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BOOKBINDING ADHESIVES AND A METHOD OF APPLYING SAME

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This invention relates to the art of book-binding, and more particularly to hot melt adhesives for use therein.

It will be understood that, where the word "book" is used herein, this includes magazines, pamphlets, writing tablets, and similar articles, as well as books themselves.

The leaves of books and similar articles of manufacture are customarily bound together by stitching with cord or by stapling. However, the former method is expensive and time-consuming and requires complicated and expensive machinery, as well as excessive storage space for intermediate steps in the manufacture. Furthermore, such bindings are not permanent since the stitching cord deteriorates during shelf storage and may be so weakened by normal use as to loosen or break and require re-binding. The stapling method, on the other hand, limits the thickness of the book, for, if the book is of substantial thickness, the center pages are insecurely bound and frequently fall out. Cheap books and pamphlets have also been made in which the leaves are embedded in an adhesive, but the adhesives heretofore used are not resistant to attack by molds, are adversely affected by moisture, and eventually fail by becoming brittle. Such adhesives have the further disadvantage of varying greatly in "setting" speed under conditions of fluctuating humidity, resulting in considerable loss of production during the manufacture of books on high speed mechanical equipment.

An object of the present invention is to provide books with an improved and permanent binding. Another object is the provision of a simple and efficient process for binding the edges of pages of paper to form a book. Still another object is the provision of a process which eliminates the need for stitching or stapling and which may be carried out with less skilled labor to produce a bookbinding at least as permanent as the highest quality stitched binding. A further object is the provision of a bookbinding process which speeds production and reduces the storage space needed between operational steps in book manufacture. Another object is the provision of a bookbinding process which does not limit the thickness of the book produced. Another object is an improved binding medium which does not cause mechanical or chemical deterioration of the paper. A further object is a binding medium which is waterproof, is unaffected by long exposure to moisture and air, and will withstand severe and numerous flexings. A still further object is the provision of a binding medium which

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is tough and flexible at high and low temperatures. Other objects will become apparent as the description proceeds.

These objects are accomplished by applying a permanently flexible, waterproof, tough, thermoplastic adhesive composition to the binding edges of a plurality of paper sheets to form a strong, adhesive, continuous film over the entire surface of these edges and with good penetration of the interstices between the fibers at the paper edges, as well as between the individual sheets, thus contributing to the greater overall strength of the binding.

In the preferred embodiment of the invention the thermoplastic adhesive composition comprises a hydrous ethanol soluble polyamide and a compatible liquefying softener and is applied in two steps, first as warm (125° F.) primer solution containing 20–40% by weight of adhesive in 80% ethanol, and second (immediately thereafter) as a volatile solvent-free hot melt coating applied at about 320° F.

Three different types of polyamides have been found useful in the adhesives of this invention.

Polyamide A is described in Brubaker et al. 2,285,009. This polyamide is formed by reacting hexamethylenediammonium adipate and hexamethylenediammonium sebacate with caprolactam or with 6-amino-caproic acid, or by reacting hexamethylenediammonium adipate, hexamethylenediammonium sebacate, 6-amino-caproic acid, and a mixture of hexamethylenediammonium suberate and hexamethylenediammonium azelate.

Polyamide B is disclosed in a co-pending application of Cairns, Serial Number 539,195, filed June 7, 1944, now Patent 2,430,860, granted November 18, 1947, and assigned to the assignee hereof. This polyamide is produced by reacting a linear polyamide, having an intrinsic viscosity of at least 0.4 and containing hydrogen-bearing amide groups as an integral part of the main polymer chain, with formaldehyde and a formaldehyde-reactive organic compound having hydrogen attached to an element of groups V and VI of series 2 and 3 of the periodic table, particularly an alcohol or a mercaptan, in the presence of a catalyst.

The term "intrinsic viscosity" used herein is defined as

$$\frac{\log_e \lambda r}{C}$$

in which λr is the viscosity of a dilute solution (e. g., 0.5% concentration) of the polymer in m-cresol divided by the viscosity of m-cresol in the same units and at the same temperature

(e. g., 25° centigrade) and C is the concentration in grams of polymer per 100 cc. of solution.

Polyamide C is disclosed in Carothers 2,130,523, and Frosh 2,388,035, and comprises a polyhexamethylene sebacamide in which 50% of the amide groups are alkylated by isobutyl groups, the distribution of alkyl groups being substantially that obtained by using approximately 40% diprimary, 20% primary-secondary, and 40% disecondary diamines in the preparation of the polyamide.

