

AMENDED



COMMONWEALTH OF AUSTRALIA

Patents Act 1953

630868

CONVENTION APPLICATION FOR A STANDARD PATENT

We, AVERY DENNISON CORPORATION, a corporation organized and existing under the laws of the State of Delaware, of 150 North Orange Grove Boulevard, Pasadena, California 91103, United States of America, hereby apply for the grant of a Standard Patent for an invention entitled

"Thermoplastic, Plasticizer-Resistant Film, and Pressure Sensitive Film Comprising the Plasticizer-Resistant Film"

which is described in the accompanying complete specification.

Details of basic application:-

Number of basic application:- 880428

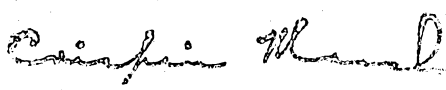
Name of Convention country in which basic application was filed:- Netherlands

Date of basic application:- 19 February 1988

Our address for service is: F.B. RICE & CO.,
28A Montague St,
Balmain N.S.W. 2041

Dated this 28 day of March 1991

AVERY DENNISON CORPORATION

By: 

Registered Patent Attorney

TO: The Commissioner of Patents,
COMMONWEALTH OF AUSTRALIA

Australia Patents Act 1990
Notice of Entitlement

(to be filed before acceptance)

We, Robert G. van Schoonenberg
being authorised by AVERY DENNISON CORPORATION
of 150 NORTH ORANGE GROVE BOULEVARD, PASADENA,
CALIFORNIA 91103, UNITED STATES OF AMERICA
the applicant in respect of an application for a patent for an invention entitled THERMOPLASTIC, PLASTICIZER-
RESISTANT FILM, AND PRESSURE SENSITIVE FILM COMPRISING THE
PLASTICIZER-RESISTANT FILM.
filed under Australian Application No. 30047/89, state the following:-

Part 1 - Must be completed for all applications.

☐ The person(s) nominated for the grant of the patent:
is/are the actual inventor(s)
or
☒ has, for the following reasons, gained entitlement from the actual inventor(s):
Avery Dennison Corporation (formerly Avery International Corporation)
is the assignee of the actual inventors O.V. Nieuwenhuize,
F. de Grunt, S. de Visser and R. Vos in respect of the invention.

Part 2 - Must be completed if the application is a Convention application.

☐ The person(s) nominated for the grant of the patent is/are:
the applicant(s) of the basic application(s) listed on the patent request form
or
☒ entitled to rely on the basic application(s) listed on the patent request form by reason of the following:
The applicant of the basic application, Avery International
Corporation, is now known as Avery Dennison Corporation by
reason of a change of name.

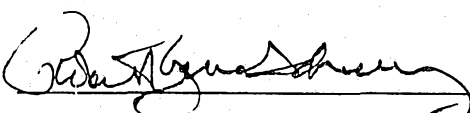
The basic application(s) listed on the request form is/are the first application(s) made in a Convention country in respect of the invention.

~~**Part 3 - must be completed if the application was made under the PCT and claims priority:-**~~

~~☐ The person(s) nominated for the grant of the patent is/are:
the applicant(s) of the application(s) listed in the declaration under Article 8 of the PCT
or
☐ entitled to rely on the application(s) listed in the declaration under Article 8 of the PCT by reason of the following:-

_____~~

~~The basic application(s) listed in the declaration made under Article 8 of the PCT is/are the first application(s) made in a Convention country in respect of the invention.~~

Signed: 

Date: 9-4-92

Status: Vice President, General Counsel & Secretary

F.B. RICE & CO. PATENT ATTORNEYS

(12) PATENT ABRIDGMENT (11) Document No. AU-B-30047/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 630868

(54) Title
THERMOPLASTIC, PLASTICIZER-RESISTANT FILM, AND PRESSURE SENSITIVE FILM COMPRISING
THE PLASTICIZER-RESISTANT FILM

International Patent Classification(s)
(51)⁴ C08L 027/06 C08J 005/18 C08L 023/28 C09J 007/02

