

19



Europäisches Patentamt
European Patent Office
Office européen des brevets

11

Publication number:

**0 357 933
A1**

12

EUROPEAN PATENT APPLICATION

21

Application number: **89113801.8**

51

Int. Cl.⁵ **B42C 9/00 , B42C 9/02 ,
C09J 193/04 , C09J 157/00 ,
//(C09J193/04,153:02,191:00),
(C09J157/00,153:02,191:00)**

22

Date of filing: **26.07.89**

30

Priority: **17.08.88 US 233175**

71

Applicant: **National Starch and Chemical
Corporation
10 FINDERNE AVENUE BOX 6500
BRIDGEWATER NEW JERSEY 08807(US)**

43

Date of publication of application:
14.03.90 Bulletin 90/11

72

Inventor: **Flanagan, Thomas P.
236 Piazza di Luna
Venice Florida 34285(US)**

84

Designated Contracting States:
DE FR GB IT NL SE

74

Representative: **Hagemann, Heinrich, Dr.
Dipl.-Chem. et al
Patentanwälte HAGEMANN & KEHL
Ismaninger Strasse 108 Postfach 860329
D-8000 München 86(DE)**

54

Toughened hot melt adhesive composition for book hinge joint.

57

A process for the formation of the hinge joints on bound book blocks using a toughened hot melt pressure sensitive adhesive comprising:

a) 10 to 40% by weight of a substantially radial styrene-butadiene block copolymer, the copolymer having a styrene content greater than about 35% by weight, a modulus at 300% elongation of at least 4.5 MPa and a solution viscosity less than about 1000 cps;

b) 20 to 65% by weight of a compatible tackifying resin;

c) 0.1 to 4% by weight stabilizer; and

d) the remainder (to 100%) comprising a plasticizing oil.

EP 0 357 933 A1

TOUGHENED HOT MELT ADHESIVE COMPOSITION FOR BOOK HINGE JOINT

The present invention is directed to toughened pressure sensitive hot melt adhesives used to form the hinge joint of a flexible covered book.

Flexible or soft covered books are generally formed by coating a layer of hot melt adhesive on the secured edge of a series of printed stocks or signatures to form a book block to which a paper backing or other suitable cover is applied to form the spine of the book. While this process produces the primary bonding of the book block to the cover, a secondary bond is often formed at the hinge or joint of the cover. This bond is produced by applying a small amount of adhesive to the outer sheet of each side of the book block immediately adjacent to the hinge area. This hinge joint formation is actually carried out in two separate steps with the adhesive being applied to the book block before the cover is affixed and the joint then being formed by application of pressure to the book cover at some point "downline" in the manufacturing operation. The purpose of this adhesive application is to conceal the binding adhesive and also to reinforce the binding and to prevent the book from falling apart relatively easily when grasped only by the flexible cover.

The adhesives used for this application must possess a variety of properties, specifically they must possess low viscosity (i.e., about 500 to 5000 cps at 350 ° F) for easy application, strong aggressive tack at the point of formation of the hinge bond, good adhesion to difficult cover stocks and resistance to creep or cold flow both at room temperature and under elevated temperature conditions. Heretofore the adhesives used have generally been either the non-pressure sensitive hot melt adhesives used in the book binding operation or emulsion adhesives. Both types of adhesives suffer from the common deficiency of their relatively short open time i.e., the time during which a bond may be found. This lack of open time creates a serious problem in the automated book binding process where interruptions, slow downs or even shut downs of the manufacturing line result in loss of aggressive tack properties with the subsequent need to discard large quantities of partially completed products. Another problem resulting from the finite open time of the adhesives of the prior art is the high rejection rate due to poorly formed joints caused by the relatively high coating weights which must be applied in order to assure the presence of the needed residual aggressive tack at the time the hinge joint is formed, particularly when slow machine speeds are involved. Additional rejects are created with finite open time products, when appropriate thin coating weights are used for

high production speeds, but when machine slows down or stops because of some other interruption in the binding line the thin coating weight causes solidification prior to bond formation and therefore no bond can be formed.

We have now found that pressure sensitive hot melt adhesive compositions prepared adhesives which comprise a substantially radial styrene-butadiene block copolymer, the copolymer having a styrene content greater than about 35% by weight, a modulus at 300% elongation of at least 4.5 MPa and a solution viscosity less than about 1000 cps are particularly useful in the formation of hinge joints for flexible books.

