United States Patent Office 3,837,994 Patented Sept. 24, 1974

3,837,994

MANUFACTURE OF PERFECT BOUND BOOKS

Thomas P. Flanagan, Green Brook, and Irving I. Kaye, Murray Hill, N.J., assignors to National Starch & Chemical Corporation, New York, N.Y.

No Drawing. Continuation-in-part of abandoned application Ser. No. 724,267, Apr. 25, 1968. This application June 12, 1972, Ser. No. 261,916

Int. Cl. B32b *27/10, 31/04;* B42c *9/00*

U.S. Cl. 161—100 12 Claims

ABSTRACT OF THE DISCLOSURE

A method for the "perfect" binding of books wherein the hot melt adhesive composition which is utilized to bind the sheets thereof comprises a blend of (a) a block polymer of monovinyl aromatic hydrocarbons and conjugated dienes; (b) a tackifying resin; (c) a stabilizer; and (d) a wax diluent.

This application is a continuation-in-part of application bearing Ser. No. 724,267, filed Apr. 25, 1968 and now abandoned.

The "perfect" binding of books is a relatively new, high speed, continuous operation used in the book-binding industry. Originally developed for the cheaper, paper-backed books of pocket size, i.e. "pocket books," its use has gradually spread to catalogs, magazines, telephone directories, manuals, brochures, etc., where high speed production is an important criteria. In this operation, the books are printed in long, continuous sheets or webs which are cut, folded and properly arranged to form a series of stacks, referred to as signatures, which are then fed into a continuous, revolving chain equipped with clamps. The free edges of the clamped sheets are first cut to remove the signature folds and then roughed so as to expose a maximum amount of fibers at the edges of the sheets and to make them more receptive to the adhesive composition. A layer, or coat, of a molten adhesive composition (hot melt) is then applied by means of a suitable applicator, after which a paper backing or other suitable cover is applied before the molten adhesive sets to form the spine of the book. The perfect bound book is then trimmed to the proper size, and the edges colored as by painting or dyeing, when desired, to give the finished product.

As noted above, hot melt compositions useful for the perfect binding of books serve at least two critical functions. In the first place, they must hold the book together during its formation. Thus, it is necessary that they be capable of forming thin films in the molten state; that they wet rapidly; that they have good adhesion (tack) for similar and dissimilar sheets ranging from waxed-glassine to high-kraft papers, metallic foils, or metal-coated sheets; that they be quick setting but not too quick so as to prevent the cover from bonding; and, that they be capable of exhibiting a wide range of viscosities in order to be applicable for use with any suitable hot melt applicator. Secondly, on cooling or setting, hot melt adhesives must be able to produce spines having good "wear potential" so as to be capable of preventing the book from falling apart. Wear potential includes the properties of high bonding strength, flexibility, high film strength (tensile strength) and resistance to aging, mold growth, "warm flow" and "cold crack."

"Warm flow" is the undesirable softness which permits the spine of a book to "flow apart" under stress as, for example, when the reader folds the book back-to-back for a period of time. This characteristic becomes especially troublesome in hot, humid atmospheric conditions.

"Cold crack" is the undesirable hardness of the spine

which prevents the opening of a book to 360°, i.e. so that the covers are back-to-back to one another, without causing the book to split. This characteristic is dependent upon temperature and is of particular importance when books are exposed to cold climates. Since the perfect bound book has no staples, rivets, stitches, etc., cracking of the spine causes the book to fall apart.

The prior art hot melt adhesive compositions are often limited in their effectiveness as hot melts for the perfect binding of books because they are only mediocre with regard to one or more of the properties enumerated above. Often it has been necessary to compromise certain properties in order to obtain products having at least a narrow range of useful properties. Thus, for example, hot melts based on polyvinyl acetate have shown poor warm flow and cold crack characteristics. In addition, hot melts based on ethylene-vinyl acetate copolymer systems have experienced various adhesion problems and the books which have been bound with the latter hot melts have exhibited poor opening properties.

