PATENT SPECIFICATION (11) 1 587 525

1 587 525

(21) Application No. 41584/77 (22) Filed 6 October 1977
(44) Complete Specification published 8 April 1981
(51) INT. CL.[3] C09K 3/00 C08K 3/16 // B32B 5/14
(52) Index at acceptance
C3V AT
B5N 0514
B8F BF
C3W 114 121 122 215 221 225 301 302 324
C3Y B230 B249 B404 G370

(72) Inventors: BENJAMIN JOHN TAYLOR
ROBERT MICHAEL LACY

(19)

(54) IMPROVEMENTS IN OR RELATING TO ADHESIVE PRODUCTS HAVING PROTECTIVE BACKINGS POSSESSING EMBRITTLED ZONES, AND THEIR MANUFACTURE

(71) We, AVERY INTERNATIONAL CORPORATION, a Corporation organised and existing under the laws of the State of Delaware, United States of America, residing at 415 Huntington Drive, San Marino, California 91108, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:–

The present invention relates to adhesive products such as label stock, labels, tapes, and the like and more particularly to adhesive products and their manufacture in which protective backings thereof are provided with embrittled zones that aid in removing the backing from the adhesive.

Many adhesive products, particularly those having pressure sensitive adhesives, are provided with a backing which is secured to the surface of the adhesive and which protects the adhesive before use. It is known to provide embrittled zones in the form of thin lines running across the backing of such adhesive products. When the adhesive product is sharply flexed along an embrittled line, the backing cracks along the line and the newly-formed edges of the backing lift up off of the adhesive layer, thereby offering gripping points for peeling the backing from the adhesive. Embrittled zones that are not sharply flexed preferably have sufficient tensile strength to permit removal in one continuous piece of a portion of backing having one or more of such embrittled zones. In this case, when two or more embrittled zones are present in the backing of a label, one of the zones can be cracked selectively and the backing can be removed in only two pieces. Until the flexing operation occurs however, the adhesive surface is protected and contained by the backing. The embrittled zones are integral with the backing and serve to protect and contain the adhesive until cracked.

U.S. Patent 3,035,957 to which reference is directed describes one such adhesive product having a fibrous backing with embrittled zones. The embrittled zones are produced by applying heat, a flame, a chemical substance such as sulfuric acid, ultraviolet radiation, or the like to partially degrade or decompose a portion of the fibrous backing. U.S. Patent 3,006,793 to which reference is also directed describes adhesive products in which embrittled zones extend diagonally across the backing from edge to edge. In one embodiment, the embrittled zones are produced by applying a chemical embrittling agent such as an aqueous solution of sulfuric acid with the use of a printing roll having raised helical printing ridges.

When an acidic solution is used to form the embrittled zones, a problem is encountered. Residual acid remains in the backing even when a volatile acid, such as hydrochloric acid, is used. When label stock having these acid embrittled zones is tolled or stacked for transfer to a label printer, for example, the backing of one layer of label stock comes into contact with the face of another layer of label stock. Residual acid tends to be transferred from embrittled zones of the backing to the face of the adjacent label stock and changes the printing characteristics of the face. When ink is subsequently applied to the label face in a printing operation, the portions of the label affected by the residual acid take on a color or intensity of color different from that of the surrounding regions. The effect is typically seen as a line of lighter or contrasting color running across the face of the printed label. The degree of this effect depends upon the chemical nature of the ink used. Some inks are so sensitive to the acid-caused changes that they cannot be used with the acid-embrittled adhesive products of the prior art.

Another problem encountered in the manufacture of the prior art products is the need to balance carefully the degree of brittleness and the tensile strength of the embrittled zones to provide a balance between good cracking per-

formance upon flexing and avoidance of unwanted cracking.

It has now been found *inter alia* that presence of a brittle, film-forming organic polymer apparently suffused into the embrittled zones, that is, between and among the fibers of the zones and not merely on the surface of the zones, may enhance the brittleness and the crackability of the embrittled zones and retard the transfer from embrittled zones of an adhesive product backing to a surface of any residual chemical embrittling agent in contact therewith, e.g. from the backing of one sheet of label stock to the face of another in a stack.

The polymer should be sufficiently brittle for the backing to crack cleanly along the embrittled zones without any bridging.

