

Australia

Patents Act 1990

NOTICE OF ENTITLEMENT

677585

I, John Gordon Hinde, of Spruson & Ferguson, St Martins Tower, 31 Market Street, Sydney, New South Wales 2000, Australia, being the patent attorney for the Applicant(s)/Nominated Person(s) in respect of Application No. 41159/93 state the following:-

The Applicant(s)/Nominated Person(s) has/have entitlement from the actual inventor(s) as follows:-

The Applicant(s)/Nominated Person(s) is/are the assignee(s) of the actual inventor(s).

The Applicant(s)/Nominated Person(s) is/are the applicant(s) of the application(s) listed in the Declaration under Article 8 of the PCT. The basic application(s) listed on the Declaration under Article 8 of the PCT is/are the first application(s) made in a Convention country in respect of the invention.

DATED this 14th day of February 1997

.....
John Gordon Hinde

IRN: 283551

INSTR CODE: 58400



AU9341159

(12) PATENT ABRIDGMENT (11) Document No. AU-B-41159/93
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 677585

- (54) Title
PLASTICIZER RESISTANT PRESSURE SENSITIVE ADHESIVE FOR VINYL MARKING FILM
- International Patent Classification(s)
(51)⁵ C09J 133/08 C09J 007/02 C09J 133/10
- (21) Application No. : 41159/93 (22) Application Date : 27.04.93
- (87) PCT Publication Number : WO93/22391
- (30) Priority Data
- (31) Number (32) Date (33) Country
4-109375 28.04.92 JP JAPAN
- (43) Publication Date : 29.11.93
- (44) Publication Date of Accepted Application : 01.05.97
- (71) Applicant(s)
MINNESOTA MINING AND MANUFACTURING COMPANY
- (72) Inventor(s)
HIROSHI MATSUDA
- (74) Attorney or Agent
SPRUSON & FERGUSON , GPO Box 3898, SYDNEY NSW 2001
- (56) Prior Art Documents
EP 338724
- (57) Claim

1. An adhesive for decorative film comprising:
100 parts by weight of a copolymer having a weight average molecular weight of 700,000-1,200,000 obtained by copolymerization of 64%-75% by weight of a (meth)acrylate having a C₄-C₈-alkyl group, 20-26% by weight of methyl methacrylate and 5-10% by weight of acrylic acid, and 0.005 to 0.1 parts by weight of a crosslinker.

OPI DATE 29/11/93 APPLN. ID 41159/93
AOJP DATE 10/02/94 PCT NUMBER PCT/US93/03882



AU9341159

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C09J 133/08, 7/02 C08F 220/18	A1	(11) International Publication Number: WO 93/22391 (43) International Publication Date: 11 November 1993 (11.11.93)
(21) International Application Number: PCT/US93/03882 (22) International Filing Date: 27 April 1993 (27.04.93) (30) Priority data: 04/109375 28 April 1992 (28.04.92) JP (71) Applicant (for all designated States except US): MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): MATSUDA, Hiroshi [JP/JP]; 539, Yanome, Tendo-city, Yamagato Prefecture 994 (JP). (74) Agents: PETERS, Carolyn, V. et al.; Office of Intellectual Property Counsel, Minnesota Mining and Manufacturing Company, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AT, AU, BB, BG, BR, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, 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 the receipt of amendments. 677585
(54) Title: PLASTICIZER RESISTANT PRESSURE SENSITIVE ADHESIVE FOR VINYL MARKING FILM (57) Abstract A decorative film that is free of deterioration of the surface film due to the generation of wrinkles even when being applied to an adherent having plasticizer migration ability, such as polyvinyl chloride, and an adhesive thereof comprising: 100 parts by weight of a copolymer having a weight average molecular weight of 700,000-1,200,000 obtained by copolymerization of 64-75 % by weight of a (meth)acrylate having a C₄-C₈-alkyl group, 20-26 % by weight of methyl methacrylate and 5-10 % by weight of acrylic acid, and 0.005 to 0.1 parts by weight of a crosslinker.		

PLASTICIZER RESISTANT PRESSURE SENSITIVE ADHESIVE FOR VINYL MARKING FILM.

Technical Field

The present invention relates to a plasticizer resistant, decorative film
5 and an adhesive therefor.

Background of the Invention

A decorative film is comprised of a surface film, such as vinyl
chloride, on which an adhesive layer is applied or laminated and, in some
10 cases, said adhesive layer is protected by a release film. In the case of
possessing a release film, this decorative film is used by applying it on the
surface of an adherent (article to be decorated) after removing the release
film.

