

[54] GLASS-RUN FOR WINDOW GLASS OF MOTOR CAR

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[57] ABSTRACT

A glass-run for a window glass moving to open and close of a motor car, which has excellent non-adhesion property is disclosed, said glass-run comprising a substrate of a high molecular material having coated on the surface thereof a film formed by hardening a specific paint composition comprising components (A), (B), (C), (D), (E) and (F) described in the specification.

16 Claims, No Drawings

GLASS-RUN FOR WINDOW GLASS OF MOTOR CAR

Matter enclosed in heavy brackets [] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

FIELD OF THE INVENTION

The present invention relates to a novel glass-run for a window glass of a motor car, more specifically to a glass-run for a window glass of a motor car, having improved abrasion resistance.

BACKGROUND OF THE INVENTION

Glass-run for a window glass of a motor car has been required various properties (such as high heat resistance and weather fastness) to be exhibited under severe conditions. In general, a glass-run applied to the window of motor car, when it is used to support the window glass, especially in the case of a window glass moving to open and close, is required to be made of materials having a low coefficient of friction. The glass-run is used at the parts to be contacted with the movable glass, while a fixed window glass is supported by window frame per se, that is, by weather strips made of rubber or plastics. The glass-run is generally coated with a film at the parts to be contacted with the movable glass. However, an abrasion resistance test of such a conventional glass-run reveals that the coated film per se is easily abraded or cracked, or the coated film is often peeled apart from the substrate.

As a result of extensive studies on glass-run to improve its abrasion resistance, some of the present inventors had found that the coated film is the determinative factor on the abrasion resistance of glass-run and that the abrasion resistance can be markedly improved by coating a paint composition comprising the following components (A), (B), (C), (D) and (E) on at least a part of the surface of a substrate of a glass-run to be contacted with the movable window glass, and hardening it. They had also proposed a glass-run prepared using a paint composition comprising, as well as the above components (A) to (E), from 0.5 to 3 parts by weight of talc (Japanese Patent Application No. 200084/83 (corresponding U.S. patent application Ser. No. 664,030 filed on Oct. 23, 1984)). However, the glass-run thus obtained tends to adhere to a movable window glass in practical use. Accordingly, a glass-run having improved properties, particularly with respect to non-adhesiveness, has been desired.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a glass-run for a window glass of a motor car, which has excellent abrasion resistance and non-adhesive properties.

As a result of further investigations on the above glass-run, it has now been found that a glass-run free from the above drawbacks can be produced by using a paint composition in which the above talc is replaced by at least one of silica, clay and calcium carbonate.

That is, the present invention provides a glass-run for a window glass moving to open and close of a motor car, which comprises a substrate of a high molecular material having a film coated on at least a part of the surface of the substrate to be contacted with the win-

dow glass, said film being formed by hardening a paint composition comprising:

(A) 100 parts by weight of an urethane polymer obtained by the reaction of a polyester polyol having hydroxy groups in its terminal and a molecular weight of 1,000 to 3,000, synthesized from a saturated diol having 2 to 6 carbon atoms and an organic dicarboxylic acid having 4 to 6 carbon atoms, with an organic diisocyanate in the molar ratio of NCO/OH of from 0.6/1 to 0.95/1;

(B) 10 to 60 parts by weight of a castor oil polyol;

(C) 1 to 100 parts by weight of an urethane prepolymer having isocyanate groups in its terminal obtained by the reaction of a low molecular polyol and an organic diisocyanate;

(D) 2 to 100 parts by weight of a fluoro carbon resin;

(E) 5 to 100 parts by weight of a silicone oil, and

(F) 0.5 to [3] 8 parts by weight of at least one member of silica, clay, and calcium carbonate.

DETAILED DESCRIPTION OF THE INVENTION

High molecular materials which can be used as a substrate of glass-run are not particularly limited, and any materials conventionally used as the substrate of glass-run can be used in the present invention. The surface of the substrate is coated with the paint composition of the present invention. The surface of the substrate is optionally cleaned up before coating the paint composition.

The urethane polymer (A) which is one of the components of the paint composition is obtained by the reaction of a polyester polyol and an organic diisocyanate in the molar ratio of NCO/OH of from 0.6/1 to 0.95/1. When the ratio is outside the above range, the resulting glass-run does not exhibit excellent abrasion resistance in a high temperature atmosphere.