The invention provides an adhesive laminate comprising a facestock, an adhesive layer on the facestock, and a removable fibrous backing in contact with the adhesive layer, the backing having at least one narrow embrittled zone integrally included in the backing, and the embrittled zone comprising an organic, brittle film-forming polymer.

The invention also provides a process for the production of an adhesive laminate comprising a facestock, an adhesive layer on the facestock, and a removable fibrous backing, with the fibrous backing having at least one embrittled zone, which process comprises: (a) applying to a narrow portion of the fibrous backing an aqueous embrittling composition containing 1 to 15 weight percent of a volatile chemical embrittling agent capable of embrittling the backing when the composition is applied thereto and is dried by heating, and an organic, brittle film-forming polymer in emulsion form; and (b) curing and drying the applied composition at 150° to 250°C to form a narrow embrittled zone comprising said brittle polymer.

The invention also provides a process for the production of an adhesive laminate comprising a facestock, an adhesive layer on the facestock, and a removable fibrous backing in contact with the adhesive layer, in which the backing is treated to form at least one narrow, integral embrittled zone therein, and an organic, brittle film-forming polymer is introduced into the embrittled zone.

The invention also provides an aqueous composition for providing an embrittled zone and a brittle polymer film deposit thereat on a removable fibrous backing of an adhesive laminate comprising also a facestock, and an adhesive layer on the facestock, the fibrous backing being in contact with the adhesive layer, which composition comprises (a) from 1 to 15 weight percent of a volatile chemical embrittling agent capable of embrittling zones of the backing when the composition is applied to the backing and is dried by heating, and (b) an organic, brittle film-forming polymer that remains as a brittle film in the embrittled zones after the composition is dried.

The invention also provides an aqueous composition for providing an embrittled zone and a brittle polymer film deposit thereat on a removable fibrous backing of an adhesive laminate comprising also a facestock, and an adhesive layer on the facestock, the fibrous backing being in contact with the adhesive layer, which composition comprises from 1 to 15 weight percent of hydrogen chloride, from 0.5 to 3 weight percent or an organic thickener, from 0.4 to 1 weight percent of wetting agent, from 0.5 to 2 weight percent of antifoam agent, and from 1 to 10 weight percent of organic, brittle film-forming polymer; the composition being such that when applied to zones of the backing and dried by heating, embrittled zones are formed on the backing, and the polymer penetrates the backing and forms a brittle film which retards the transfer of residual hydrochloric acid from the embrittled zones.

There now follows a description of embodiments of the invention. This description, which is illustrative of product, process and composition aspects of the invention, is given by way of example only, and not by way of limitation of the invention.

Adhesive products embodying the present invention are laminated structures comprising a facestock bearing printed matter, an adhesive layer on the facestock, and a removable fibrous backing in contact with the adhesive layer which protects the adhesive layer before the produced is used; the printed matter is applied after lamination and is on the side of the facestock remote from the adhesive. Examples of facestock include paper plastics and cloth. Examples of adhesive include natural and synthetic rubber-based adhesives, acrylics, and polyurethanes. When elevated curing and drying temperatures are involved, the facestock and adhesive are chosen from materials that can withstand such temperatures. The backing comprises a fibrous material having integral embrittled zones that are embrittled by application of heat, a flame, a chemical substance, or radiation so that the embrittled zones crack upon flexing but retain sufficient tensile strength to maintain the integrity of the backing during ordinary handling, such as removal of the backing from a label. Useful backing materials include paper and cloth, A fibrous backing of paper or a similar cellulosic material is preferred. The side of the backing that contacts the adhesive is typically coated with a release agent such as a silicone to prevent the adhesive from sticking to the removable backing.

The adhesive laminate is first assembled in a known manner. Conveniently, a web of facestock is continuously coated with adhesive and then laminated to the release-coated side of a continuous web of backing; alternatively the adhesive coating is applied to the backing web prior to lamination rather than to the facestock. Then, either in separate operations or

in a combined operation, narrow embrittled zones are formed in the backing and an organic, brittle film-forming polymer is suffused into the embrittled zones. Preferably, substantially all of the polymer in the backing is within the embrittled zones.

As indicated above, the embrittled zones may be formed by the application of heat, for example, by contacting the backing with a flame of hot wire or stylus; by directing an intense beam of radiation such as infrared radiation, visible light, or ultraviolet radiation, at the backing; or by applying a chemical embrittling agent, for example, a solution of an organic or mineral acid such as acetic acid, sulfuric acid or hydrochloric acid. The use of an aqueous solution of hydrochloric acid is preferred because, as described below, the polymer may be incorporated in the acid solution so that the embrittled zones are formed and the polymer is suffused into the zones in a single operation.