(21) Application No. : 30047/89 (22) Application Date : 17.02.89

(30) Priority Data

(31) Number (32) Date (33) Country
880428 19.02.88 NL THE NETHERLANDS

(43) Publication Date : 24.08.89

(44) Publication Date of Accepted Application : 12.11.92

(71) Applicant(s)
AVERY DENNISON CORPORATION

(72) inventor(s)
O.V NIEUWENHUIZE; S. DE VISSER; F. DE GRUNT; R. VOS

(70) Nominated Person(s)
RPC CONTAINERS LIMITED

(74) Attorney or Agent
F B RICE & CO , 28A Montague Street, BALMAIN NSW 2041

(56) Prior Art Documents
US 4680234
GB 1406841

(57) Claim

1. A plasticizer-resistant film comprised of a layer formed of a blend of polyvinyl chloride and chlorinated polyethylene in respective weight ratios of 10:90 to 65:35 in which the polyvinyl chloride has a K-value of 45 to 80 and the chloride content of the chlorinated polyethylene is from 30 to 45% by weight, said film being receptive to retaining diffused plasticizer from a plasticized substrate without becoming sticky and in contact with said layer, a plasticizer-resistant, pressure-sensitive adhesive which retains adhesion in the presence of a plasticizer, said adhesive comprising a polymer containing an alkyl acrylate or alkyl methacrylate or mixtures thereof.

2. A pressure-sensitive adhesive film as claimed in claim 1 in which the weight ratio of polyvinyl chloride to chlorinated polyethylene is from 35:65 to 65:35.

COMMONWEALTH OF AUSTRALIA

Patent Act 1952

630868

C O M P L E T E S P E C I F I C A T I O N

(ORIGINAL)

Class Int. Class

Application Number :
Lodged :
Complete Specification Lodged :
Accepted :
Published :
Priority : 19 February 1988
Related Art :



Name of Applicant : ^{Dennison} AVERY ~~INTERNATIONAL~~ CORPORATION

Address of Applicant : 150 North Orange Grove Boulevard
Pasadena, California 91103
United States of America

Actual Inventor/s : O.v Nieuwenhuize,
S. de Visser, F. de Grunt
R. Vos

Address for Service : F.B. RICE & CO.,
Patent Attorneys,
28A Montague Street,
BALMAIN 2041.

Complete Specification for the invention entitled:
Thermoplastic, plasticizer-resistant film, and pressure sensitive film
comprising the plasticizer-resistant film

The following statement is a full description of this invention
including the best method of performing it known to us/me:-

Field of the Invention

The invention relates to a thermoplastic plasticizer-resistant film. The film will not change its dimensions or turn sticky when plasticizer molecules penetrate the film. In particular, the invention relates to a pressure-sensitive film adapted for adherence to a vinyl substrate plasticized with monomeric plasticizer without change of dimension.

Background of the Invention

Vinyl substrates plasticized with monomeric plasticizers have found extensive use for interior surfaces such as wall coverings and exterior surfaces such as vinyl coated canvas for trucks. these vinyl substrates contain as much as 25-75 parts of monomeric plasticizer, of the vinyl resin. Letters, figures or drawings are applied to said vinyl substrates by hand painting or by printing with screen printing inks. For this object also a pressure-sensitive vinyl film optionally printed with letters, etc., can be used.

In the latter case, vinyl film wrinkles and turns sticky, and that the adhesive layer loses adhesion.

These problems are substantially attributable to the migration of plasticizers from the substrate into the film.

European Patent Specification 103.407, incorporated herein by reference, discloses a pressure-sensitive film adapted for adherence to vinyl substrate plasticized with monomeric plasticizer. This film comprises a first layer of polyvinyl chloride, a second layer of a plasticizer-resistant, pressure-sensitive adhesive and a third layer between said first and second layers serving as a barrier for migration of the plasticizer from the vinyl substrate. This film meets the following demands. It is capable of maintaining adhesion and a wrinkle-free surface when adhered to a plasticizer substrate, and is receptive to conventional screen printing inks.

Summary of the Invention

This invention relates to a thermoplastic plasticizer-resistant film comprising a blend of polyvinyl chloride and chlorinated polyethylene with plasticizer-resistant, pressure-sensitive adhesive.

In particular, this invention relates to a pressure-sensitive adhesive film combination consisting of only two layers, which film meets the three-layer product performance of the '407 patent publication.

The plasticizer-resistant film comprises a layer formed of a blend of polyvinyl chloride and chlorinated polyethylene in respective weight ratios of 10:90 to 65:35 in which the polyvinyl chloride has a K-value of 45 to 80 and the chloride content of the chlorinated polyethylene is from 30 to 45% by weight, said film being receptive to retaining diffused plasticizer from a plasticized substrate without becoming sticky and in contact with said layer, a plasticizer-resistant, pressure-sensitive adhesive which retains adhesion in the presence of a plasticizer, said adhesive comprising a polymer containing an alkyl acrylate or alkyl methacrylate or mixtures thereof.



The pressure-sensitive film, according to the invention, meets the three previously mentioned product demands. First, the blend of polyvinyl chloride and chlorinated polyethylene is receptive to conventional
5 screen printing inks.