Hot melt adhesives utilizing the block polymers described herein are taught in U.S. Pat. 3,239,478 to J. T. Harlan, Jr. The hot melt adhesives taught in the patent, however, exhibit pressure sensitive properties and are unsuitable for use in the perfect binding of books. A pressure sensitive adhesive is one which remains tacky for prolonged periods (or permanently) after being coated upon a surface. It will be seen from the description of the perfect binding process found herein that the semi-finished books must be trimmed to the desired, final size after application of the adhesive. A tacky adhesive (i.e. one that is pressure sensitive) cannot be used for book binding because the adhesive would undesirably accumulate on the knives or blades used in the cutting operation and the random spreading of the adhesive would ruin the books. It is essential that the adhesives used in the process of the present invention be non-pressure sensitive.

In order to distinguish the present hot melt adhesives from those described in the aforementioned Harlan patent, it is noted that the pressure sensitive adhesives of Harlan are formulated with oils which are liquid at room temperature. The adhesives of this invention, in contrast, do not require any oils, but rather incorporate waxes which are solid at room temperature. The waxes employed herein are termed "wax diluents" and function to modify properties in the described adhesives. The waxes are not merely "diluents" since they serve to provide a lowering of viscosity, a necessary dryness at room temperatures, as well as a rigidity balanced with softness desirable in the hot melt adhesives used in the perfect binding of books.

It is to be pointed out that the hydrogenated vegetable, animal and fish fats and oils found to be useful in the adhesives herein are solid materials at ambient temperatures by virtue of their being hydrogenated. As such, the hydrogenated materials are often referred to in the adhesive industry as "animal or vegetable waxes."

It is, thus, the prime object of this invention to deposit upon the clamped edges of a plurality of similar and dissimilar sheets, a molten adhesive layer which, upon cooling or setting, forms a spine characterized by good tack, excellent bond strength and superior resistance to "warm flow" and "cold crack" characteristics. It is a further object that the adhesive layer may be deposited on the edges of such sheets by means of applicator equipment conventional in the perfect binding industry. It is still a further object that the adhesive may be handled in bulk form for the premelting equipment presently available in the industry; or, it may be pelletized, diced or granulated for convenient premelting in an applicator of the extruder type; or, in rope or cord form for applica-

tors designed to handle adhesives in the latter physical forms. Various other objects and advantages of this invention will become apparent from the following detailed description thereof.

We have now discovered that by utilizing hot melt adhesive compositions, as hereinafter described, in the perfect binding of books, it is possible to overcome substantially all of the difficulties previously encountered in such an operation and thereby to obtain spines for perfect bound books which exhibit superior properties. Such hot melt adhesives are capable of forming thin films at conventional application temperatures; they have good heat stability; they set quickly but not too quickly so as to enable the cover to be bonded to the sheets; they display excellent adhesion to a variety of sheets including all varieties of paper stocks, waxed-glassine sheets, metallic foils, metalized sheets of paper and polyester sheets, etc.; and, they produce spines characterized by high tensile strength, excellent adhesion, low temperature flexibility, and insensitivity to high humidity conditions as well as resistance to warm flow, cold crack, mold formation and deterioration by aging.

The hot melt adhesive compositions utilized in the novel process of this invention consists essentially of a blend of: (1) a block polymer of monovinyl aromatic hydrocarbons and conjugated dienes, which represents the basic component of the system; (2) at least one tackifying resin which serves to extend the adhesive properties of the system; (3) at least one stabilizer; and (4) at least one wax diluent.