The polyester polyol which constitutes the urethane polymer (A) has hydroxy groups in its terminal and a molecular weight of from 1,000 to 3,000 and is obtained by reacting a saturated diol having 2 to 6 carbon atoms and an organic dicarboxylic acid having 4 to 6 carbon atoms. Examples of saturated diols include propylene glycol, butanediol, pentanediol, hexanediol and the like, and examples of organic dicarboxylic acids include adipic acid, succinic acid and the like.

Examples of organic diisocyanates which constitutes the urethane polymer (A) include 4,4'-diphenylmethane diisocyanate, 4,4'-diphenyl ether diisocyanate and the like.

The castor oil polyol (B) is a copolymer composed of castor oil, phthalic anhydride and glycerol, and the molecular weight and number of OH groups of castor oil polyol may be changed by altering the molar ratio of the three monomer components. The number of OH groups is generally more or less 100.

The urethane prepolymer (C) has isocyanate groups in its terminal and is obtained by reacting a low molecular polyol (generally a molecular weight of less than 1,000) and an organic diisocyanate. Examples of low molecular polyols include glycerine, trimethylol propane and the like. As the organic diisocyanate, those described in the preparation of the urethane polymer (A) can be used.

Examples of the fluoro carbon resin (D) include polytetrafluoroethylene, tetrafluoroethylene/hexafluoro-

propylene copolymer, polytrifluoro-chloro-ethylene, polyvinylidene fluoride and the like.

Examples of the silicon oil (E) include dimethyl silicone oil, methyl chloro silicone oil, methyl hydrogen silicone oil, methyl phenyl silicone oil, fluoro silicone oil and the like.

In the paint composition used in the present invention, component (B) is used in an amount of 10 to 60 parts by weight per 100 parts by weight of component (A). When component (B) is used in an amount outside the above range, the abrasion resistance of the resulting glass-run is deteriorated. The amount of component (C) used is 1 to 100 parts by weight, preferably 4 to 20 parts by weight, per 100 parts by weight of component (A). Component (D) is used in an amount of 2 to 100 parts by weight, preferably 10 to 60 parts by weight, more preferably 2 to 20 parts by weight, per 100 parts by weight of component (A). The use of less than 2 parts by weight component (D) results in deterioration of the abrasion resistance and the use of more than 100 parts by weight of component (D) degrades the stability of the paint composition and precipitations of component (D) occurs significantly. Component (E) is used in an amount of 5 to 100 parts by weight, preferably 10 to 50 parts by weight, more preferably 2 to 20 parts by weight, per 100 parts by weight of component (A). When it is less than 5 parts by weight, the abrasion resistance of the resulting glass-run is degraded, and when it is more than 100 parts by weight, the resulting paint composition becomes unstable and component (E) is separated from the composition as well as in the case of component (D). Component (F) is used in an amount of 0.5 to **[3.0]** 8 parts by weight per 100 parts by weight of component (A) to have the effect preventing adhesion to a movable window glass. When the amount of component (F) is less than 0.5 parts by weight, the resulting glass-run tends to lose the effect. On the other hand, when it is more than **[3.0]** 8 parts by weight, physical properties of the resulting glass-run is deteriorated.

In the preparation of the paint composition, a catalyst capable of accelerating the urethanizing reaction may also be added, such as dibutyltin diacetate, dibutyltin dioctoate, dibutyltin dilaurate, dibutyltin diesterate, tributyltin acetate, tributyltin octoate, tributyltin laurate, dioctyltin diacetate, dioctyltin dilaurate, diethyltin oleate, monomethyltin dioleate, etc. In addition, fillers such as carbon black, silicon dioxide etc. may further be added.

Organic solvents which can be used as a diluent for the paint composition include acetone, methyl ethylketone, methyl isobutyl ketone, benzene, toluene, xylene, ethyl acetate, methyl acetate, isopropyl acetate, trichloroethylene, 1,1,1-trichloroethane, dimethylformamide etc. The amount of organic solvents may be selected in accordance with a desired viscosity of the composition used for processing.

As coating method for the paint composition used in the production of glass-run, dip coating method, spray coating method, brush coating method, knife coating, roller coating etc. can be used, but the coating method is not limited thereto. The paint composition is used in the form of a solution diluted with the organic solvent as described above. The paint composition is coated on the substrate to form a film generally having a dry thickness of from 10 to 100 μm and preferably from 30 to 50 μm .