Owing to the lack of a barrier layer, monomeric plasticizer will diffuse from the vinyl substrate into the film. However, the plasticizer concentration will reach an equilibrium, and this concentration of plasticizer does
10 not lead to a sticky or wrinkling film or adversely impact the pressure-sensitive adhesive layer. The pressure-sensitive adhesive used with film is typically acrylic based and resists loss of adhesion due to entry of the plasticizer.



1 Detailed Description

Hereinbelow is a more detailed description of both the thermoplastic plasticizer-resistant film and the layer of the pressure-sensitive film according to the invention.

5 A suitable weight ratio of polyvinyl chloride:chlorinated polyethylene is 10:90 to 90:10, preferably ^{10:90 to 65:35, more preferably} 35:65 to 65:35. The ratio of polyvinyl chloride:chlorinated polyethylene which gives the best film properties, depends on other parameters, such as the K value of the polyvinyl chloride, the melting viscosity of the chlorinated polyethylene and the processing conditions of the polymer blend. Thus, using polyvinyl chloride having a high K-value(a) relatively more chlorinated polyethylene is necessary to get good film properties.

10 The already mentioned K-value or inherent viscosity of the polyvinyl chloride is a measure of the average molecular weight. This K-value can amount to 45-80, preferably to 50-65. By applying polyvinyl chloride having K-values higher than 80 it costs much power to prepare a blend having the required distribution of polyvinyl chloride and chlorinated polyethylene. In addition in that case a somewhat more rigid film is produced.

25 The polyvinyl chloride can be prepared in any conventional manner, that is, by suspension-, mass- or emulsion polymerization. Usually polyvinyl chloride produced by suspension polymerization is used.

30 The chlorinated polyethylene that is applied, can be produced according to known methods by chlorination of polyethylene. Suitable chlorinated polyethylenes

35 (a) A measure of molecular weight based on viscosity "Encyclopedia of Polymer Science and Technology," Vol. 14, John Wiley & Sons (1971).



1 have a chloride content of 30-45% by weight and
preferably about 42% by weight, and a melt viscosity of
600-3,000 Pa.s.

5 The blend of chlorinated polyethylene and polyvinyl
chloride usually comprises furthermore UV- and/or heat-
stabilizers, antioxidant, pigment or other usual
additives. Plasticizers are, in general, not present or
substantially not present because of the self-
plasticizing effect of the chlorinated polyethylene.

10 Ethylene/vinyl acetate copolymers in an amount of
up to 10% by weight may be added to the polymer blend
without affecting the properties of the film. The blend
of chlorinated polyethylene and polyvinyl chloride may
be prepared with any conventional blending apparatus.
15 Therefore, the two polymers in the appropriate amount in
the form of, for example, powders together with further
usual additives are added to the blending apparatus.
The blend is thoroughly mixed until a homogeneous melt
is obtained, preventing decomposition of primarily the
20 polyvinyl chloride. Subsequently, a film is
manufactured from the homogeneous melt by any
conventional manner including casting, extruding and
calendering.

25 The thickness of said film may be 0.01-1.15 mm and
preferably 0.60-0.10 mm.

The adhesive used in the pressure-sensitive film
according to the invention, must be pressure-sensitive
(self-adhesive) and plasticizer-resistant; the latter
means that the adhesive should have an adhesion level
30 which is sufficiently high independent of the
plasticizer concentration.

Adhesives described in the European Patent
Specification 104 407, incorporated herein by reference,
discloses adhesives functional for this purpose.
35 Generally, adhesives which have proved to function,

1 comprise polymers of a combination of the following
monomers; acrylic acid, methacrylic acid, acrylamide,
methacrylamide (preferably present in amounts from 1.0%
to about 10% by weight, alkyl acrylates, alkyl
5 methacrylates containing at least 4 carbon atoms
(preferably present in amounts of about 35% to 85% by
weight), and other unsaturated monomers, like N-vinyl
pyrrolidone (5 to 15% by weight), methyl acrylate (15 to
10 50% by weight) and vinyl acetate (20.0-50.0% by weight).
Fumaric acid and/or mono-and diesters of unsaturated
dicarboxylic acids like dibutyl fumarate may also be
present.

A specific adhesive composition found suitable in
the practice of this invention is a terpolymer made from
15 52.2 parts n-butylacrylate, 37.5 parts methyl acrylate,
and 10 parts of acrylic acid. For economy this adhesive
may be prepared at a low inherent viscosity and cross-
linking agent. Another adhesive found suitable in the
practice of this invention is a linear terpolymer
20 consisting of 56.0 parts of isooctylacrylate, 40.1 parts
of vinyl acetate and 4.0 parts of acrylic acid. Yet
another adhesive is a terpolymer prepared from 85.0
parts of n-butylacrylate or methylbutylacrylate, 10.0
parts of N-vinyl pyrrolidone and 5.0 parts of acrylic
25 acid.