In this case, since the adherend is comprised of a resin having a strong
15 plasticizer migration ability, such as a vinyl chloride resin, when the surface
film is a film having a low plasticizer resistance, such as a vinyl chloride
sheet, the plasticizer is migrated from the adherent to the surface film,
generating wrinkles on the surface sheet and, thereby resulting in the
impairment of its decorative characteristics and weathering characteristics.
20 For this reason, a means is required to prevent the deterioration of the surface
film due to the migration of the plasticizer from the adherent.

Japanese Unexamined Patent Publication (Kokai) No. 59-5944 discloses
a decorative film which prevents the migration of a plasticizer from an
adherent to the film by placing a barrier layer comprising a urethane resin
25 between a vinyl chloride surface film and an adhesive layer. In such an
aspect, however, the production cost become unduly expensive because of the
addition of the barrier layer. Japanese Unexamined Patent Publication (Kokai)
No. 3-45671 discloses a decorative film which utilizes a surface film having
improved plasticizer resistance due to the content of a urethane resin, and an
30 adhesive containing a plasticizer resistant monomer, such as vinyl acetate.

However, the cost of this decorative film tends to be expensive due to the use of the surface film containing a urethane resin.

Summary of the Invention

5 The present invention provides an adhesive film having high plasticizer resistance and capable of preventing the deterioration of a film without placing any barrier layer against a plasticizer, and to provide a decorative film using said adhesive comprising 100 parts by weight of a copolymer having a weight average molecular weight of 700,000-1,200,000 obtained by copolymerization
10 of 64-75% by weight of a (meth)acrylate having a C₄-C₈-alkyl group, 20-26% by weight of methyl methacrylate and 5-10% by weight of acrylic acid, and 0.005 to 0.1 parts by weight of a crosslinker.

Description of the Preferred Embodiment

15 The "(meth)acrylate having a C₄-C₈-alkyl group" which is used in the present invention means an alkyl acrylate or alkyl methacrylate having 4-8 carbon atoms in the alkyl group, the alkyl moiety of which is butyl, pentyl, hexyl, heptyl, or octyl, it being possible for these alkyl groups to be a linear or branched chain. Typical examples of such alkyl acrylates and alkyl
20 methacrylates include 2-ethylhexyl acrylate, n-butyl acrylate, and butyl methacrylate.

 The reasons why the amount of the (meth)acrylate having a C₄-C₈-alkyl group should be defined to be 64 to 75% by weight based on 100% by weight the total monomer amount are as follows: if the amount is more than the
25 upper limit, the performance of plasticizer resistance deteriorates, and if it is less than the lower limit, the glass transition point increases and, thus, the adhesion at a low temperature decreases. More preferably, the amount of (meth)acrylate having a C₄-C₈-alkyl group is 70 to 72 parts by weight.

 The amount of methyl methacrylate is to be defined in the range of 20-
30 26% by weight based on 100% by weight the total monomer amounts, because the adhesion decreases if it is less than 20% by weight, and

conversely the adhesion characteristics at a low temperature decrease if it is more than 26% by weight. The amount of acrylic acid is to be defined in the range of 5-10% by weight based on 100% by weight the total monomer amount, because the adhesion drastically decreases if it is less than 5% by weight, and conversely, the adhesion characteristics at a low temperature decrease if it is more than 10% by weight.

In the copolymerization of the above-described monomer components, a catalyst is preferably used in order to accelerate the polymerization. As such a catalyst, peroxybenzoyl, azobisisobutyronitrile, or the like is used, typical examples of which include Benper W75 (produced by Daiichi Kasei Kogyo Co., Ltd.), Lucido L-70 (produced by Pennwal), and the like. The amount of the catalyst used varies depending on the type of the catalyst, but usually is 0.01 to 5 parts by weight, preferably 0.01 to 0.5 part by weight, based on 100 parts by weight of the total monomer amount.

For the purpose of improving the coherent strength, the molecular weight of the polymer is preferably in the range of 700,000 to 1,200,000 because if it is less than 700,000, it is difficult to effectively prevent the generation of wrinkles on the surface film due to the migration of the plasticizer, and if it exceeds 1,200,000, the viscosity increases so much that a solution polymerization can be carried out only with difficulty, which leads to a disadvantage from the viewpoint of production. The weight average molecular weight herein is measured by the gel permeation chromatographic method.