The polymer may be introduced into the embrittled zones in a variety of ways. When the embrittled zones are formed by the application of intense heat or radiation, it is desirable to introduce the polymer after the embrittled zones are formed so as to avoid degradation of the polymer by heat or radiation. The polymer may be applied to the embrittled zones by a printing process, as a hot melt or dissolved in an organic solvent or preferably, emuslified in water. The adhesive product with applied polymer is then passed through a heating zone where the polymer penetrates into the backing within the boundaries of embrittled zones and where solvent or water is removed.

The fibrous backings used in the adhesive products include a minor amount, typically less than 10 volume percent, of void volume between and among the fibers of the backing. Apparently polymer is suffused into the backing so as to occupy at least a portion of the void volumes within the boundaries of the embrittled zones, rather than merely lying on the surface. It is indeed preferred to avoid a raised line of polymer protruding above the surface of the backing, because such a raised line can interfere with stacking and printing operations.

The entire backing may be suffused with polymer to assure that the embrittled zones are included, but the cost of materials may render this approach uneconomical.

In a preferred embodiment of this invention, an embrittling composition comprising both a chemical embrittling agent and a polymer is used to form the embrittled zones and to incorporate the polymer into the zones in one operation. Specially preferred is an aqueous embrittling composition comprising a volatile acid, notably hydrochloric acid, and a polymer in emulsion form.

In the practice of this preferred embodiment, the assembled laminate is first dried. An aqueous composition comprising hydrochloric acid and a polymer emulsion is applied to portions of the backing of the dried laminate and the laminate is heated to dry the embrittling zones and form the embrittled zones. The laminate is then passed through a humidification chamber to raise the moisture content of the laminate to prevent curling.

The preferred chemical embrittling composition is an aqueous mixture containing a volatile acid, notably hydrochloric acid, and an acid resistant polymer in emulsion form. To improve the handling properties of the composition, an organic thickening agent and minor amounts of a wetting agent and an anti-foam agent are usually added. The composition contains from 1 to 15 weight percent, preferably from 2 to 5 percent acid. The lower concentrations are preferred in order to minimise problems of acid transfer. The polymer is present in amounts of from 1 to 10 percent by weight of composition preferably from 5 to 7 percent by weight. Sufficient organic thickening agent is added to provide a composition having a desired viscosity that depends upon the method of application used. Between 0.5 and 3 weight percent of thickener is added, preferably between 1 and 2 weight percent. Minor amounts of antifoam agent and wetting agent are used. The antifoam agent is included in amounts of between 0.5 and 2.0 percent preferably 1.percent. The wetting agent is included in amount of between 0.4 and 1 percent, preferably 0.5 percent. The thickener, wetting agent and antifoam agents are added so that the composition can be applied in a controlled manner in the form of narrow zones or lines, preferably between 0.2 and 2 millimetres wide, on the backing of the laminate. Consequently the relative proportions of these ingredients can be varied to provide optimum results with the particular method of application being employed.

During the heating of the laminate to form the embrittled zones, not only the liquid content of the composition evaporates, but also there is a loss of the more volatile solids. Preferably the dry solids remaining in the embrittled zones after the heating are less than 8 percent by weight of the original composition. Higher residual solids in the embrittled zones can leave a raised line of solids above the surface of the backing. The proportion of polymer solids in the total solids of the embrittling composition should advantageously be kept as high as possible.

The embrittling composition is normally prepared in a two stage operation. First, the required water, thickening agent, antifoam agent, wetting agent, and polymer emulsion are combined as a master batch having a higher viscosity than is desired for the working composition. The master batch has a reasonable shelf life for storage. When a new batch of working composition is called for, the required amount of hydrochloric acid is added slowly with agitation. This reduces the viscosity to the desired level, for example, 2,000 to 3,000 centipoises.

The composition when so prepared has a limited service life but normally at least 4 hours. If desired, the polymer may be added to the composition in the second stage of mixing. The acid is added to the composition shortly before use because it gradually hydrolyzes the organic thickener, causing the viscosity of the composition to drop eventually below a useful level.