The best results are obtained when such a
polyacrylate is blended with a certain amount,
preferably 10-35%, of a phthalic acid ester of hydro-
abietyl alcohol and with a certain amount, preferably
30 0.5-5%, of a dialkyl phthalate.

The polyacrylate and the additional blends are
present in the form of a 25-35% solution in suitable
solvents, like isopropanol, hexane, toluene, ethyl
acetate, etc. The required cross-linking is effected
35 with conventional methods such as irradiation by

1 electron beams or addition of metal organic compounds
such as aluminum acetyl acetate of the solution.

The adhesive is in general present in an amount of
30-50 g/m² film. The adhesive can be applied to the
5 film by any conventional coating method to obtain a
regular distribution of the adhesive upon the surface.

Test Methods

10 In the following Example, the pressure-sensitive
films manufactured according to the invention are
subjected to the following tests:

1. 90° Peel Adhesion

15 The adhesion is the force needed to peel a
pressure-sensitive film applied to a substrate. Test
specimen having a length of 150 mm and a width of 25 mm
are used, and the adhesion is determined in N/25 mm.
Test specimen are peeled under 90° at a rate of 300
mm/min. using a tester at a temperature 23 ± 2°C. The
20 test is carried out 24 hours after applying to the
substrate, in which time the adhesion has been
sufficiently built up. In addition the test is carried
out after three weeks (accelerated) aging of adhered
film and substrate at 70°C in a hot air oven. It is
25 assumed that three weeks at 70°C is highly sufficient to
produce an equilibrium situation of the plasticizer
distribution in substrate, adhesive and CPE^a/PVC^b layer,
as will be reached in practice after a period of time.

30 2. Appearance

Appearance of adhered films is evaluated after
staying in a hot air oven at 70°C for one, two, and

^aChlorinated polyethylene

35 ^bPolyvinyl chloride

1 three weeks; reference is an unaged film. Evaluation
criteria are wrinkling, shrinkage and stickiness of the
CPE/PVC layer. All the films mentioned in the Example
were evaluated as good after three weeks at 70°C.

5
3. Flexibility

As there is no standard test for evaluation of the
flexibility, the flexibility is provisionally evaluated
by manual movement. It appeared that films wherein the
10 amount of chlorinated polyethylene was somewhat higher
and the K-value of the polyvinyl chloride was somewhat
lower are most satisfactory.

Example

15 A number of representative pressure-sensitive films
according to the invention has been manufactured. The
first layer consisting of a blend of chlorinated
polyethylene and polyvinyl chloride has a thickness of
100 m. The types of polyvinyl chloride (prepared by
20 suspension-, mass- or emulsion- polymerization, s, m and
e respectively), the K-value of the PVC, the chloride
content of the CPE and the weight ratio of CPE/PVC are
mentioned in the following table. The CPE/PVC- blends
comprise per 100 parts by weight a stabilization package
25 consisting of 1.5 part by weight of processing aid
(methacrylate) and 2.5 parts by weight of fatty acid
esters.

30 The CPE/PVC-layer is provided in a conventional way
with such a layer of adhesive that the weight of the
adhesive regularly distributed upon the surface is 40
g/m². The adhesive composition is 72% by weight of
polyacrylate, 24% by weight of phthalic acid ester of
hydro-abietyl alcohol, 3.5% by weight of dialkyl

1 phthalate and 0.5% by weight of aluminum acetyl
acetate.

5 The resulting pressure-sensitive films are
laminated on vinyl substrates. The basis of the
substrates (tarpaulins) used in the tests is a woven
canvas structure, to which and within which plasticized
PVC is applied. The tarpaulins may ^{optionally} ~~optimally~~ be
10 provided with coatings. Said coatings (acrylate) affect
indeed the adherence level which does not have very
large consequences for the initial adherence, but they
do affect distinctly the adherence as a function of
time, as said coatings somewhat provide diffusion
barriers which means that the equilibrium situation is
15 reached less rapidly. This is also shown by plasticizer
concentration determinations at certain times of
accelerated aging in identical film samples adhered to
coated and uncoated plasticized PVC substrates. This
means that pressure-sensitive films adapted for
application on uncoated plasticized PVC substrates are
20 certainly adapted for application on coated plasticized
PVC substrates.