All three of these types of polyamides are characterized by being soluble to at least 15% in hot 80% ethanol, and by having a high degree of pliability.

Although the bookbinding adhesives of my invention may be produced by using any of the three types of polyamides described above, polyamide A is preferred.

The term "liquefying softener" is used herein to describe the property possessed by certain softeners, or solvent plasticizers, of accelerating the normal melting rate of the special polyamides and lowering their fluid temperature to a practical level.

The following examples are given by way of illustration.

Example 1

	Per cent by weight
Coumarone indene-phenolic condensate ("Nevillac" TS)	35
Resorcinol (technical grade)	5
Polyamide A	60
	100

The composition was prepared by charging the first portion into an oil-jacketed paddle mixer, heating to about 320° F., and slowly adding the polyamide with agitation until a homogeneous hot melt solution was obtained.

An assembly of about 200 pages was tightly clamped between two parallel flat plates, with about ⅛ inch of the binding edge of the assembly exposed. After roughing the binding edges slightly with a sharp saw blade, a prime coat of a 30% solution by weight of the composition of Example 1 in 80% ethanol heated to 125° F. was applied with a brush. The excess was immediately scraped off and the primed area allowed to dry for about three seconds. A knife coating of the composition of Example 1 heated to 320° F. was applied immediately thereafter. The coating was permitted to cool for a few seconds and the pressure means were then removed. The binding was already sufficiently strong for all ordinary handling, including trimming of the pages. After standing for two days, during which period the plastic melt set up to a hard film, the binding was exceptionally strong, as pages could only be removed by tearing the paper, there being no separation at the juncture of the edges of the pages and the adhesive coating. The latter was tough and flexible and withstood repeated flexing and hard usage. The binding was completely waterproof, and remained unaffected in usefulness over the temperature range of 0°–150° F.

Example 2

	Per cent by weight
Chlorinated diphenyl (40–65% Cl)	46
Polyamide C	54
	100

This composition was prepared by mixing the ingredients in an oil-jacketed paddle mixer and heating to about 160° C. with agitation until a homogeneous hot melt solution was obtained. The hot melt solution was then applied to the binding edge of a book over a prime coat comprised of a 30% solution of the composition of Example 2 in 80% ethanol in the same manner as described in Example 1. This binding was fully as tough and strong as that described above, but even more flexible and resilient. The binding was allowed to cool, and, in contrast to Example 1, after one or two minutes, it had reached its maximum strength.

Example 3

	Per cent by weight
Coumarone indene-phenolic condensate ("Nevillac" OA)	45
Polyamide C	55
	100

This composition was prepared in a manner similar to that of Example 2 and applied as described in Example 1, again using a primer prepared as above from the composition under test. This binding was somewhat "softer" and more flexible than those described above, but otherwise equal in all respects.

Example 4

	Per cent by weight
Coumarone indene-phenolic condensate ("Nevillac" TS)	35
Polyamide B	65
	100

This composition was prepared in a manner similar to that of Example 2 and applied on its individual primer as described in the previous examples. This binding was very soft and flexible but still retained sufficient toughness to permit its use for binding periodicals and the like.

Example 5

	Per cent by weight
Diamyl benzene sulphonamide	45
Polyamide A	55
	100

This composition was prepared in a manner similar to that of Example 2 and applied over its individual primer as described in the previous examples. This binding "set" after 48 hours to a remarkably tough and leathery state. Its shape-retaining characteristics were equal to Examples 1 and 2.

Example 6

	Per cent by weight
Octyl phenol	45
Polyamide A	55
	100

This composition was prepared in a manner similar to that of Example 2 and applied over its individual primer as described in the previous examples. A highly tough and resilient binding was produced which was suitable for periodicals and the like.

Pages prepared as above, wherein the generally unsatisfactory stapling method or the expensive, time-consuming step of stitching is dispensed with, may then be combined with a suit-

able cover to form a book by methods customarily employed; in some cases, prior to adding the outside cover, a fabric reinforcement is placed over the film of adhesive and embedded therein while the latter is hot and sufficiently softened or tacky to be receptive and adherent to the fabric layer.