A wide variety of polymers may be used. Exemplary polymers include plasticized and unplasticized polyvinyl chlorides, polyvinyl alcohols, polyvinyl acetates, styrene acrylate copolymers, and thermoplastic and self-cross linking acrylic polymers. Acrylic polymers tend to be acid sensitive. Polyvinyl acetate polymers are preferred. The polymers are typically added to the embrittling composition in the form of an aqueous emulsion. Useful emulsions are sufficiently acid stable so that the polymer remains in emulsion in the embrittling composition for the normal service life of the solution, for example, at least four hours.

The polymers form films that are brittle at normal ambient temperatures, e.g. 15 to 30°C. The brittleness of the polymer film enhances the brittleness (the crackability) of embrittled zones containing the polymer. When the embrittled zones are formed chemically, for example with acid, the polymers are resistant to the embrittling agent; that is, the polymers are chemically stable in the presence of residual chemical embrittling agent in the embrittled zones and retard the transfer of residual embrittling agent to a surface in contact with the embrittled zones.

It is believed, without intending to be bound by the theory, that the polymers form a film or coating on the fibers of the backing in the embrittled zone to trap residual embrittling agent, e.g. acid, that is present in the fibers, thereby retarding the transfer of the residual acid out of the backing to another surface. The polymer does not exhibit any tackiness after drying or in the presence of high humidity.

The organic thickening agent is sufficiently acid-stable to provide a composition having a working life of at least four hours. Examples of thickening agents include vegetable gums, such as xanthan gum and gum arabic, ethylene oxide polymers, and various cellulose derivatives such as methylcellulose, hydroxypropyl methylcellulose, hydroxybutyl methylcellulose and hydroxyethyl cellulose. Hydroxypropyl methylcellulose is preferred and is normally present in an amount of 1 to 2 weight percent, preferably between 1.2 and 1.4 weight percent. When hydroxypropyl methylcellulose is used as a thickener, a minor amount of ammonia, less than 0.05 weight percent, can be added to the composition in order to help dissolve the thickener.

Examples of wetting agents include anionic sulphosuccinates, alkylarylpolyether alcohols such as isooctyl phenoxy polyethoxy ethanol, ethoxylated nonyl phenol, and naphthalene sulphonates, and conventional antifoam agents such as silicone antifoam agents.

To establish the embrittled zone the laminate is passed as a web preferably under tension in contact with a suitable applicator which applies the embrittling composition. Preferably the applicator is a roller having helical grooves. The grooves receive the composition from a dip bath with excess composition being wiped away from the surface of the roller by a doctor blade in firm contact with the surface of the applicator. Upon contact with the backing of the laminate, the grooves release the embrittling composition to the paper backing.

The pattern produced is a series of parallel lines which traverse the web at some angle to its direction of travel. Spacing between the zones will vary depending upon the size of the label to be cut from the stock and is adjusted to assure that each label cut will have at least one embrittled zone on its backing. Following application of the embrittling composition the web is passed through a curing zone which is maintained at a temperature of from 150 to 250°C preferably from 180 to 200°C. Upon heating, the zones are cured, the lines of embrittlement are established, and the polymer present in the embrittling composition forms a protective film on the fibers of the backing. The web is maintained at the curing temperature for a time between 0.5 and 5 minutes, preferably from 1 to 2 minutes.

The minimum film-forming temperature of the polymer is for example not greater than 50°C; but since, as described above, during curing a temperature of up to 250°C may be achieved, polymers having minimum film-forming temperatures well in excess of 50°C may be feasible.

After the embrittled zones are cured, the web is passed through a moisturizing zone. The moisturizing is conveniently accomplished by passing the web through a chamber maintained at a relative humidity of 90 percent. The resultant moisturized label stock will lie flat for subsequent printing and cutting operations.

WHAT WE CLAIM IS:–

1. An adhesive laminate comprising a facestock, an adhesive layer on the facestock, and a removable fibrous backing in contact with the adhesive layer, the backing having at least one narrow embrittled zone integrally included in the backing, and the embrittled zone comprising an organic, brittle film-forming polymer.

2. An adhesive laminate according to Claim 1, wherein the embrittled zone comprises residual chemical embrittling agent and the polymer retards transfer of residual chemical embrittling agent from the embrittled zone.

3. An adhesive laminate according to Claim 2, wherein the backing is paper, the residual embrittling agent comprises hydrogen chloride, and the polymer is a poly (vinyl acetate).