The production of glass-run according to the present invention has an advantage that a film having excellent properties with respect to abrasion resistance, non-adhesion property, water-repellancy and lubricity can be formed on the substrate by a simple operation, i.e., merely by coating and allowing to stand at a room temperature for several hours or heating at 180° C. or the less for several minutes. The term "room temperature" herein means a normal temperature in the room affected from usual climate and without using heating means such as dryer and heating oven. The coated film is preferably hardened at a room temperature since a heating apparatus is not required and the operation is simplified. However, heating means may be used when a great deal of the treatment is required. In the case, the temperature must be maintained below 180° C. because the heating at a temperature of more than 180° C. might deteriorate the substrate. Some kinds of substrate are softened at a temperature of more than 100° C., and therefore it is preferred to treat it by heating at a temperature of less than 100° C. The heating means may properly be selected.

The present invention will be described in more detail by reference to the following Examples. In the Examples, all parts are by weight. With regard to the substrates used in Examples, EPDM rubber (hardness JIS, A 80 degree) was used in Examples 1-8 and Comparative Example, and an extruded product of a mixture of polyvinyl chloride (100 parts), dioctyl phthalate (75 parts), barium stearate (2 parts), zinc stearate (1 part) and dibutyltin dilaurate (1 part) (the extrusion temperature: 130°-140° C.) was used in Example 9.

Urethane polymer (A) and urethane prepolymer (C) employed in Examples were prepared in the following manner.

Urethane polymer (A) having terminal hydroxy groups was obtained by reacting 1000 parts of polyester polyol (hydroxyl value: 56.0) synthesized from 1,4-butanediol and adipic acid, and 100 parts of 4,4'-diphenylmethane diisocyanate (MDI), in 2000 parts of toluene under dried nitrogen atmosphere at 80° C. for 3 hours.

Urethane prepolymer (C) having terminal NCO groups was obtained by reacting 100 parts of trimethylolpropane and 553 parts of 4,4'-diphenylmethane diisocyanate in 487 parts of ethyl acetate under dried nitrogen atmosphere at 80° C. for 3 hours.

EXAMPLE 1

25.0 parts of urethane polymer (A), 8.0 parts of castor oil polyol ("2310-50T" produced by Tokushima Seiyu Co., Ltd.), 10 parts of urethane prepolymer (C), 8.0 parts of polytetrafluoroethylene resin, 8.0 parts of silicone oil, 0.5 part of carbon black, 0.065 part of dibutyltin dilaurate, 0.065 part of phenol salt of 1,8-diazabicycloundecene-7, were mixed by a propeller type mixer at 23° C. for 30 minutes using a solvent consisting of 1.3 parts of toluene, 3.0 parts of cyclohexanone, 15.0 parts of tetrachloroethylene and 118.9 parts of trichloroethylene, to prepare a paint composition. This paint composition was coated on a substrate and hardened to produce a glass-run for a window glass of motor car.

Abrasion resistance and non-adhesion property of the product were examined by an abrasion resistance test and an adhesion test and the results are shown in the Table 1.

Abrasion Resistance Test

The coated surface of the product was abraded by moving the glass abrasor (thickness: 5 mm) in reciprocal manner under the following conditions.

Charged weight: 3 kg.

Cycle of abrasor: 60 times/minute

Stroke of abrasor: 145 mm

Adhesion Test

A test piece (5×50×50 mm) of the glass-run was held between a glass plate and a metal plate by clip and water was poured between the glass plate and the metal plate. The assembly was then allowed to stand at 80° C. for 1 hour. Thereafter the glass plate was pulled with a pushpull scale to measure the adhesion strength which the glass was peeled apart from the test piece of glass-run.

Examples 2-9 and Comparative Examples

Experiments were carried out in the same manner as in Example 1 except using the paint composition shown in the Tables 1 and 2, and the results are also shown in the Tables 1 and 2.