The adhesive of the present invention further contains a bisamide crosslinker or a isocyanate crosslinker in order to improve the coherent strength. Examples of bisamide type crosslinkers include 1,4-bis(ethyleneiminocarbonylamino)benzene, 4,4'-bis(ethyleneiminocarbonylamino)diphenylmethane, 1,8-bis(ethyleneiminocarbonylamino)octane, and the like, and typically RD1054 (produced from 3M Company, U.S.A.) can be used. As the isocyanate type crosslinker, 1,4-tolylene diisocyanate and hexamethylene diisocyanate can be

mentioned, and typically Coronate L (produced by Nippon Polyurethane) and Coronate L-55E (produced by Nippon Polyurethane) may be used.

As the crosslinker of the present invention, the bisamide type is preferable because it has a higher reactivity with the copolymer and, thus, its effect can be exhibited by using a smaller amount, and because it is minimally influenced by moisture in air, etc., in the air, and only a small variability of crosslinking efficiency can be attained.

The amount of the crosslinker to be added is defined to be in the range of 0.005 to 0.1 part by weight based on 100 part by weight the copolymer. If the amount is less than 0.05 part by weight, the coherent strength does not sufficiently increase, and the migration of the plasticizer and the generation of wrinkles on the surface film resulting therefrom cannot sufficiently be prevented. Conversely, if it is more than 0.1 part by weight, the adhesion retention after the migration of the plasticizer significantly decreases.

In the production of the adhesive of the present invention, the above-mentioned monomers are dissolved in an appropriate solvent, e.g., acetic acid, acetone, hexane, benzene, or a mixture thereof, and the polymerization is initiated by the addition of the above-described catalyst. The polymerization temperature is 40-100°C, and preferably 50-80°C, and the polymerization time is 6-24 hours, and preferably 12-20 hours.

After the polymerization has ended, the crosslinker is added to the formed polymer, after which it is applied on the surface film to produce a decorative film of the present invention. As the surface film, any desired decorative film, such as a polyvinyl chloride film, a polyurethane film, or a polyester film, may be used. Particularly, when a film having a relatively low plasticizer resistance, such as a polyvinyl chloride film, is used, the effect of the present invention is attained.

For coating the adhesive of the present invention on a film, a usual means for applying an adhesive can be used. For example, a knife coater, roll coater, curtain flow coater, or the like can be used. The film thickness is 20-200 μm , and preferably 30-100 μm , and the thickness of the adhesive layer is 10-50 μm , and preferably 30-40 μm . On the surface of the adhesive layer

5

of the decorative film according to the invention, a release sheet for protecting the adhesive layer, such as a silicone type release paper or a fluorine release paper, may be applied.

Objects and advantages of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All materials are commercially available or known to those skilled in the art unless otherwise stated or apparent.

10

Examples

Production of Film

The production was carried out as follows: prescribed monomeric components and a peroxybenzoyl polymerization catalyst (both varying in their amounts) were dissolved in such an amount of ethyl acetate as to be substantially equal to the total amount of the monomers and catalyst, and the polymerization was carried out at the boiling point of the reaction mixture for 18 hours. After the polymerization, more ethyl acetate was added to the formed polymer to adjust the viscosity of the polymer to an appropriate coating viscosity (2500-3500 cps/25°C). To this was added a bisamide crosslinker (RD 1054, 3M Company, U.S.A.), etc., and the mixture was thoroughly agitated. The polymer was applied on a separator by a knife coater to a thickness of 35 μm after drying, dried in an oven at 90°C for 2 minutes, after which the formed layer was transferred to a 50 μm thick soft polyvinyl chloride film having been primer-coated, to produce an adhesive film.

Evaluation

(1) Initial Adhesion

The film produced as described above was cut into 1 inch wide pieces, and each piece was adhered on a polyvinyl chloride adherent

6.

containing 55 PHR of dioctylphthalate (55 parts by weight based on 100 parts by weight of the resin) at 20°C at a 65% relative humidity to produce a test piece. This adherent was fixed on an aluminum plate by means of a double sided adhesive tape. The test piece was left standing at 20°C at a 65% relative humidity for 48 hours, and then peel strength was measured at a peeling angle of 180° at a peeling rate of 300.0 mm/min. The scoring criteria was as follows:

- o . . . 3.0 kg/inch or more of the initial adhesion
- Δ . . . 1.0 kg/inch or more of the initial adhesion
- x . . . less than 1.0 kg/inch of the initial adhesion

(2) Heat Aged Adhesion

The test piece produced as described in the paragraph of the initial adhesion was aged at 65°C for 1 week, and the peel strength was measured at 20°C at a 65% RH at a peeling angle of 180° at a peeling rate of 300.0 kg/min by using a tensile tester. The rating criteria was the same as those of the initial adhesion.