Thus, the present invention is directed to a process for the formation of hinge joints on bound book blocks comprising the steps of applying a molten film of a hot melt pressure sensitive adhesive to the outer sheet of each side of the book block on an area immediately adjacent the bound edges and for a length substantially coterminus with the bound edges; applying a cover thereto; and exerting pressure on the book cover in the area of the pressure sensitive hot melt film; wherein the pressure sensitive hot melt adhesive comprises:

a) 10 to 40% by weight of a substantially radial styrene-butadiene block copolymer, the copolymer having a styrene content greater than about 35% by weight, a modulus at 300% elongation of at least 4.5 MPa and a solution viscosity less than about 1000 cps;

b) 20 to 65% by weight of a compatible tackifying resin;

c) 0.1 to 4% by weight stabilizer;

d) the remainder (to 100%) comprising a plasticizing oil.

The block copolymers useful herein are comprised of styrene and butadiene blocks arranged in a substantially radial configuration and contain at least 35%, and generally up to about 50%, by weight of the styrene moiety. Of greater significance however, the copolymers selected should exhibit a modulus at 300% elongation of at least about 4.5 MPa and a solution viscosity less than about 1000 cps (25% in toluene at 23 ° C using a Brookfield viscometer). These copolymers may be prepared using methods taught, for example, in U.S. Pat. Nos. 3,239,478; 3,427,269; 3,700,633; 3,753,936 and 3,932,327. Alternatively they are available from Shell Chemical Co. under the trademark Kraton DX1122 (37% styrene, modulus of 4.8 MPa, viscosity 670 cps) and from Eni Chem Americas (Agip USA Inc.) as Europrene SOL T 162LW/1 (40% styrene, modulus of 5.0 MPa, viscosity 750

cps) or SOI T 162 LW/2 (40% styrene, modulus of 4.6 MPa, viscosity (640 cps). While the optimum amounts of the copolymer used in the adhesive will vary depending on the end use application, the copolymer will generally be present in the adhesive formulation at levels of 10 to 40% by weight, preferably 15 to 25% by weight.

The tackifying resins useful in the adhesive compositions can be hydrocarbon resins, hydrogenated hydrocarbon resins, synthetic polyterpenes, rosin esters, natural polyterpenes, and the like. More particularly, the useful tackifying resins include any compatible resins or mixtures thereof such as (1) natural and modified rosins such, for example, as gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin, and polymerized rosin; (2) glycerol and pentaerythritol esters of natural and modified rosins, such, for example as the glycerol ester of pale, wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerized rosin, the pentaerythritol ester of hydrogenated rosin, and the phenolic-modified pentaerythritol ester of rosin; (3) copolymers and terpolymers of natured terpenes, e.g. styrene/terpene and alpha methyl styrene/terpene; (4) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from 80 to 150 °C; the latter polyterpene resins generally resulting from the polymerization of terpene hydrocarbons, such as the bicyclic monoterpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low temperatures; also included are the hydrogenated polyterpene resins; (5) phenolic modified terpene resins and hydrogenated derivatives thereof such, for example, as the resin product resulting from the condensation, in an acidic medium, of a bicyclic terpene and a phenol; (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from 70 to 135 °C.; the latter resins resulting from the polymerization of monomers consisting of primarily of olefins and diolefins; also included are the hydrogenated aliphatic petroleum hydrocarbon resins; (7) aromatic petroleum hydrocarbon resins and the hydrogenated derivatives thereof; and (8) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof. Mixtures of two or more of the above described tackifying resins may be required for some formulations. The tackifier is used in amounts of 20 to 65% by weight.

The remainder (up to about 60% by weight) of the hot melt adhesive comprises at least one oil diluent. Suitable plasticizing or extending oils include not only the usual plasticizing oils but also olefin oligomers and low molecular weight polymers as well as vegetable and animal oil and their derivatives. The petroleum derived oils which may

