufficient to maintain the first glass sheet and the second glass sheet in spaced-apart relationship.

6. A method according to claim 5, wherein the interleaving material has an average particle size of at least 20 microns.

7. A method according to claim 6, wherein the interleaving material has an average particle size of between about 100 to 300 microns.

8. A method according to claim 6, wherein the interleaving material is in the form of a ground powder.

9. A method according to claim 6, wherein the interleaving material is in the form of generally spherical beads.

10. The method according to claim 1, further comprising the step of applying a coating of a stain inhibitor to the first glass sheet prior to bringing the second glass sheet into face-to-face relation with the major surface of the first glass sheet.

11. The method according to claim 10, wherein the stain inhibitor is an acid.

12. The method according to claim 11, wherein the acid is adipic acid.

13. A method for protecting stacked glass sheets, each of said glass sheets having a tin oxide coated glass surface, comprising the steps of:

a) applying an interleaving material to a major surface of a first glass sheet, said interleaving material being comprised of a high molecular weight polymer having a number average molecular weight of at least 100,000; and

b) bringing a major surface of a second glass sheet into face-to-face relation with said major surface of the first glass sheet.

14. The method according to claim 13, wherein said interleaving material is applied to the tin oxide coated surface of said first glass sheet.

15. The method according to either of claims 13 or 14, wherein the interleaving material is ultra-high molecular weight polyethylene having a number average molecular weight of at least 1,000,000.

16. The method according to either of claims 13 or 14, wherein the interleaving material is poly(methyl methacrylate) having a number average molecular weight of at least 1,000,000.

17. The method according to any of claims 13 to 16, wherein the interleaving material has a number average molecular weight of between about 3,000,000 and 6,000,000.

18. A method according to any of claims 13 to 17, wherein the interleaving material is a particulate having an average particle size sufficient to maintain the first glass sheet and the second glass sheet in spaced-apart relationship.

19. A method according to claim 18, wherein the interleaving material has an average particle size of at least 20 microns.

20. A method according to claim 19, wherein the interleaving material has an average particle size of between about 100 to 300 microns.

21. The method according to claim 13, further comprising the step of applying a coating of a stain inhibitor to the first glass sheet prior to bringing the second glass sheet into face-to-face relation with the major surface of the first glass sheet.

22. The method according to claim 21, wherein the stain inhibitor is applied to the tin oxide coated surface of said first glass sheet.

23. The method according to either of claims 21 or 22, wherein the stain inhibitor is an acid.

24. The method according to claim 23, wherein the acid is adipic acid.

25. An article of manufacturing comprising:

a) a plurality of glass sheets; and

b) an interleaving material interposed between said glass sheets, said interleaving material being comprised of a high molecular weight polymer having a number average molecular weight of at least 100,000.

26. The article according to claim 25, wherein the interleaving material is ultra-high weight polyethylene having a number average molecular weight of at least 1,000,000.

27. The article according to claim 25, wherein the interleaving material is poly(methyl methacrylate) having a number average molecular weight of at least 1,000,000.

28. The article according to any of claims 25 to 27, wherein the interleaving material has a number average molecular weight of between about 3,000,000 and 6,000,000.

29. The article according to any of claims 25 to 28, wherein the interleaving material is a particulate having an average particle size sufficient to maintain the first glass sheet and the second glass sheet in spaced-apart relationship.

30. The article according to claim 29, wherein the interleaving material has an average particle size of at least 20 microns.

31. The article according to claim 30, wherein the interleaving material has an average particle size of between about 100 to 300 microns.

32. The article according to any of claims 25 to 31, further comprising a coating of a stain inhibitor interposed between said glass sheets.

33. The article according to claim 32, wherein the stain inhibitor is an acid.

34. The article according to claim 33, wherein the acid is adipic acid.

INTERNATIONAL SEARCH REPORT

Int. ational application No.
PCT/US94/14306

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :BO5D 1/12; B32B 17/06, 17/10

US CL :427/180; 428/426, 432, 441

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 427/180; 428/426, 432, 441

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,489,106 (DUFFER ET AL) 18 December 1984, abstract; column 2, line 66 to column 3, line 2.	1-16, 21-28
Y	US, A, 4,011,359 (SIMPKIN ET AL) 08 March 1977, abstract; column 3, lines 4-10.	25-28
A	US, A, 4,447,496 (FRANZ ET AL) 08 May 1984, see entire document.	1-16, 21-28

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

Int. ational application No.
PCT/US94/14306

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos::
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 17-20, 29-34
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.