The basic polymer component of our adhesive systems may be described as an unvulcanized elastomeric block polymer wherein the respective monomeric moieties are arranged in an alternating sequence having the general configuration A-B-A wherein A is a non-elastomeric polymer block derived from the moieties of a monovinyl aromatic hydrocarbon monomer and B is an elastomeric polymer block derived from the moieties of a conjugated diene monomer; the total concentration of the A block therein ranging from about 20 to 50%, as based on the total weight of the polymer. An additional configuration which has been applied to these three unit block polymers is $(SSS)_n$-$(BBB)_n(SSS)_n$ wherein S represents the moieties derived from the vinyl substituted aromatic hydrocarbon monomer in which the vinyl group is attached to a nuclear carbon atom and B represents the moieties derived from the conjugated diene monomer. It should be noted that, in these polymers, styrene is ordinarily used as the monovinyl aromatic hydrocarbon member while butadiene-1,3 and isoprene are the most frequently used conjugated diene members. Thus, for example, styrene-butadiene-styrene polymers are commercially available under the trademarks "Kraton 101" and "Kraton 102," while styrene-isoprene-styrene polymers are commercially available under the trademarks "Kraton 107" and "Kraton 84–0554." All of the latter designated block polymers are sold by the Shell Chemical Company.

Methods for preparing the latter block polymers are well known to those skilled in the art; typical procedures being disclosed in U.S. Pat. 3,265,765, issued Aug. 9, 1966. These procedures generally involve the solution polymerization of a mixture containing the monovinyl aromatic hydrocarbon monomer and the conjugated diene monomer in the presence of a catalyst of the formula $R(Li)_x$ wherein x is an integer having the value of from 1 to 4 and R is a hydrocarbon radical selected from the group consisiting of aliphatic, cycloaliphatic and aromatic radicals.

The tackifying resins which are present in our hot melt systems serve to extend the adhesive properties of the block polymer. As contemplated in this invention, the term "tackifying resin" includes: (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) polyterpene resins having a softening point, as determined by ASTM method E28–58T, of from about 80 to 150° C.; the latter polyterpene resins generally resulting from the polymerization of terpene hydrocarbons, such as the bicyclic mono-terpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low temperatures; (4) chlorinated terphenyl resins containing from about 42 to 60%, by weight, of chlorine; (5) phenolic-modified terpene resins such, for example, as the resin product resulting from the condensation, in an acidic medium, of a bicyclic terpene and a phenol; and (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from about 70 to 135° C.; the latter resins resulting from the polymerization of monomers consisting primarily of olefins and diolefins.

The stabilizers which are present in the hot melt systems of this invention serve to protect the otherwise vulnerable block polymer, and thereby the total adhesive system, from the thermal and oxidative degradation which is frequently encountered during the manufacture and application of the adhesive as well as in the ordinary exposure of the final adhered product. Such degradation is usually manifested by deterioration in appearance, physical properties and performance. Among the applicable stabilizers are included 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;
pentaerythrityl tetrakis-3(3,5-di-tert-butyl-4-hydroxyphenyl)propionate;
n-octadecyl-3(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate;
4,4'-methylenebis (2,6-di-tert-butyl phenol);
2,2'-methylenebis (4-methyl-6-tert-butylphenol);
4,4'-thiobis (6-tert-butyl-o-cresol);
2,6-di-tert-butylphenol;
6-(4-hydroxyphenoxy)-2,4-bis(n-octylthio)-1,3,5-triazine;
2,4,6-tris-(4-hydroxy-3,5-di-tert-butylphenoxy)-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-hydroxybenzoate; and
sorbitol hexa-[3-(3,5-di-tert-butyl-4-hydroxy-phenyl)propionate].

The performance of these stabilizers may be further enhanced by utilizing, in conjunction therewith: (1) synergists such, for example, as thiodipropionate esters and phosphites; and (2) chelating agents and metal deactivators such, for example, as ethylenediamine tetraacetic acid, salts thereof, and disalicylalpropylenediimine.