be employed are relatively high boiling materials containing only a minor proportion of aromatic hydrocarbons (preferably less than 30% and, more particularly, less than 15% by weight of the oil). Alternatively, the oil may be totally non-aromatic. The oligomers may be polypropylenes, polybutenes, hydrogenated polyisoprene, hydrogenated polybutadiene, or the like having average molecular weights between 350 and 10,000. Among the applicable stabilizers or antioxidants included herein are high molecular weight hindered phenols and multifunctional phenols such as sulfur and phosphorous-containing phenols. Hindered phenols are well known to those skilled in the art and may be characterized as phenolic compounds which also contain sterically bulky radicals in close proximity to the phenolic hydroxyl group thereof. In particular, tertiary butyl groups generally are substituted onto the benzene ring in at least one of the ortho positions relative to the phenolic hydroxy group. The presence of these sterically bulky substituted radicals in the vicinity of the hydroxyl group serves to retard its stretching frequency and, correspondingly, its reactivity; this steric hindrance thus providing the phenolic compound with its stabilizing properties. Representative hindered phenols include: 1,3,5-trimethyl 2,4,6-tris (3,5-di-tert-butyl-4-hydroxybenzyl)benzene; pentaerythritol tetrakis-3(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate; n-octadecyl-3,5-di-tert-butyl-4-hydroxyphenyl-propionate; 4,4'-methylenebis (2,6-tert-butylphenol); 4,4'-thiobis (6-tert-butyl-o-cresol); 2,6-di-tertbutylphenol; 6-(4-hydroxyphenoxy)-2,4-bis(n-octylthio)-1,3,5-triazine; di-n-octadecyl 3,5-di-tert-butyl-4-hydroxy-benzylphosphonate; 2-(n-octylthio)-ethyl 3,5-di-tert-butyl-4-hydroxy-benzoate; and sorbitol hexa[3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate]. The stabilizer is present in amounts of 0.1 to 4% by weight, preferably less than about 2%.

Optional additives may be incorporated into the hot melt compositions in order to modify certain properties thereof. Among these additives may be included colorants such as titanium dioxide; and fillers such as talc and clay, etc. as well as minor amounts (e.g. less than about 5%) of a petroleum derived wax.

These hot melt adhesive compositions may be formulated using techniques known in the art. An exemplary procedure involves placing approximately half of the total tackifying resin concentration in a jacketed mixing kettle, preferably in a jacketed heavy duty mixer of the Baker-Perkins or Day type, which is equipped with rotors and thereupon raising the temperature to a range of from 250 ° to 350 ° F., the precise temperature utilized depending on the melting point of the particular tackifying resins. When the resin has melted, stirring is initiated and

the block polymer and stabilizer are added together with any optional additives whose presence may be desired, the addition of the latter components being extended over a prolonged period in order to avoid the formation of lumps. Mixing and heating are continued until a smooth, homogeneous mass is obtained whereupon the remainder of the tackifying resin and the oil are thoroughly and uniformly admixed therewith. The resultant hot melt adhesives are generally produced with an oil in bulk form and packaged in release coated tube or boxes.

In the following illustrative examples all parts are given by weight and all temperatures in degrees Celsius unless otherwise noted.

EXAMPLE I

The following example illustrates the preparation of adhesives of the invention in formulations suitable for use in the bookbinding industry as discussed above.

In preparing the following samples, a heavy duty mixer which had been heated to 150° C and which was equipped with a stirring paddle was charged with half of the tackifying resin. After melting of the resins, stirring was then initiated whereupon the block copolymers and the antioxidants were added slowly. Heating and stirring were continued until a homogeneous mass was obtained whereupon the remainder of the tackifying resin and the oil were admixed therewith. The molten mixture was then poured into a siliconized paper tube and cooled to room temperature.

Adhesives were prepared from the materials and amounts shown in Table I using the general procedure described above. Viscosity measurements were determined using a Brookfield viscometer (Spindle 27) at 325° F. The adhesives were subjected to the following tests to determine the heat resistance of the adhesive under a constant load and static stress and elevated temperature.

The adhesive was heated to 320° F and a lamination of kraft paper was made using heated rollers. The adhesive thickness was 50 mil and the bonds having an adhesive area of one square inch. The bonds were aged overnight at 72° F and 50% RH. The peel mode samples were then hung in a 105° F oven using 300 gram/inch weights. The time at which the bond failed was noted as was the mode of failure.

The tensile strength of the hot melt adhesive was determined on samples cast from the hot melts and molded in silicone rubber molds into the shape of dog bones. After cooling, the dog bone shaped specimens were removed from the mold

and tested using an Instron Tensile Tester. The force required to start to stretch the specimen is recorded as the "tensile yield", the force required to break the specimen as "tensile break". This procedure also provides a measurement of percent elongation, which is the percentage stretch of the hot melt sample at the point of rupture in obtaining the ultimate tensile strength.