TABLE 1

	Comparative Example	Example				
		1	2	3	4	5
Urethane polymer (A)	25.0	25.0	25.0	25.0	25.0	25.0
Castor oil polyol	8.0	8.0	8.0	8.0	8.0	8.0
Urethane prepolymer (B)	10.0	10.0	10.0	10.0	10.0	10.0
Fluorine resin	8.0	8.0	8.0	8.0	8.0	8.0
Silicone oil	8.0	8.0	8.0	8.0	8.0	8.0
Carbon black	0.5	0.5	0.5	0.5	0.5	0.5
Silica (A)	—	0.5	1.0	2.0	—	—
Silica (B)	—	—	—	—	1.0	—
Silica (C)	—	—	—	—	—	1.0
DBTDL	0.065	0.065	0.065	0.065	0.065	0.065
SA No. 1	0.065	0.065	0.065	0.065	0.065	0.065
Toluene	1.3	1.3	1.3	1.3	1.3	1.3
Cyclohexanone	3.0	3.0	3.0	3.0	3.0	3.0
Tetrachloroethylene	15.0	15.0	15.0	15.0	15.0	15.0
Trichloroethylene	118.9	118.9	118.9	118.9	118.9	118.9
Adhesion strength (kg)	5.6	2.8	1.0	0.4	0.8	0.8
Abrasion resistance (times)	25.000	20.000	15.000	10.000	15.000	15.000

TABLE 2

	Example			
	6	7	8	9
Urethane polymer (A)	25.0	25.0	25.0	25.0
Castor oil polyol	8.0	8.0	8.0	8.0
Urethane prepolymer (B)	10.0	10.0	10.0	10.0
Fluorine resin	8.0	8.0	8.0	8.0
Silicone oil	8.0	8.0	8.0	8.0
Carbon black	0.5	0.5	0.5	0.5
Clay	1.0	—	—	—
Calcium carbonate	—	1.0	—	—
Porous silica	—	—	1.0	1.0
DBTDL	0.065	0.065	0.065	0.065
SA No. 1	0.065	0.065	0.065	0.065
Toluene	1.3	1.3	1.3	1.3
Cyclohexanone	3.0	3.0	3.0	3.0
Tetrachloroethylene	15.0	15.0	15.0	15.0
Trichloroethylene	118.9	118.9	118.9	118.9
Adhesion strength (kg)	0.7	0.5	0.4	0.4

TABLE 2-continued

	Example			
	6	7	8	9
5 Abrasion resistance (times)	20.000	20.000	35.000	50.000

[Note]

Castor oil polyol: 2310-50T produced by Tokushima Setyu Co., Ltd. (hydroxyl value: 80)

Silica (A): Aerosil #200 produced by Nippon Aerosil Co., Ltd.

Silica (B): Aerosil #300 produced by Nippon Aerosil Co., Ltd.

Silica (C): Aerosil R972 produced by Nippon Aerosil Co., Ltd.

10 Clay: Clay F produced by Sobue Co., Ltd.

Calcium carbonate: Whiton B produced by Shiraishi Calcium Co., Ltd.

Porous silica: Cyloyd 308 produced by Fuji Devision Chemical Co., Ltd.

DBTDL: dibutyltin dilaurate

SA No. 1: phenol salt of 1,8-diazabicycloundecene-7

Further, the paint composition of Examples 8 and 9 had a long pot life. That is, the time taken for the viscosity (at 25° C.) of the composition to reach 400 cps (above which it cannot be sprayed) was 5 hours (initial viscosity: 50 cps) as compared to that of Example 2 (2.5 hours (initial viscosity: 50 cps)).

It can be seen from the above results that the glass-run of the present invention has markedly improved non-adhesive property.

While the invention has been described in detail and

with reference to specific embodiments thereof, it will be apparent to one skilled in the art that various changes and modifications can be made therein without departing from the spirit and scope thereof.

What is claimed is:

1. A glass-run for a window glass moving to open and close of a motor car, which comprises a substrate having a film coated on at least a part of the surface of the substrate to be contacted with the window glass, said film being formed by hardening a paint composition comprising:

- 55 (A) 100 parts by weight of an urethane polymer obtained by the reaction of a polyester polyol having *terminal* hydroxy groups [in it's terminal] and a molecular weight of 1,000 to 3,000, synthesized from a saturated diol having 2 to 6 carbon atoms and an organic dicarboxylic acid having 4 to 6 carbon atoms, with an organic diisocyanate in the molar ratio of NCO/OH of from 0.6/1 to 0.95/1;
- 60 (B) 10 to 60 parts by weight of a castor oil polyol;
- (C) 1 to 100 parts by weight of an urethane prepolymer having *terminal* isocyanate groups [in it's terminal] obtained by the reaction of a low molecular polyol and an organic diisocyanate;
- 65 (D) 2 to 100 parts by weight of a fluoro carbon resin;

(E) 5 to 100 parts by weight of a silicone oil; and
(F) 0.5 to [3] 8 parts by weight of at least one member of silica, clay, and calcium carbonate.