Wax diluents are employed in order to reduce the melt viscosity or cohesive characteristics of the hot melt adhesive compositions without appreciably decreasing their ad-

hesive binding characteristics. Among the applicable wax diluents are included: (1) low molecular weight, e.g. 1000–6000, polyethylene having a hardness value, as determined by ASTM method D–1321, of from about 0.1 to 120 and an ASTM softening point of from about 150–250° F.; (2) petroleum waxes such as paraffin wax having a melting point of from about 130 to 165° F. and microcrystalline wax having a melting point of from about 140 to 200° F.; the latter melting points being determined by ASTM method D127–60; (3) atactic polypropylene having a Ball and Ring softening point of from about 120 to 160° C.; and synthetic waxes made by polymerizing carbon monoxide and hydrogen such as Fischer-Tropsch wax. Each of these wax diluents is solid at room temperatures. Hydrogenated animal, fish and vegetable fats and oils such as hydrogenated tallow, lard, soya oil, cottonseed oil, castor oil, menhadin oil, cod liver oil, etc., are solid materials at ambient temperature by virtue of their being hydrogenated and are also found to be useful to function as the wax diluent equivalent. These hydrogenated materials are often referred to in the adhesive industry as "animal or vegetable waxes."

The procedure for preparing these hot melt adhesive compositions 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 about 250 to 350° F., the precise temperature utilized depending on the melting point of the particular tackifying resin. 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 wax diluent are thoroughly and uniformly admixed therewith. The resulting hot melt adhesive composition is drawn off and may be used immediately in hot pots; or, it may be molten-extruded into rope form or converted into pellets, rods, cylinders, slugs or billets depending on the equipment which will be subsequently used to apply the hot melt during the perfect binding operation; or, it may be placed in cooling pans and held in bulk form for later use; or, it may be granulated or diced.

With regard to proportions, the hot melt systems of this invention typically contain a concentration of the block polymer ranging from about 20 to 50%, a concentration of tackifying resin ranging from about 20 to 59% and a concentration of stabilizer ranging from about 1 to 4%; the latter concentrations being based on the total weight of the hot melt composition. Wax diluents are present from about 20 to a maximum concentration of about 50%, as based on the total weight of the hot melt composition.

Optional additives may be incorporated into the hot melt compositions of this invention 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.

The hot melts of this invention are typically applied at temperatures ranging from about 300 to 400° F., a preferred melt viscosity of from about 5,000 to 30,000 centipoises, and at a wet film thickness of from about 5 to 35 mils when utilized in the perfect binding operation of this invention. As previously noted, the basic perfect binding technique, as conceived by the novel process of this invention, comprises the steps of: (1) printing, cutting, folding and arranging the signatures; (2) cutting the signatures to remove the signature folds and to expose a fully squared backbone; (3) roughing the backbone so as to expose the fibers at the back edge and make them more receptive to the hot melt composition; (4) applying the hot melt composition by means of any conventional equipment employed in the perfect binding industry so as to provide a continuous film or coating over the entire back surface of the sheets; (5) applying a suitable cover, for example, paper backing, kraft, crash or full cover, to the molten hot melt coating; (6) allowing the adhesive to solidify thereby forming the spine of the book; and (7) trimming the perfect bound book to the proper size. Subsequently, the edges of the front and ends of the sheets may be dyed, or painted, when desired.

As an optional step in the latter procedure, a coating of an emulsion or latex adhesive, e.g. a polyvinyl acetate emulsion, may be applied to the roughed backbone resulting from step (3) and then dried in order to aid in the eventual binding operation. In addition, the roughed backbone may be preheated prior to the application of the hot melt adhesive. Furthermore, it should be noted that for a continuous operation, the application of the hot melt, the application of the cover and the setting of the adhesive may all be completed within a matter of seconds.

In a variation of the above described process, the application of the backing or cover to the molten hot melt coating in step (5) is omitted so that the molten adhesive on the spine is simply permitted to solidify. An additional coating (or coatings) of hot melt adhesive (either the same or other formulation) is subsequently applied on top of the first coating and while the adhesive film is still in its molten form a layer of crash and paper are bonded to the spine. The book as this stage is termed a "lined-up" book in book binding terminology and is thereafter "cased-in" by means of the secured crash and end-sheets in conventional fashion.

The following examples will further illustrate the embodiment of this invention. In these examples all parts given are by weight unless otherwise noted.

EXAMPLE I

This example illustrates the preparation of a hot melt adhesive composition typical of the products of this invention as well as the improved properties thereof which enable it to be effectively utilized in a perfect binding operation.