4. An adhesive laminate according to Claim

1 or Claim 2, wherein the polymer enhances the brittleness of the embrittled zone.

5. An adhesive laminate according to any one of the preceding Claims, wherein substantially all of the polymer present is within the embrittled zone.

6. An adhesive laminate according to any one of the preceding Claims, wherein the facestock bears printed matter.

7. An adhesive laminate according to Claim 1 and substantially as hereinbefore described.

8. A process for the production of an adhesive laminate comprising a facestock, an adhesive layer on the facestock, and a removable fibrous backing, with the fibrous backing having at least one embrittled zone, which process comprises: (a) applying to a narrow portion of the fibrous backing an aqueous embrittling composition containing 1 to 15 weight percent of a volatile chemical embrittling agent capable of embrittling the backing when the composition is applied thereto and is dried by heating, and an organic, brittle film-forming polymer in emulsion form; and (b) curing and drying the applied composition at 150° to 250°C to form a narrow embrittled zone comprising said brittle polymer.

9. A process according to claim 8, wherein the applied composition contains hydrogen chloride as its embrittling agent.

10. A process according to claim 8 or claim 9, wherein there is 1 to 10 weight percent of the polymer in the applied composition.

11. A process according to claim 8, 9 or 10, wherein there is 0.5 to 3 weight percent of an organic thickener in the applied composition.

12. A process for the production of an adhesive laminate comprising a facestock, an adhesive layer on the facestock, and a removable fibrous backing in contact with the adhesive layer, in which the backing is treated to form at least one narrow integral embrittled zone therein, and an organic, brittle film-forming polymer is introduced into the embrittled zone.

13. A process according to claim 12, in which the polymer is introduced by applying a solution of polymer in solvent to the embrittled zone and removing the solvent.

14. A process according to claim 12, in which the polymer is introduced by applying an aqueous emulsion of the polymer to the embrittled zone and drying the applied emulsion.

15. A process according to claim 12, 13 or 14, wherein treatment of the backing to form said embrittled zone comprises applying an acid thereto.

16. A process for the production of an adhesive laminate according to claim 8 or claim 12 and substantially as hereinbefore described.

17. An adhesive laminate produced by a process according to any one of claims 8 to 16.

18. An aqueous composition for providing an embrittled zone and a brittle polymer film deposit thereat on a removable fibrous backing of an adhesive laminate comprising also a facestock, and an adhesive layer on the facestock, the fibrous backing being in contact with the adhesive layer, which composition comprises (a) from 1 to 15 weight percent of a volatile chemical embrittling agent capable of embrittling zones of the backing when the composition is applied to the backing and is dried by heating, and (b) an organic, brittle film-forming polymer that remains as a brittle film in the embrittled zones after the composition is dried.

19. A composition according to claim 18, in which the embrittling agent is an aqueous solution of an acid.

20. A composition according to claim 19, in which the acid is hydrochloric acid.

21. An aqueous composition for providing an embrittled zone and a brittle polymer film deposit thereat on a removable fibrous backing of an adhesive laminate comprising also a facestock, and an adhesive layer on the facestock, the fibrous backing being in contact with the adhesive layer, which composition comprises from 1 to 15 weight percent of hydrogen chloride, from 0.5 to 3 weight percent of an organic thickener, from 0.4 to 1 weight percent of wetting agent, from 0.5 to 2 weight percent of antifoam agent, and from 1 to 10 weight percent of organic, brittle film-forming polymer; the composition being such that when applied to zones of the backing and dried by heating, embrittled zones are formed on the backing, and the polymer penetrates the backing and forms a brittle film which retards the transfer of residual hydrochloris acid from the embrittled zones.

18. A composition according to any one of claims 14 to 17, wherein the polymer is a poly (vinyl acetate).

19. An aqueous composition comprising a chemical embrittling agent and an organic, brittle film-forming polymer and substantially as hereinbefore described.

GRAHAM WATT & CO.
Chartered Patent Agents,
3, Gray's Inn Square,
London, WC1R 5AH

For the Applicant.

Printed for Her Majesty's Stationery Office by MULTIPLEX techniques ltd., St. Mary Cray, Kent. 1981. Published at the Patent Office, 25 Southampton Buildings, London WC2 1AY, from which copies may be obtained.