5

10

15

20

25

30

35

40

45

50

55

TABLE I

Sample	Polymer	Amount	Resin	Amount	Oil	Tensile Strength (MPa)		K/K (hrs)	Viscosity (cps)
						Y	U		
1	DX1122X	23	Permalyn 305 ⁽¹⁾	59	18	0.06	1.17	3-1/2	2975
2	Sol T162 LW/ ⁽²⁾	23	Permalyn 305	59	18	0.09	1.27	6-1/2	3365
3	Stereon 840A	23	Permalyn 305	59	18	0.04	0.59	3-1/2	2915
4	DX1122X	23	Permalyn 305	57	20	0.05	1.16	5-1/2	2950
5	Firestone SR 7360 ⁽³⁾	23	Permalyn 305	57	20	0.04	0.86	2-1/2	2525
6	DX1122X	21	ECR 149B ⁽⁴⁾	60	19	0.05	1.17	2	2400
7	Sol T162 LW/2	21	ECR 149B	60	19	0.07	1.27	2-3/4	2420
8	Stereon 840A	21	ECR 149B	60	19	0.04	0.62	3-1/2	2470
9	DX1122X	15	ECR 149A ⁽⁵⁾	30	25	0.03	0.82	1	760
			ECR 149B	30					
10	Stereon 840A	21	ECR 149A	30	19	0.05	0.72	5-1/3	2630
			ECR 149B	30					
11	Stereon 840A	15	ECR 149A	30	25	0.02	0.38	1-2/3	685
			ECR 149B	30					
12	DX1122X	21	ECR 149A	30	19	0.07	1.3	7-1/4	3010
			ECR 149B	30					
13	DX1122X	15	Kristalex ⁽⁶⁾	8	25	0.04	1.14	8-3/4	570
			ECR 149B	52					
14	Sol T162 LW/2	15	Kristalex	8	25	0.04	1.22	6-1/4	805
			ECR 149B	52					
15	Firestone SR 7360	15	Kristalex	8	25	0.03	0.73	3-1/4	765
			ECR 149B	52					

TABLE I (continued)

Sample	Polymer	Amount	Resin	Amount	Oil	Tensile Strength (MPa)		K/K (hrs)	Viscosity cps
						Y	U		
16	Stereon 840A	15	Kristalex ECR 149B	8 52	25	0.03	0.59	2-1/4	690
17	DX1122X	15	Kristalex ECR 149A	8 52	25	0.06	1.24	25	1025
18	DX1122X	21	M 105 (7)	60	19	.06	1.19	16	2310
19	SOL T162X LW/2	21	M 105	60	19	.08	1.39	16	2320
20	Stereon 840A	21	M 105	60	19	.04	0.83	4-1/2	2450
21	Stereon 840A	21	Res D2105 (8)	60	19	.05	0.91	20-1/2	2470
22	Stereon 840A	22.5	Res D2105	60	17.5	.06	1.06	40	2950
23	SOL T168	22.5	Res D2105	60	17.5	.06	1.32	82	3535
24	SOL T168	18	Res D2105	60	22	.02	0.85	4-1/2	1390
25	DX1122X	18	Res D2105	60	22	.04	1.14	32-1/3	935
26	DX1122X	15	Res D2105	60	22*(9)	.03	0.98	8	600

(1) Permalyne 305 is a pentaerythritol ester of rosin from Hercules

(2) Stereon 840A is a styrene butadiene multi-block copolymer containing 43% styrene, having a modulus of 2.4 MPa and a solution viscosity of 650 cps. from Firestone

(3) Firestone SR 7360 is a styrene-butadiene polymer containing 43% styrene, having a modulus at 300% elongation of 3.7 MPa and a solution viscosity of 990 cps.

(4) ECR 149B is an aliphatic/aromatic C₅/C₉ resin from Exxon (95°C)

(5) ECR 149A is an aliphatic/aromatic C₅/C₉ resin from Exxon (softening pt. 105°C)

(6) Kristalex 5140 is an alpha methyl styrene resin from Hercules (140°C)

(7) M 105 is a styrenated terpene resin from Reichhold

(8) Res D2105 is a styrenated terpene resin from Hercules

(9) Also contained 3 parts ECR 143H, a liquid aliphatic tackifying resin available from Exxon

The testing results of Samples 1-8 show significantly higher ultimate tensile strength of the adhesives of the present invention when contrasted with presently commercially utilized adhesive compositions containing similar amounts of raw materials.