A heavy duty mixer which had been heated to 300° F. and which was equipped with a stirring paddle was charged with 22.5 parts of rosin dimer. This tackifying resin was completely melted. Stirring was then initiated whereupon 35 parts of a styrene-butadiene-styrene block polymer commercially available under the trademark "Kraton 102" sold by Shell Chemical Company and 3.0 parts of a 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl - 4 - hydroxybenzyl) benzene stabilizer were added slowly in order to prevent the formation of lumps. Heating and stirring were continued until a homogeneous mass was obtained whereupon 22.5 additional parts of rosin dimer and 20 parts of paraffin wax having a melting point of 150° F. were admixed therewith; the presence of the paraffin wax serving to reduce the melt viscosity of the system.

The resulting homogeneous hot melt composition had a melt viscosity of 10,000 centipoises (cps.) at 350° F., as determined by a Brookfield Viscometer using a #6 spindle at 20 r.p.m. Upon coating the above prepared molten hot melt composition onto the edges of compressed sheets of paper, an adhesive film was formed which, upon setting or cooling, produced an excellent spine binding for the various sheets.

In order to further demonstrate the applicability of the above prepared hot melt to a perfect binding operation, it was subjected to the following test procedures:

Low temperature flexibility.—The molten hot melt was cast, by means of a heated Bird applicator, onto a polytetrafluoroethylene-coated steel sheet yielding a film having a dry film thickness of 20 mils. After cooling, the film specimen was stripped from the plate and cut into ½ x 2 inch test specimens. A representative specimen was then placed in a temperature controlled, carbon dioxide cabinet for a period of 10 minutes whereupon it was immedi-

ately flexed at a 30° angle. Where the specimen did not crack as a result of this procedure, a second identical specimen was placed in the cabinet at a lower temperature and the flexing procedure repeated. The temperature at which the specimen eventually cracked was thus viewed as its "low temperature flexibility" value. Thus, as the latter value is decreased, there is a corresponding increase in the flexibility and stability which can be expected upon exposing these films and the books bound therewith to low temperature conditions.

Tensile strength.—This property was determined on films cast from the hot melts according to Test Method A of ASTM procedure D882–56T utilizing an Instron Tensile Tester; the latter films having been prepared according to the method set forth in the above described "Low Temperature Flexibility" test.

Warm flow.—The hot melt adhesive was utilized, as in the previously described perfect binding procedure, in order to prepare two perfect bound books. The resulting books were then opened at identical pages and parted till the backbone was exposed. Thereafter, the front and back cover of each book were placed back-to-back to one another and maintained in that position by means of a rubber band which was positioned around the length of the book. The thus conditioned books were placed in an oven set at a temperature of 100° F. for a period of 24 hours, whereupon they were examined in order to determine whether their adhesive spines had failed, i.e. whether they had distorted to the point that the books fell apart. Books that survived this initial test were then subjected to increasingly higher temperatures.

Cold crack.—Four perfect bound books, prepared as in the "Warm Flow" procedure hereinabove, were placed in a refrigerator set at a temperature of 40° F. for a period of 16 hours whereupon they were removed and immediately opened back-to-back in the center of the book. A record was kept of the number of books that cracked as a result of the flexing procedure. Books that did not crack were thereafter exposed to lower temperatures and the flexing procedure repeated.

Films derived from the hot melt adhesive whose preparation was described in this example exhibited a tensile strength of 730 p.s.i. and a low temperature flexibility value below —50° F. The "warm flow" and "cold crack" values of the latter hot melt are presented in the following table. The table also presents the results obtained from submitting two commercially utilized bookbinding adhesives to the identical test procedures.

	Warm flow (No. of book failures)		Cold crack (No. of book failures)		
Adhesive composition	16 hours at 100° F.	48 hours at 120° F.	16 hours at 40° F.	6 hours at 35° F.	48 hours at 35° F.
Hot melt described hereinabove.	0 of 2	0 of 2	0 of 4	0 of 4	0 of 4.
Polyvinyl acetate-based hot melt.	2 of 2		3 of 4	4 of 4	
Ethylenevinyl acetate-based hot melt.	0 of 2	0 of 2	0 of 4	2 of 4	4 of 4.

