(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 December 2002 (19.12.2002)

PCT

(10) International Publication Number
WO 02/100961 A1

(51) International Patent Classification⁷: C09D 133/04, C09J 133/04

(21) International Application Number: PCT/US02/18218

(22) International Filing Date: 7 June 2002 (07.06.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
2001-174301 8 June 2001 (08.06.2001) JP

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(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PRIMER COMPOSITION FOR PAINTED SUBSTRATES

(57) Abstract: A composition which makes it possible to use an adhesive tape to be adhered to substrates painted with any of acidic paints and alkaline paints and is capable of improving the adhesion strength of the adhesive tape to the painted surface and especially improving the durability to the shearing force. A primer composition contains (A) a graft copolymer of an acrylic copolymer grafted with an aminoalkyl group having a primary amino group in the terminal; (B) an acrylic copolymer having carboxyl group in the molecular chain; and (C) a solvent capable of dissolving or dispersing the component (A) and the component (B) therein as essential constituent components.

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PRIMER COMPOSITION FOR PAINTED SUBSTRATES

Field of the Invention

The present invention relates to a primer composition to be used for improving the adhesion strength of an adhesive tape, and more particularly a decorative adhesive tape, to a substrate painted with a melamine resin paint or an anti-acid rain paint. The primer composition is applied to the painted substrate before the adhesive tape is adhered to the painted substrate.

Background

Conventionally, it has been popular that the peripheral portions (for example, door pillars) of side windows are coated to be black as a design of an automobile. In recent years, it has tended to become common to stick a black color adhesive tape on the peripheral portions in place of coating with a paint owing to environmental requirements to decrease the use of organic solvents in coating and owing to the reasons regarding the work processes.

Sticking such an adhesive tape for decoration can be carried out by directly sticking an adhesive tape, having an acrylic adhesive in an adhesion face, to object faces of the peripheral portions of the side windows, already coated with a ground color of the body. It can also be carried out by applying a resin composition, having a prescribed adhesive property to improve the adhesion force, to the adhesive tape to the object faces and then sticking an adhesive tape thereto.

Generally, known as a resin composition usable as an adhesive are compositions containing a copolymer having carboxyl groups in the molecule, a copolymer having amino groups, and the like as constituent components.As one example of such compositions, Japanese Patent Laid-Open No. 59-30872 discloses an aqueous composition for coating, which is an aqueous solution or an aqueous dispersion of an addition copolymerized resin obtained by reaction of a carboxyl-containing copolymer with an unsaturated aliphatic primary amine. Further, Japanese Patent Laid-Open No. 6–322342 discloses a binary solution type adhesive composition containing (A) an aqueous solution of a polymer compound having carboxyl groups and/or sulfonic acid groups in the molecule and (B) an aqueous solution of an amino groupcontaining acrylic copolymer in the molecule and Japanese Patent Laid-Open No. 2655574 discloses an acrylic copolymer containing primary amine groups and carboxylic acid groups, respectively.

Summary of the Invention

High shearing force can be applied partially between the side window peripheral portions to which an adhesive tape is adhered and the rim portions of the side windows through rubber members. When this occurs, the adhesion strength of the adhesive tape in the relevant portions can be low, and the adhesive tape can become wrinkled.

Further, the adhesive tape is to be adhered to the coating to be the ground color of an automobile and there exist as the coating of the automobile are an acidic coating using an anti-acid rain paint and an alkaline coating using a melamine resin paint and a composition capable of improving the adhesion strength of the adhesive tape to the painted substrate painted with any of these paints is desired to be made available.

However, conventional resin compositions disclosed in the above mentioned Japanese Patent Laid-Open No. 59-30872, Japanese Patent Laid-open No. 6-322342, and Patent No. 2655574 are not proposed for a presumed purpose to adhere an adhesive tape to a painted substrate, so that the effect in such a purpose is not made clear.

The present invention has been developed taking such a conventional situation into consideration, and the purpose of the present invention is to provide a composition capable of improving the adhesion strength of an adhesive tape, especially the durability to shearing force in relation to the painted surface and making the adhesive tape usable for the case where the adhesive tape is adhered to any of the acidic paint and the alkaline paint.

