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(54) Title: THERMOSET CROSS-LINKABLE PRE-APPLIED ADHESIVE

(57) Abstract

This invention is a preapplied liquid adhesive whose components, when dried and heated, react to form a polymer. Laminates made with the thermoset adhesive withstand exposure to 240 °F (116 °C). The adhesive combines urethane dispersions, carboxyl functional acrylic latices and tertiary amine blocking agent.

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THERMOSET CROSSLINKABLE PRE-APPLIED ADHESIVE

This invention relates to thermoset adhesives preapplied to vinyl substrates or release films supplied as free films for subsequent heat reactivating application and bonding to another substrate.

BACKGROUND OF THIS INVENTION

Most pre-applied adhesives are pressure-sensitive adhesives and are not heated after application by the consumer. A recent development with pre-applied adhesives is a heat activated adhesive. Pre-applied adhesives may be prepared from hot melt adhesives; either non-reactive thermoplastic adhesive or reactive thermoset adhesive. They may also be prepared from water borne emulsions or dispersions, which are currently available only as the non-reactive thermoplastic systems. No reactive thermoset water borne pre-applied adhesives are currently available. Reactive hot melt adhesives are on the market although not in the form of a pre-applied storage stable adhesive. There is a need to fill this void for a reactive thermoset water borne pre-applied system.

In this invention, water borne adhesive systems are applied to the surface of a metal, vinyl, wood or plastic substrate. For example, a thin film of liquid adhesive is applied to and dried on a roll of vinyl. This roll which now has the pre-applied adhesive on the back of the vinyl is shipped to a manufacturer who heat laminates the vinyl usually to a rigid substrate, such

as, a wood door or sheets of cold rolled steel or plastic. The advantage of the pre-applied method is elimination of all liquid chemicals from the final manufacturer's laminating facility. The pre-applied method also provides uniformity in application which results in improved quality of the final product.

This invention is a water borne pre-applied system that when heat activated (at the final manufacturers facility) forms a thermoset adhesive bond. This thermoset bond, in contrast to commercially available thermoplastic bond coats, adds additional performance properties that are needed in the market place. The most critical performance need for pre-applied adhesives, second only to the adhesive bond strength, is heat resistance of the final product. The pre-applied adhesive is applied and dried on a roll of vinyl, foam or cloth. The end user of this roll of goods would like to have a processing procedure to heat activate and bond the unrolled goods to a surface at some minimum activation temperature. The lower the heat activation temperature the less the distortion of the final product. The service conditions of the final product often encounter elevated temperatures. In automotive applications for example, it is not uncommon to need performance properties for heat resistance for interior parts of 200°F because car interiors can reach such a temperature in the summer.

This invention is a waterborne thermoset system that can be dried on rolled goods, stored, and then heat activated at a later date at a relatively low activation temperature. The laminate exhibits unique elevated temperature heat resistant properties superior to the heat resistance of conventional

thermoplastic adhesives. Longer press times permit lower activation temperatures and shorter press times require higher activation temperatures.

Detailed Description of the Invention

The first ingredient of the adhesive of the invention is a urethane dispersion such as the aliphatic polyester waterborne urethane dispersions available from Zeneca Resins as NEOREZ R-9617 and R9621 dispersions.

The second ingredient of the adhesive of this invention is a carboxy-modified reactive acrylic latex such as that available as Hycar 26084 carboxy-modified acrylic latex from BF Goodrich, Cleveland, Ohio. The preferred latex lacks any other functionality than carboxyl functionality at 6.3 acid value, and hydroxyl functionality at hydroxyl value 5.

The third ingredient of the adhesive of this invention is a tertiary amine such as N,N-Diethylethanolamine or N-N-Dimethylethanolamine. The preferred amines have vapor pressures from 1 to 4 mm mercury at 20°C. The most preferred amine is diethyl ethanolamine.

The fourth ingredient is a melamine-formaldehyde resin having imino (-NH) functionality such as Cymel 327 resin or Cymel 323 resin from Cytec, West Paterson, NJ. The preferred resin has 1 to 2.5 triazine units per molecule. The most preferred resin has methoxy methyl-imino functionality and 1.75 triazine groups per molecule.

Laminates using the adhesive of the invention can be made with vinyl and metal or wood. Useful vinyl substrates are available from Uniroyal Engineered Products, Port Clinton, Ohio. Useful foam backed vinyl

substrates include those from Foamex International, Auburn, Indiana. Among the useful wood substrates are those from Mills Pride, Waverly, Ohio. Useful metal substrates are available from ACT Laboratories, Hillsdale, Michigan.

In the following Examples all measurements are in the metric system and all parts are by weight unless otherwise noted. All references mentioned herein are specifically incorporated by reference.

EXAMPLE 1

The control water-borne thermoplastic preapplied adhesive was a mixture of:

60g Zeneca R9621 urethane dispersion[1]

20g Zeneca R9617 urethane dispersion[1]

0.02g Proxel 6XL 1,2 benzisothiazolin-3-one preservative[2]

0.02g Drewplus L-407 foam control agent[3]

0.06g Aquasperse 11877-7226 phthaloblue color[4]

0.25g Nopco DSX-1550 rheology modifier[5]

20.0g Hycar 26084 carboxy-modified reactive acrylic latex[6]

The adhesive was prepared by blending the ingredients in the order listed.