It is thus evident that the hot melt compositions utilized in the process of this invention are particularly well-suited for used in the perfect binding of books.

EXAMPLE II

This example illustrates the preparation of a number of hot melts of this invention utilizing a variety of block polymers, tackifying resins, stabilizers and wax diluents. It also illustrates the applicability of these hot melts to the perfect binding operation.

The general procedure set forth in Example I, hereinabove, was utilized in preparing each of the following hot melt compositions. The characteristics of the resulting hot melts were then determined by submitting the compositions to one or more of the following test procedures:

Melt viscosity.—Determined at 350° F. on a Brookfield Viscometer using a #6 spindle at 20 r.p.m., unless otherwise indicated.

Tensile strength.—Determined by means of the procedure described in Example I.

Elongation.—This property is defined as the percentage increase in the length of the test specimen which is observed during the tensile strength determination prior to the breaking of the film specimen. Higher elongation values are indicative of excellent rubbery characteristics in the hot melt and of increased film continuity as well as of an increased ease with which books bound with the particular hot melt composition may be opened.

Warm flow.—Determined by means of the procedure described in Example I.

Cold crack.—Determined by means of the procedure described in Example I.

Composition A

	Parts
Styrene-butadiene-styrene block polymer (Kraton 102)	40
Polyterpene resin—ASTM softening point of 115° C.	30
Paraffn wax—melting point of 150° F.	30
Pentaerythrityl tetrakis - 3(3,5-di-tert-butyl - 4 - hydroxyphenyl)propionate	2
Distearylthiodipropionate	0.5
Calcium salt of ethylenediamine tetraacetic acid	0.25

Melt viscosity—9125 cps.

Composition B

	Parts
Styrene-buatdiene-styrene block polymer (Kraton 102)	40
Chlorinated terphenyl resin containing 60%, by wt., of chlorine	30
Parraffin wax—melting point of 150° F.	30
n-Octadecyl 3(3,5-di-tert-butyl - 4 - hydroxyphenyl) propionate	2
Tri(mixed mono- and dinonylphenyl)phosphite	0.5

Melt viscosity—13,000 cps.
Tensile strength—635 p.s.i.

Composition C

	Parts
Styrene-isoprene-styrene block polymer	50
Rosin dimer	25
Paraffin wax—melting point of 150° F.	25
1,3,5 - trimethyl - 2,4,6-tris(3,5 - di-tert-butyl - 4 - hydroxybenzyl)benzene	2
Distearylthiodipropionate	0.5

Melt viscosity—12,750 cps.
Tensile strength—220 p.s.i.

Composition D

	Parts
Styrene-butadiene-styrene block polymer (Kraton 102)	37.5
Rosin dimer	37.5
Paraffin wax—melting point of 150° F.	25.0
1,3,5-trimethyl-2,4,6-tris(3,5 - di - tert - butyl - 4-hydroxybenzyl)benzene	3.0

Melt viscosity—8,500 cps.
Tensile strength—500 p.s.i.
Warm flow (16 hrs. at 100° F.)—0 of 2.
Cold crack (6 hrs. at 35° F.)—0 of 4.

Composition E

	Parts
Styrene-butadiene-styrene block polymer (Kraton 101)	37.5
Pentaerythritol ester of stabilized rosin	37.5
Microcrystalline wax—melting point of 195° F.	25.0
1,3,5-trimethyl-2,4,6 - tris(3,5 - di - tert.butyl - 4-hydroxy benzyl)benzene	3.0

Melt viscosity—30,750 cps.
Tensile strength—210 p.s.i.

Composition F

	Parts
Styrene-butadiene-styrene block polymer (Kraton 102)	40
Phenolic-modified terpene resin	35
Paraffin wax—melting point of 150° F.	20
Microcrystalline wax—melting point of 195° F.	5
4,4'-methylenebis (2,6-di-tert-butyl phenol)	2

Melt viscosity—17,750 cps.
Tensile strength—920 p.s.i.
Elongation—2400%.