Sample 9 shows that it is possible to use less polymer to obtain a lower viscosity adhesive without sacrifice of tensile strength. (Compare to Sample 11 prepared with 15 parts Stereon). Note however the product did suffer with respect to Kraft-Kraft adhesive and hence would not be readily useful for certain end use applications where stringent heat resistance values are required.

Samples 12, 13 and 14 show results similar to those of Sample 9, additionally overcoming the deficiency of Sample 9 with respect to heat resistance by use of a different tackifier system.

Sample 17 shows a further formulation according to the invention using a different tackifying system. Note, in particular, the high heat resistance value.

Samples 18 through 26 again shown the improved heat resistance and ultimate tensile strength achieved using adhesive compositions of the invention as contrasted to conventionally employed Stereon containing adhesive systems with Samples 24, 25 and 26, also showing that lower levels of the Kraton D1122X may be used to obtain lower viscosity products without sacrifice to the tensile strength.

All of samples 1-22, on testing, gave entirely cohesive modes of failure in the Kraft to Kraft heat resistance test, i.e., adhesive residue was observed on both substrates after bond failure.

The resultant adhesives may be used to form the hinge joint using methods conventional in the book binding art and without limitation to the particular binding method employed. Thus the book block may be bound by any of the usual procedures, including, but not limited to, perfect binding with hot melt adhesive, burst binding with emulsion adhesive and then with hot melt adhesive; sewn and glued off with emulsion adhesive; or perfect or burst bound with emulsion adhesive. The hinge joint may be formed on any book, construction, i.e., a flexible or soft cover book or a book block which will eventually be hard bound or case bound book, but wherein a hinge joint is formed between the book block and the combined end sheets. In general, regardless of the method of construction, a film of a non-pressure sensitive adhesive is coated on the secured edges of the book block; then a molten film of the hot melt pressure sensitive adhesive described previously is coated on the outer sheet of each side of the book block on an area immediately adjacent the secured edges and for a length substantially coterminus

therewith; the flexible cover is applied to the first film while the latter is still in the uncured state and pressure is exerted on the book cover in the area of the pressure sensitive hot melt film to form the hinge joint. Alternatively, the hinge or joint hot melt may be applied in appropriate lines to the flexible cover as the cover is fed on the binder to next to the book block.

Claims

1. A process for the formation of hinge joints on bound book blocks comprising the steps of applying a molten film of a hot melt adhesive to the outer sheet of each side of the book block on an area immediately adjacent the bound edges and for a length substantially coterminus with the bound edges; applying a cover thereto and exerting pressure on the book cover in the area of the hot melt film wherein the a hot melt adhesive is a pressure sensitive adhesive composition comprising:

a) 10 to 40% by weight of a substantially radial styrene-butadiene block copolymer, the copolymer having a styrene content greater than about 35% by weight, a modulus at 300% elongation of at least 4.5 MPa and a solution viscosity less than about 1000 cps;

b) 20 to 65% by weight of a compatible tackifying resin;

c) 0.1 to 4% by weight stabilizer; and

d) the remainder (to 100%) comprising a plasticizing oil.

2. The process of Claim 1 wherein the tackifier in the hot melt pressure sensitive adhesive composition is any compatible resin or mixture thereof selected from the group consisting of (1) natural and modified rosins; (2) glycerol and pentaerythritol esters of natural and modified rosins; (3) copolymers and terpolymers of natural terpenes; (4) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from about 80° to 150° C; (5) phenolic modified terpene resins and hydrogenated derivatives thereof; (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from about 70° to 135° C.; (7) aromatic petroleum hydrocarbon resins and the hydrogenated derivatives thereof; and (8) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof.

3. A book produced by the process of Claim 1.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-4 712 808 (BEH-FORREST et al.) * Claims 5-12 * ---	1-3	C 09 J 193/04 C 09 J 157/00 //
Y	US-A-3 950 291 (JURRENS) * Claim 6; example 1 run A,B,C * -----	1-3	B 42 C 9/02 B 42 C 9/00 (C 09 J 193/04 C 09 J 153:02 C 09 J 191:00) (C 09 J 157/00 C 09 J 153:02 C 09 J 191:00)
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 09 J B 42 C
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 16-11-1989	Examiner LOISELET-TAISNE S.M.T.
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

EPO FORM 1503 03.82 (P0401)