The present invention provides a primer composition comprising (A) a graft copolymer of an acrylic copolymer grafted with an aminoalkyl group having a primary amino group in the terminal; (B) an acrylic copolymer having carboxyl group in the molecular chain; and (C) a solvent capable of dissolving or dispersing the component (A) and the component (B) therein as essential constituent components.

Detailed Description

Since the primer composition of the present invention contains the component (A) excellent in adhesion to an acidic paint-coated surface (an anti-acid rain paint) and an acrylic adhesive (acidic) and the component (B) excellent in adhesion to an alkaline paint-coated surface (a melamine resin paint) in a single solution, the composition allows an adhesive tape containing an acrylic adhesive to be adhered to both of the alkaline paint-coated surface and the acidic paint-coated surface and improves the adhesion strength of the adhesive tape to the respective painted surfaces, especially the durability to the shearing force.

Incidentally, the respective compositions disclosed in the above mentioned Japanese Patent Laid-Open No. 59-30872 and Patent No. 2655574 are basically different in terms of the constitution from the primer composition of the present invention in a point that they contain only one type of component as a copolymer and the composition disclosed in the Japanese Patent Laid-Open No. 6-322342 is different in a point that it is a two-solution-type adhesive composition.

In the present invention, acrylic copolymers usable as the component (A) and the acrylic copolymers having carboxyl groups in the molecular chain -and usable as the component (B) are determined based on the amino group content (amine-H equivalent = molecular weight per an amino group) of the graft copolymer grafted with an aminoalkyl group having a primary amino group in the terminal for the former and the carboxyl group content (acid value) of the acrylic copolymer for the latter as to keep both (A) and (B) compatible with each other and even in a solution when both are mixed in the solution.

More particularly, it is preferable to use those having the amine-H equivalent from 350 to 1800 as the component (A) and those having the acid value (mg KOH/g) from 10 to 110 as the component (B). The ratio of the component (A) and the component (B) by weight is preferable as to satisfy the component (A) : the component (B) = 6:4 to 9:1.

If the molecular weights of the component (A) and the component (B) are high, the stability (the coating strength, the heat resistance, the waterproofness, the weathering resistance, and the like) of the primer coating is improved, however the molecular weights are too high, that causes decrease of their solubility and increase of the viscosity of their solution, so that it is preferably to use those having weight average molecular weight of about 100, 000 for the component (A) and those having weight average molecular weight of 4600 to 14,000, for the component (B).

In consideration of the practical temperature range of the primer coating, the glass transition temperature (Tg) of the component (A) and of the component (B) is preferably around room temperature. Practically, it is preferable to use those having Tg of 40 to 100°C for the component (A) and those having Tg of 50 to 750°C for the component (B).

In the present invention, the solvents usable for the component (C) is those capable of dissolving or dispersing the two types of copolymers of the component (A) and the component (B) and normally, organic solvents are used, however in the case where hydrophilic groups are introduced in the component (A) and the component (B) to make them water-soluble resin or these components are emulsified, water may also be used. Incidentally, theprimercomposition of the present invention may further contain a variety of additives such as an ultraviolet ray adsorbent, a heat stabilizer, a thickener and the like based on the necessity.

Examples

Hereinafter, the present invention will be described more particularly according to examples, however the present invention is not at all restricted to these examples.

Preparation of primer composition solution

Example 1

Polyment (a registered trade mark) NK-350 resin solution (amino-H equivalent weight about 1,800; the weight average molecular weight around 100,000; Tg approximately 400°C), manufactured by Nippon Shokubai Co., Ltd., was used as the component (A) and SCX (a registered trade mark) 804 acrylic resin (acid value about 10; the weight average mlecular weight 14,000; and Tg approximately 60°C), manufactured by Johnson Polymer Corporation was used as the component (B). The component (A) and the component (B) were mixed at the weight ratio (A) : (B) = 6 : 4 on the bases of the resin solid matter by weight and diluted to 5% of solid by adding methyl ethyl ketone to obtain a primer composition solution in uniform solution state.