Composition G

	Parts
Styrene-butadiene-styrene block polymer (Kraton 102)	40
Aliphatic petroleum hydrocarbon resin—Ball and Ring softening point of 100° C.	35
Paraffin wax—melting point of 150° F.	20
Microcrystalline wax—melting point of 195° F.	5
2,2'-methylenebis(4-methyl-6-tert-butylphenol)	3
Disalicylalpropylenediimine	0.25

Melt viscosity—23,500 cps.
Tensile strength—880 p.s.i.
Elongation—3400%.

Composition H

	Parts
Styrene-isoprene-styrene block polymer (Kraton 107)	35
Rosin dimer	45
Polyethylene grease—softening point of 195° F. and a hardness value of 80	20
2,2'methylenebis(4-methyl-6-tert-butyl phenol)	2

Melt viscosity—23,625 cps.
Tensile strength—530 p.s.i.
Elongation—5000%.

Composition I

	Parts
Styrene-isoprene-styrene block polymer (Kraton 107)	35
Rosin dimer	45
Paraffin wax—melting point of 150° F.	20
n-Octadecyl 3(3,5-di-tert-butyl-4 - hydroxyphenyl) propionate	2
Distearylthiodipropionate	0.5
Calcium salt of ethylenediamine tetraacetic acid	0.25

Melt viscosity—12,175 cps.
Tensile strength—320 p.s.i.
Elongation—5000%.

Composition J

	Parts
Styrene-isoprene-styrene block polymer (Kraton 84–0554)	40
Polyterpene resin — ASTM softening point of 115° C.	35
Paraffin wax—melting point of 150° F.	20
Microcrystalline wax—melting point of 190° F.	5
4,4'-methylenebis (2,6-di-tert-butylphenol)	4

Melt viscosity—1500 cps.
Tensile strength—810 p.s.i.
Elongation—>5000%.

Summarizing, it is seen from the testing data presented above that this invention provides the practitioner with improved adhesive compositions for use in the perfect binding of books.

Variations may be made in proportions, procedures and materials without departing from the scope of this invention which is defined by the following claims.

We claim:

1. In the process of binding books containing a plurality of sheets by means of the perfect binding method, the steps for producing a spine for said books which comprise;

(A) applying to the secured edges of said sheets a molten film of a hot melt non-pressure sensitive adhesive composition consisting essentially of a blend of: (1) a block polymer having the general configuration

A-B-A

wherein A is a non-elastomeric polymer block derived from the moieties of a monovinyl aromatic hydrocarbon monomer, and B is an elastomeric polymer block derived from the moieties of a conjugated diene monomer; (2) at least one tackifying resin; (3) at least one stabilizer for said block polymer; and, (4) at least one wax diluent selected from the group consisting of polyethylene having a molecular weight of from about 1,000 to 6,000, petroleum waxes, atactic polypropylene, and Fischer-Tropsch wax, said wax diluent being a solid at room temperature;

(B) applying a cover to said film while the latter is still in molten state; and

(C) allowing said film to solidify.

2. The process of claim 1, wherein said hot melt adhesive composition is applied at a temperature of from about 300 to 400° F. and at a melt viscosity of from about 5,000 to 30,000 centipoises.

3. The process of claim 1, wherein said block polymer is present in said adhesive composition in a concentration of from about 20 to 50%, said tackifying resin is present in a concentration of from about 20 to 59%, said stabilizer is present in a concentration of from about 1 to 4%, and, said wax diluent is present in a concentration of from about 20 to 50%; the latter concentrations all being based on the total weight of said adhesive composition.

4. The process of claim 1, wherein step (B) is omitted and the cover is not directly adhered to the spine.

5. The process of claim 1, wherein said tackifying resin in said adhesive composition is selected from the group consisting of natural and modified rosins; glycerol esters of natural and modified rosins; pentaerythritol esters of natural and modified rosins; polyterpene resins having an ASTM softening point of from about 80 to 150° C.; chlorinated terphenyl resins containing from about 42 to 60%, by weight, of chlorine; phenolic-modified terpene resins; and, aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from about 70 to 135° C.; and, wherein said stabilizer is a hindered phenol.