In commercial use, the pages may be assembled between flat metal plates held together under pressure and adjusted to leave about $\frac{1}{16}$ inch to $\frac{1}{4}$ inch of the edges exposed after they are trimmed. The assembled pages are then passed through a cutter to trim the edges, and then to "roughers" to open up the fibers at the edges of the pages to make them more receptive to the adhesive composition, so it will slightly penetrate into the interstices. The edges are next brushed with rotating brushes to remove any loose fibers resulting from the roughing operation. The edges of the pages are then coated with a warmed (125° F.) liquid primer consisting of a solution of the hot melt adhesive in 80% ethanol, the surface excess removed with flexible scrapers, and then the hot melt itself is applied at about 320° F. by a conventional revolving applicator consisting of a flat-surfaced wheel about one-half immersed in the hot melt composition. The thickness of the adhesive film applied is regulated by an adjustable scraper knife. If additional reinforcement is desired, a sheet of fabric, such as cheesecloth, may be pressed into the surface of the applied adhesive film while the latter is still hot. The outside book cover is finally combined with the improved cemented book pages by conventional means.

A modification of this process involves preheating the binding edges to a temperature higher than the adhesive application temperature, and then immediately applying the hot melt at 320° F. without the use of primer. The resultant binding penetrates the paper almost as well as where a liquid primer is used, and for many purposes will be satisfactory. Fabric reinforcement and/or the outside book cover may then be applied as described above.

The proportion of polyamide to compatible liquefying softener is limited by the maximum viscosity of the melt, which must be held at about 320° F. (higher temperatures are quite possible, but at the expense of pot stability), and by the minimum degree of toughness and tensile strength required at temperatures (0°–150° F.) in which a bookbinding adhesive might conceivably be used. The examples illustrate compositions formulated to give good application viscosities with excellent stability at 320° F., as well as films of high tensile strength, toughness, and flexibility in the range of 0°–150° F. It is essential that the ratio of polyamide to softener be between 45:55 and 65:35. Ratios higher or lower than these appreciably affect either application viscosity or room temperature toughness.

The liquefying softeners disclosed above function primarily to cause rapid melting of the adhesive composition to a mobile liquid state above about 265° F. without detracting greatly from the natural toughness and tensile strength of the polyamide resin film at room temperature.

Nonyl phenol, decyl phenol, diamyl phenol and other substituted phenols and related substances are also suitable for use as liquefying softeners for the polyamide hot melts of this invention.

For most purposes, about 3 mils to 10 mils film thickness of final adhesive film gives the superior binding properties provided in the present invention. This film thickness may be conveniently obtained by applying the adhesive composition at about 200 to 500 poises viscosity. This is obtained and controlled by heating the composition to proper temperature; for example, 320° F. for the compositions of the examples.

The invention is characterized by numerous valuable advantages. Of primary importance is the elimination of the time-consuming and expensive stitching operation for binding book pages. The new binding means is permanently flexible and tough and will not deteriorate from long exposure to air and variations in temperature. Due to the high degree of flexibility and elasticity of the new adhesive compositions, they will successfully withstand the severe rounding and backing operations required in the manufacture of hard bound books. They are also waterproof, and are unaffected by exposure to high humidity. Complicated machinery and highly skilled labor are not required in the process of the present invention, thus contributing to the appreciable economies which may be realized in the manufacture of the improved book construction. Books and like articles bound by the new means are more generally durable and will withstand severe usage for longer periods than books bound by prior adhesive methods. Less manufacturing space is needed since, in contradistinction to earlier methods requiring stitching, there is no delay at any point in the operational steps in the improved binding process.

It will be apparent that many widely different embodiments of this invention can be made without departing from the spirit and scope thereof; and, therefore, it is not intended to be limited except as indicated in the appended claims.

I claim:

1. A solvent-free, hot melt adhesive composition particularly adapted for binding books, comprising an ethanol-soluble synthetic linear polyamide having an intrinsic viscosity of at least 0.4 and containing amide groups separated by an average of at least two carbon atoms as an integral part of the main polymer chain and a compatible liquefying softener therefor, the ratio of polyamide to softener being between 45:55 and 65:35.

2. The composition of claim 1, in which the polyamide is the reaction product of hexamethylenediammonium adipate, hexamethylenediammonium sebacate, and caprolactam.

3. The composition of claim 1, in which the polyamide is the reaction product of a linear polyamide, which has an intrinsic viscosity of at least 0.4 and contains hydrogen-bearing amide groups as an integral part of the main polymer chain, with formaldehyde and a formaldehyde-reactive organic compound having hydrogen attached to an element of groups V and VI of series 2 and 3 of the periodic table, in the presence of a catalyst.