Example 2

A primer composition solution was produced in the same manner as the foregoing Example 1 except that Joncryl (a registered trade mark) 611 acrylic resin (acid value about 53; the weight average molecular weight 8,100; and Tg approximately 50°C), manufactured by Johnson Polymer Corporation was used as the component (B).

Example 3

A primer composition solution was produced in the same manner as the foregoing Example 1 except that the component (A) and the component (B) were mixed at the resin solid matter ratio by weight of (A) : (B) = 7 : 3.

Example 4

A primer composition solution was produced in the same manner as the foregoing Example 1 except that the component (A) and the component (B) were mixed at the resin solid matter ratio by weight of (A) : (B) = 8 : 2.

Example 5

A primer composition solution was produced in the same manner as the foregoing Example 1 except that the component (A) and the component (B) were mixed at the resin solid matter ratio by weight of (A) : (B) = 9 : 1.

Example 6

A primer composition solution was produced in the same manner as the foregoing Example 1 except that Polyment (a registered trade mark) NK-380 resin solution (amino-H equivalent weight about 700; the weight average molecular weight around 100,000; Tg approximately 100°C) , manufactured by Nippon Shokubai Co., Ltd., was used as the component (A) and Joncryl (a registered trade mark) 611 acrylic resin, manufactured by Johnson Polymer Corporation was used as the component (B).

Comparative Example 1

Polyment (a registered trade mark) NK-350 resin solution, manufactured by Nippon Shokubai Co., Ltd., was used as the component (A) and Joncryl (a, registered trade mark) 683 acrylic resin (acid value about 160; the weight average molecular weight 8,000; and Tq approximately 75°C), manufactured by Johnson Polymer Corporation. was used as the component (B). The component (A) and the component (B) were mixed at the weight ratio (A) : (B) = 6 : 4 on the bases of the resin solid matter by weight and diluted to 5% of solid by adding methyl ethyl ketone to obtain a mixed solution in which white precipitation was formed and which was found being in uneven solution state.

Comparative Example 2

A primer composition solution containing 5% of solid matter and being in even solution state was produced using Polyment (a registered trade mark) NK-350 resin solution, manufactured by Nippon Shokubai Co., Ltd., was used as the component (A) but using no component for the component (B) and then diluting the resin solution to 5% of solid by methyl ethyl ketone.

Preparation of Test Panel

The respective primer composition solutions (except the solution of the comparative example 1 by which no uniform solution state could not be obtained) produced by the above described examples and comparative examples were applied to melamine resin-painted steel plates and anti-acid rain paint-painted steel plates and dried at a room temperature to prepare test panels.

Measurement of Durability to Shearing Force

As an adhesive tape, Scotchcal (a registered trade mark) FTA 9031J black out film, manufactured by Sumitomo 3M Ltd., was adhered to the respective test panels. The adhering method was according to JIS Z 0237 8.2.3. Controls were prepared by directly sticking only the adhesive tape to the melamine resin-painted steel plate and the anti-acid rain paintpainted steel plate without applying any primer composition solutions.

Measurement of the durability to shearing force was carried out according to JIS Z 0237 11.3, except that the adhesion surface area was 10 x 10 mm. After the adhesive tape was adhered, the respective test panels were subjected to aging under the respective aging conditions shown in Table 1 and according to the loading conditions shown in the same table for the respective tests of the durability of shearing face, the duration to the time when the adhesive tape was dropped off the test panels was measured. The results were shown in Tables 2 to 9.

Table 1

Test	Aging Condition	Load Condition for Test for Durability Toe Shearing Force
1	At 80°C for 24 hours	applying load of 2.1 Kg at 80°C
2	At 20°C for 3 hours	applying load of 1 Kg at 80°C
3	At 20°C for 3 hours and then immersion in water at 40°C for 48 hours	applying load of 1 Kg at 80°C and 95% relative humidity

Table 2

(Without application of primer composition)

Test	Melamine Resin-Painted Steel Plate	Anti-Acid Rain Paint-Painted Steel Plate
1	200 minutes	25 minutes
2	1 minute	1 minute
3	1 minute	1 minute

Table 3

(Example 1).