6. The process of claim 1, wherein the monovinyl aromatic hydrocarbon monomer moieties in said block polymer are derived from styrene and the conjugated diene monomer moieties are derived from the group of monomers consisting of butadiene-1,3 and isoprene.

7. A perfect bound book comprising a plurality of sheets and a cover therefor which is adhesively bound to the edges of said sheets by means of the dried residue of a hot melt non-pressure sensitive adhesive composition consisting essentially of a blend of: (1) a block polymer having the general configuration

A-B-A

wherein A is a non-elestomeric polymer block derived from the moieties of a monovinyl aromatic hydrocarbon monomer, and B is an elastomeric polymer block derived from the moieties of a conjugated diene monomer; (2) at least one tackifying resin; (3) at least one stabilizer for said block polymer; and, (4) at least one wax diluent selected from the group consisting of polyethylene having a molecular weight of from about 1,000 to 6,000, petroleum waxes, atactic polypropylene, and Fischer-Tropsch wax, said wax diluent being a solid at room temperature.

8. The perfect bound book of claim 7 wherein the melt viscosity of said adhesive composition is in the range of from about 5,000 to 30,000 centipoises at a temperature of from about 300 to 400° F.

9. The prefect bound book of claim 7, wherein said random block polymer is present in said adhesive composition in a concentration of from about 20 to 50%, said tackifying resin is present in a concentration of from about 20 to 59%, said stabilizer is present in a concentration of from about 1 to 4%, and said wax diluent is present in a concentration of from about 20 to 50%; the latter concentrations all being based on the total weight of said adhesive composition.

10. The perfect bound book of claim 7, wherein the monovinyl aromatic hydrocarbon monomer moieties in said block polymer are derived from styrene and the conjugated diene monomer moieties are derived from the group of monomers consisting of butadiene-1,3 and isoprene.

11. The perfect bound book of claim 7, wherein said tackifying resin in said adhesive composition is selected from the group consisting of natural and modified rosins; glycerol esters of natural and modified rosins; pentaerythritol esters of natural and modified rosins; polyterpene resins having an ASTM softening point of from about 80 to 150° C.; chlorinated terphenyl resins containing from about 42 to 60%, by weight, of chlorine; phenolic-modified terpene resins; and, aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from about 70 to 135° C.; and, wherein said stabilizer is a hindered phenol.

12. A perfect bound book comprising a plurality of sheets, the edges of said sheets being adhesively bound by means of the dried residue of a hot melt non-pressure sensitive adhesive composition comprising a blend of: (1) a block polymer having the general configuration

A-B-A

wherein A is a non-elastomeric polymer block derived from the moieties of a monovinyl aromatic hydrocarbon monomer, and B is an elastomeric polymer block derived from the moieties of a conjugated diene monomer; (2) at least one tackifying resin; (3) at least one stabilizer for said block polymer; and (4) at least one wax diluent selected from the group consisting of polyethylene having a molecular weight of from about 1,000 to 6,000, petroleum waxes, atactic polypropylene, and Fischer-Tropsch wax, said wax diluent being a solid at room temperature.

References Cited

UNITED STATES PATENTS

1,858,685	5/1932	Semon	281—21
3,239,478	3/1966	Harlan	260—27
3,262,996	7/1966	Kurtz et al.	260—28.5
3,265,765	8/1966	Holden et al.	260—28.5
3,292,951	12/1966	Schoenberger	281—21
3,390,035	6/1968	Sands	156—334
3,632,540	1/1972	Unmuth et al.	260—27

CHARLES E. VAN HORN, Primary Examiner

R. A. DAWSON, Assistant Examiner

U.S. Cl. X.R.

11—1 AD; 156—334; 161—69, 250, 255; 260—27 BB, 28.5 B, 876 B; 281—21 R