The concentration of plasticizer in the PVC of the
substrate is 30-40% by weight. All the used
plasticizers are phthalic acid esters of alkanols having
25 at least 8 carbon atoms. Frequently applied
plasticizers are dioctyl phthalate and didecyl
phthalate, the first mentioned having the highest
diffusion rate in otherwise identical conditions.

30 The substrate used for aging comprises a blend of
substantially these two plasticizers.

The adherence level of the pressure-sensitive film
with the substrate after lamination and 24 hours at room
temperature to build up said adherence is satisfying for
all these films and it varies between 11 and 17 N/25 mm.
35 the constructions comprising substrate, adhesive layer



1 and CPE/PVC layer as indicated in the table are
subjected to accelerated aging for three weeks (500
hours) at 70°C. After said aging, the adherence of the
pressure-sensitive films with the substrates is
5 determined.

10

15

20

25

30

35

PVC		CPE	PVC/CPE	90° Peel adhesion (after ageing)	
				uncoated substrate	coated substrate
type	K-value	(% by weight)	(% by weight)	(N/25 mm)	(N/25 mm)
s	50	42	40/60	21.9	10.4
s	50	36	20/80	12.5	10.0
s ¹	50	42	45/55	10.1	9.8
m	58	36	40/60	8.0	7.0
s	58	42	40/60	9.0	8.4
e	60	42	40/60	8.1	9.1
m	60	36	40/60	12.6	7.4
m	60	42	20/80	8.7	8.4
s	65	36	60/40	14.2	8.5
s	70	36	80/20	7.9	7.8
s	80	36	20/80	15.7	11.1
s	80	42	20/80	11.9	9.3

1 = addition of 25% parts by weight of titanium dioxide (rutile) per 100 parts by weight of CPE/PVC.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A plasticizer-resistant film comprised of a layer formed of a blend of polyvinyl chloride and chlorinated polyethylene in respective weight ratios of 10:90 to 65:35
- 5 in which the polyvinyl chloride has a K-value of 45 to 80 and the chloride content of the chlorinated polyethylene is from 30 to 45% by weight, said film being receptive to retaining diffused plasticizer from a plasticized
- 10 layer, a plasticizer-resistant, pressure-sensitive adhesive which retains adhesion in the presence of a plasticizer, said adhesive comprising a polymer containing an alkyl acrylate or alkyl methacrylate or mixtures thereof.
- 15 2. A pressure-sensitive adhesive film as claimed in claim 1 in which the weight ratio of polyvinyl chloride to chlorinated polyethylene is from 35:65 to 65:35.
3. A pressure-sensitive adhesive film as claimed in claim 1 in which the polyvinyl chloride polymer has a
- 20 K-value of 50 to 65.
4. A pressure-sensitive adhesive film as claimed in claim 1 in which the chlorinated polyethylene has a chlorine content of 42% by weight and a melt viscosity of 600 to 3,000 PaS.
- 25 5. A pressure-sensitive adhesive film as claimed in claim 1 in which there is present in the film an ethylene vinyl acetate polymer present in an amount up to 10% by weight of the polymers.
6. A pressure-sensitive adhesive film as claimed in
- 30 claim 1 in which the pressure-sensitive adhesive is applied at a coat weight of 30 to 50 g/m².
7. A pressure-sensitive adhesive as claimed in claim 1 in which the pressure-sensitive adhesive comprises a polyacrylate.
- 35 8. A pressure-sensitive adhesive film as claimed in



claim 1 in which the adhesive includes a dialkyl phthalate and from 10 to 35% by weight of a phthalic acid ester of hydroabretyl alcohol.

9. A pressure-sensitive adhesive film as claimed in
5 claim 8 in which the dialkyl phthalate is present in an amount of from 0.5 to 5% by weight of the pressure-sensitive adhesive.

10. A pressure-sensitive adhesive film as claimed in
10 claim 7 in which the adhesive includes a dialkyl phthalate and from 10 to 35% by weight of a phthalic acid ester of hydroabretyl alcohol.

11. A pressure-sensitive adhesive film as claimed in
claim 10 in which the dialkyl phthalate is present in an amount of from 0.5 to 5% by weight of the
15 pressure-sensitive adhesive.

12. A pressure-sensitive adhesive film as claimed in
claim 14 in which the pressure-sensitive adhesive contains
72% by weight polyacrylate 24% by weight of phthalic acid
ester of hydroabretyl alcohol, 3.5% by weight dialkyl
20 phthalate and 9.5% by weight aluminum acetyl acetate.

DATED this 25th day of August 1992

AVERY DENNISON CORPORATION
Patent Attorneys for the
Applicant:

F.B. RICE & CO.