2. A glass-run as claimed in claim 1, wherein said component (F) is silica.

3. A glass-run as claimed in claim 1, wherein said component (F) is clay.

4. A glass-run as claimed in claim 1, wherein said component (F) is calcium carbonate.

5. A glass-run for a window glass of a motor car comprising:

a substrate having a film coated on at least a part of the surface of the substrate to be contacted with the window glass, said film being formed by hardening a paint composition comprising:

(A) 100 parts by weight of an urethane polymer obtained by the reaction of a polyester polyol having terminal hydroxy groups and a molecular weight of 1000 to 3000, synthesized from a saturated diol having 2 to 6 carbon atoms and an organic dicarboxylic acid having 4 to 6 carbon atoms, with an organic diisocyanate in the mole ratio of NCO/OH of from 0.6/1 to 0.95/1;

(B) 10 to 60 parts by weight of a castor oil polyol;

(C) 1 to 100 parts by weight of a urethane prepolymer having terminal isocyanate groups obtained by reacting a low molecular weight polyol and an organic diisocyanate;

(D) 2 to 100 parts by weight of a fluoro carbon resin;

(E) 5 to 100 parts by weight of a silicone oil; and

(F) 2 to 8 parts by weight of at least one member of silica, clay, and calcium carbonate.

6. The glass-run for a window glass according to claim 1, wherein in said component (A) said saturated diol is selected from the group consisting of propylene glycol, butanediol, pentanediol and hexanediol and wherein said organic dicarboxylic acid is adipic acid or succinic acid.

7. The glass-run for a window glass according to claim 5, wherein in said component (A) said organic diisocyanate is 4,4'-diphenyl methane diisocyanate or 4,4'-diphenyl ether diisocyanate.

8. The glass-run for a window glass according to claim 5, wherein in said component (C) said low molecular weight polyol is glycerine or trimethylol propane; and

said organic diisocyanate is 4,4'-diphenyl methane diisocyanate or 4,4'-diphenyl ether diisocyanate.

9. The glass-run for a window glass according to claim 5, wherein said component (F) is silica.

10. The glass-run for a window glass according to claim 5, wherein said component (F) is clay.

11. The glass-run according to claim 5, wherein said component (F) is calcium carbonate.

12. The glass-run for window glass of a motor car comprising:

a substrate having a film coated on at least one part of the surface of the substrate to be contacted with the window glass; said film being formed by hardening a paint composition comprising:

(A) 100 parts by weight of a urethane polymer obtained by reacting a polyester polyol having terminal hydroxy groups and a molecular weight of 1000 to 3000 synthesized from a diol selected from a group consisting of propylene glycol, butanediol, pentanediol, hexanediol and an organic dicarboxylic acid selected from the group consisting of adipic acid and succinic acid with an organic diisocyanate selected from the group consisting of 4,4'-diphenylmethane diisocyanate and 4,4'-diphenyl ether diisocyanate in the molar ratio of NCO/OH from 0.6/1 to 0.95/1;

(B) 10 to 60 parts by weight of a castor oil polyol comprising a copolymer of castor oil, phthalic anhydride and glycerol;

(C) 1 to 100 parts by weight of a urethane prepolymer having terminal isocyanate groups obtained by reacting a low molecular weight polyol with an organic diisocyanate;

(D) 2 to 100 parts by weight of a fluoro carbon resin selected from the group consisting of polytetrafluoroethylene, tetrafluoroethylene/hexafluoropropylene copolymer, polytrifluorochloro-ethylene and polyvinylidene fluoride;

(E) 5 to 100 parts by weight of a silicone oil selected from the group consisting of a dimethyl silicone oil, methyl chloro silicone oil, methyl hydrogen silicone oil, methyl phenyl silicone oil, fluoro silicone oil; and

(F) 2 to 8 parts by weight of at least one member of silica, clay, and calcium carbonate.

13. The glass-run according to claim 12, wherein said component (F) comprises silica.

14. The glass-run according to claim 12, wherein said component (F) comprises clay.

15. The glass-run according to claim 12, wherein said component (F) comprises calcium carbonate.

16. The glass-run according to claim 12, wherein said component (F) comprises four parts by weight of said at least one member.

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