Test	Melamine Resin-Painted Steel Plate	Anti-Acid Rain Paint-Painted Steel Plate
1	2510 minutes	1840 minutes
2	2380 minutes	2370 minutes
3	73 minutes	No test

Table 4

(Example 2)

Test	Melamine Resin-Painted Steel Plate	Anti-Acid Rain Paint-Painted Steel Plate
1	2510 minutes	2520 minutes
2	2400 minutes	2380 minutes
3	10 minutes	5 minutes

Table 5

(Example 3)

Test	Melamine Resin-Painted Steel Plate	Anti-Acid Rain Paint-Painted Steel Plate
1	7400 minutes	3950 minutes
2	1460 minutes	1460 minutes
3·	150 minutes	10 minutes

Table 6

(Example 4)

Test	Melamine Resin Painted Steel Plate	Anti-Acid Rain Paint-Painted Steel Plate
1	4310 minutes	3370 minutes
2	1460 minutes	1460 minutes
3	1500 minutes	1500 minutes

Table 7

(Example 5)

Test	Melamine Resin-Painted Steel Plate	Anti-Acid Rain Paint-Painted Steel Plate
1	3000 minutes	4110 minutes
2	1440 minutes	1640 minutes
3	200 minutes	No test

Table 8

(Example 6)

Test	Melamine Resin-Painted Steel Plate	Anti-Acid Rain Paint-Painted Steel Plate
1	4200 minutes	4170 minutes
2	1480 minutes	1490 minutes
3	17 minutes	7 minutes

Table 9

(Comparative example 2)

Test	Melamine Resin-Painted Steel Plate	Anti-Acid Rain Paint-Painted Steel Plate
1	2200 minutes	No test
2	28 minutes (however the primer was stripped from the paint)	No test
3	2 minutes (however the primer was stripped from the paint)	No test

As shown in Tables 2 to 9, the test pieces coated with the primer compositions of the Examples 1 to 6 according to the present invention showed higher durability to shearing force than the test pieces coated with the primer composition of the comparative Example 2 containing no component for the component (B) and also found that the test pieces were provided with the effect of improving adhesion strength to both the melamine resin-painted steel plate and the anti-acid rain paint-painted steel plate. Regarding the test piece coated with the primer composition of the comparative Example 2, it took place a phenomenon that the primer composition was stripped from the melamine resin-painted steel plate (in other words, the primer composition was stripped while being left in the adhesive tape side) in tests 2 and 3. Such parting manner would be a serious problem in use of the adhesive tape to be adhered to an automobile.

As described above, the primer composition of the present invention contains a copolymer excellent in adhesion to the acidic paint-coated surface and a copolymer excellent in adhesion to the alkaline paint-coated surface in a single solution, so that the primer composition can be used preferably for sticking an adhesive tape to substrates painted any of the acidic paint and the alkaline paint and can improve the adhesion strength of the adhesive tape to the painted surface and especially remarkably improve the durability to the shearing force.

It Is Claimed:

1. A primer composition comprising:

(A) a graft copolymer of an acrylic copolymer grafted with an aminoalkyl group having a primary amino group in the terminal;

(B) an acrylic copolymer having carboxyl group in the molecular chain; and

(C) a solvent capable of dissolving or dispersing said component (A) and component (B) therein as essential constituent components.

2. The primer composition as claimed in claim 1, wherein said component (A) contains amino group in an amount of amino-H equivalent from 350 to 1800.

3. The primer composition as claimed in claim 1 or 2, wherein said component (B) has an acid value (mg KOH/g) of 10 to 110.

4. The primer composition as claimed in claim 1, wherein the ratio of said component (A) and component (B) by weight is (A) : (B) = 6 : 4 to 9 : 1.

INTERNATIONAL SEARCH REPORT

In tional Application No
PCT/US 02/18218

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D133/04 C09J133/04

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)
IPC 7 C09D C09J

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	EP 0 336 428 A (NIPPON PAINT CO LTD) 11 October 1989 (1989-10-11) the whole document ---	1
A	US 4 826 921 A (ANDREWS ADRIAN F ET AL) 2 May 1989 (1989-05-02) the whole document -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search 8 October 2002	Date of mailing of the international search report 18/10/2002
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Meulemans, R

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
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