4. The composition of claim 1, in which the polyamide is a polyhexamethylene sebacamide in which 50% of the amide groups are alkylated by isobutyl groups and which is obtained from a mixture of approximately 40% diprimary, 20% primary-secondary, and 40% disecondary diamines.

5. The composition of claim 1, in which the liquefying softener is a coumarone indene-phenolic condensation product.

6. The composition of claim 1, in which the liquefying softener is comprised of 87 parts of

a coumarone indene-phenolic condensation product and 13 parts of resorcinol.

7. The composition of claim 1, in which the liquefying softener is chlorinated diphenyl.

8. The composition of claim 1, in which the liquefying softener is diamyl benzene sulphonamide.

9. A process for binding books without stitching or stapling, which comprises clamping together under pressure, with a small portion of the binding edges exposed, the pages which are to form a book, coating the exposed binding edges with a warm primer composition comprising a synthetic linear polyamide having an intrinsic viscosity of at least 0.4 and containing amide groups separated by an average of at least two carbon atoms as an integral part of the main polymer chain and being soluble in 80% ethanol, a compatible liquefying softener, and a volatile solvent therefor, removing substantially all unabsorbed coating, evaporating the volatile solvent, and applying at about 320° F. a solvent-free, hot melt adhesive to the primer coated edges of the paper, said adhesive comprising a synthetic linear polyamide having the same characteristics as that above and a compatible liquefying softener, the ratio of polyamide to softener in both the primer composition and the hot melt adhesive being between 45:55 and 65:35.

10. The process of claim 9 in which the polyamide is the reaction product of hexamethylenediammonium adipate, hexamethylenediammonium sebacate, and caprolactam.

11. The process of claim 9, in which the liquefying softener is a coumarone indene-phenolic condensation product.

12. A process for binding books without stitching or stapling, which comprises clamping together under pressure, with a small portion of the binding edges exposed, the pages which are to form a book, roughing the exposed binding edges, coating said binding edges with a warm primer composition, comprising a synthetic linear polyamide having an intrinsic viscosity of at least 0.4 and containing amide groups separated by an average of at least two carbon atoms as an integral part of the main polymer chain and being soluble in 80% ethanol, a compatible liquefying softener, and a volatile solvent therefor, removing substantially all unabsorbed coating, evaporating the volatile solvent, and applying at above 320° F. a solvent-free, hot melt adhesive to the primer coated edges of the paper, said adhesive comprising a synthetic linear polyamide having the same characteristics as that above and a compatible liquefying softener, the ratio of polyamide to softener in both the primer composition and the hot melt adhesive being between 45:55 and 65:35.

13. A process for binding books without stitching or stapling, which comprises clamping together under pressure, with a small portion of the binding edges exposed, the pages which are to form a book, preheating the exposed binding edges, and applying at about 320° F. a solvent-free, hot melt adhesive to the exposed edges, said adhesive comprising a synthetic linear polyamide having an intrinsic viscosity of at least 0.4 and containing amide groups separated by an average of at least two carbon atoms as an integral part of the main polymer chain and being soluble in 80% ethanol and a compatible liquefying softener therefor, the ratio of polyamide to softener being between 45:55 and 65:35 and the temperature of the preheating treatment being higher than the hot melt application temperature.

14. The process of claim 13, in which the polyamide is the reaction product of hexamethylenediammonium adipate, hexamethylenediammonium sebacate, and caprolactam.

15. An article of manufacture, having a plurality of pages bound together by a solvent-free, hot melt adhesive composition comprising a synthetic linear polyamide having an intrinsic viscosity of at least 0.4 and containing amide groups separated by an average of at least two carbon atoms as an integral part of the main polymer chain and being soluble in 80% ethanol and a compatible liquefying softener for the said polyamide, the ratio of polyamide to softener being between 45:55 and 65:35.

16. A book having its pages embedded in a matrix of an adhesive and a cover firmly bonded thereto, the said adhesive being self-sufficient as the sole binding means and consisting of a substantially solvent-free composition containing a synthetic linear polyamide having an intrinsic viscosity of at least 0.4 and containing amide groups separated by an average of at least two carbon atoms as an integral part of the main polymer chain, and being soluble in 80% ethanol; and a compatible liquefying softener for the said polyamide, the ratio of the said polyamide to the said liquefying softener being within the range of 45 to 55 and 65 to 35.

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