(3) Appearance Changes (Test for Generation of Wrinkles)

Each sample was applied on a separator to a thickness of 35 μm after drying, dried in an oven at 90°C for 5 minutes, and then laminated on a 50 μm thick soft vinyl chloride film to produce an adhesive film. The adhesive film was cut into 12 x 13 cm pieces, and adhered on a vinyl adherend containing 55 PHR of DOP measuring 15 x 15 cm in size by means of rollers. This was left standing at 65°C for 72 hours, and the generation of wrinkles after the temperature had been cooled to room temperature was visibly observed. The rating criteria was as follows:

- o . . . not changed
- Δ . . . slight generation of wrinkles
- x . . . significant generation of wrinkles.

Table 1 shows the compositions used in Examples (1-8) and

Comparative Examples (C1-C7). Table II summarizes the evaluation of the examples.

Table I Glossary

- AA . . . acrylic acid
- 5 MMA . . methyl methacrylate
- 2EHA . . 2-ethylhexyl acrylate
- RD1054 a bisamide crosslinker
- L-55E . . an isocyanate crosslinker

- Various modifications and alterations of this invention will become
- 10 apparent to those skilled in the art without departing from the scope and principles of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth hereinabove. All publications and patents are herein incorporated by reference to the same extent as if each individual publication or patent was specifically and
- 15 individually indicated to be incorporated by reference.

		Composition					
Examples		AA	MMA	BA	2EHA	RD10054	L55E
5	1	7	22	47	24	0.005	---
	2	7	22	47	24	0.01	---
	3	7	22	47	24	0.05	---
	4	8	20	50	22	0.07	---
	5	10	26	40	24	0.07	---
10	6	5	20	50	25	---	0.01
	7	10	20	35	35	---	0.05
	8	6	25	48	21	---	0.1
	C1	3	40	30	27	0.003	---
	C2	15	30	40	15	0.25	---
15	C3	15	15	60	10	0.01	---
	C4	30	10	40	40	0.08	---
	C5	10	25	45	20	---	0.001
	C6	0	18	65	17	---	0.2
	C7	6	25	46	21	---	---

Evaluation

	Examples	Mw (10 ³)	Initial Adhesion	Adhesion After Aging	Appearance Changes
5	1	797	o	o	o
	2	797	o	o	o
	3	797	o	o	o
	4	1150	o	o	o
	5	851	o	o	o
10	6	1030	o	o	o
	7	995	o	o	o
	8	813	o	o	o
15	C1	502	x	x	x
	C2	822	x	x	o
	C3	980	o	Δ	x
	C4	886	o	Δ	x
	C5	1010	o	x	x
	C6	532	x	x	x
	C7	813	o	x	x
20					

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. An adhesive for decorative film comprising:
100 parts by weight of a copolymer having a weight average molecular weight of 700,000-1,200,000 obtained by copolymerization of 64%-75% by weight of a (meth)acrylate having a C_4-C_8 -alkyl group, 20-26% by weight of methyl methacrylate and 5-10% by weight of acrylic acid, and 0.005 to 0.1 parts by weight of a crosslinker.
2. The adhesive for decorative film as set forth in claim 1, wherein said crosslinker is a bisamide type crosslinker.
3. A decorative film characterized by having the adhesive of claim 1 or 2 applied or laminated on a surface film.
4. A decorative film as set forth in claim 3, wherein said surface film is a polyvinyl chloride.
5. An adhesive, substantially as described herein with reference to any one of the Examples other than comparative examples.
6. A decorative film characterized in that the adhesive of claim 5 is applied or laminated on a surface film.

DATED this FOURTEENTH day of OCTOBER 1994
Minnesota Mining and Manufacturing Company

Patent Attorneys for the Applicant
SPRUSON & FERGUSON



INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/03882

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C09J133/08; C09J7/02; C08F220/18		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C09J ; C08F ; C08G	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	EP,A,0 338 724 (MINNESOTA MINING) 25 October 1989 see claims 1-5 ---	1,3,4
A	US,A,4 983 656 (JAP. SYNTH. RUBBER CO.) 8 January 1991 see claims 1-7,10,12; examples 1,comp.7,8 ---	1,3
A	DE,A,2 407 494 (BEIERSDORF AG) 21 August 1975 see page 2, paragraph 2 see page 5, paragraph 2 see examples 1,4,5 see claims 1,3 -----	1,3,4
¹⁰ Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "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. "&" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
26 AUGUST 1993	1 0. 09. 93	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	ENGEL S.L.	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9303882
SA 74066

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

26/08/93

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0338724	25-10-89	JP-A- 1271472 DE-U- 6890479	30-10-89 25-03-93
US-A-4983656	08-01-91	JP-A- 1234485	19-09-89
DE-A-2407494	21-08-75	None	