EXAMPLE 2

The thermoset adhesive of this invention was prepared by combining

44g Zeneca R-9621 urethane dispersion

33g Zeneca R9617 urethane dispersion

0.01 Proxel 6XL 1,2 benzisothiazolin-3-one preservative

0.01 Drewplus L-407 foam control agent

0.11g Aquasperse 11877-7226 phthaloblue color

0.33g Nopco DSX-1550 rheology modifier

20.4g Hycar 26084 carboxy-modified reactive acrylic latex

0.55g Diethylethanolamine

1.54g Cymel 327 melamine resin crosslinker

0.20g Surfynol 440 wetting agent

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1 Zeneca, Wilmington, MA
2 ICI, Wilminton, DE
3 Ashland Inc., Boonton, NJ
4 HÜLS America, Piscataway, NJ
5 Henkel, Ambler, PA
6 BF Goodrich, Cleveland, OH
7 Union Carbide, Danbury, CT
8 Cytec, West Paterson, NJ
9 Air Products & Chemicals, Allentown, PA

These formulations were applied to the foam side of foam backed vinyl from Foamex International, Auburn, Indiana and then to vinyl from Uniroyal Engineered Products, Port Clinton, Ohio, then dried, and were then heat activated. Both adhesives showed the same adhesive bond at room temperature, but only the Example 2 crosslinked thermoset adhesive formulation passed the following heat resistance tests:

TABLE 1 - HEAT RESISTANCE TEST

	OVEN TEMP	TIME IN OVEN	HANGING WEIGHT	RESULT
Example 2 Thermoset Adhesive	225°F 101°C 225°F 101°C 185°F 85°C	24 Hours 24 Hours 24 Hours 24 Hours	30 Grams 30 Grams 30 Grams 30 Grams	PASS PASS PASS PASS

	185°F 85°C			
Example 1	185°F 85°C	4 Hours	30 Grams	FAIL
Control Thermoplastic	185°F 85°C	3 Hours	30 Grams	FAIL
Adhesive	185°F 85°C	6 Hours	10 Grams	FAIL

The heat resistance is believed to derive from some crosslinking of the amino resin. The choice of amino resin and its stabilization in the formula are unique aspects of the system. Most amino resins will react under acidic conditions. Even a weak acid such as a carboxyl group can catalyze the reaction. To maximize stability of the formulation an amine such as diethylethanol amine with the proper vapor pressure of from 1 to 4mm Hg at 20°C serves to block or neutralize any acidic groups. The amine blocking agent being fugitive can be driven off at certain higher temperatures, but remains in the adhesive film at ambient temperatures. The choice of amino resin is also important. The partially methylated melamine-formaldehyde resins require very strong acid catalysis, heat and dwell time and although are quite stable, they are difficult to react. High imino melamine-formaldehyde resins are best. The best of both worlds can be achieved, i.e. the balance of shelf stability vs. cure response.

The following Table 2 shows shelf stability of the dried film at elevated temperatures.

TABLE 2

	STORAGE STABILITY TIME	SUBSEQUENT ABILITY TO CROSS LINK

Example 1 (Thermoplastic)	13 Days/120°F	PASS
Example 2 (Thermoset)	12 Days/120°F	FAIL
	a) 30 Days/95°F at 30 Days R.T. and then b) 10 Days/95°F	PASS PASS

Table 2 shows that the dried film adhesive of this invention is stable at 120°F for 12 days. It passed 40 days of shelf stability testing at 95°F. The preferred formulation according to Table 3 below had heat resistance up to 240°F at 60 seconds.

TABLE 3

TIME & TEMPERATURE FOR CROSSLINK OF FILM

FROM PREAPPLIED THERMOSET ADHESIVE OF EXAMPLE 2

CURE CONDITIONS OF DRIED FILM			HEAT RESISTANCE 240°F/250 gr LOAD
PLATEN (°F)	DWELL (SEC.)	PSI	
280	20	4	PASS
270	20	4	PASS
260	20	4	FAIL
260	30	4	PASS
240	30	4	FAIL
240	60	4	PASS
230	60	4	PASS
220	60	4	FAIL

The dried adhesive film was placed between a Bondrite-1000 iron phosphated steel panel and vinyl, then placed on the platen for 10 seconds to bring it up to temperature. It was then pressed, the adhesive bond line temperature was very close to the platen temperature. The test was run at room temperature . The film was 7 days old.

Review of Table 3 reveals that a certain temperature and certain time are required to crosslink the adhesive film of the invention.

TABLE 4

THERMOSET vs THERMOPLASTIC HEAT RESISTANCE

	CURE CONDITIONS OF DRIED FILM			***HEAT RESISTANCE 240°F/250GR LOAD***
	PLATEN (°F)	***DWELL (SEC)***	***PSI***	
Example 2 thermoset adhesive	230	60	4	PASS
Example 1 thermoplastic adhesive	230	60	4	30 min. - fail (no crosslinker)

Review of Table 4 reveals that the melamine formaldehyde resin crosslinker and amine are essential in the adhesive of this invention.

The dried adhesive film of this invention has been shown to be shelf stable on rolled vinyl goods for as long as 120 days at 70°F. The stored vinyl film rolls, after application to a solid substrate and heat activation at 230°F, passes the overnight heat resistance test at 240°F with a 250 gm load.

I CLAIM:

1. A thermoset adhesive composition useful for laminating substrates comprising

   a) an acrylic latex having carboxyl functional groups,

   b) a polyurethane dispersion,

   c) an excess of tertiary amine, and

   d) a methoxymethyl imino melamine formaldehyde resin.

2. The adhesive of claim 1 dispensed onto a release liner as a cast film.

3. The adhesive of claim 1 having ph $\geq$ 7.

4. The adhesive of claim 1 wherein said acrylic latex has carboxyl and hydroxyl functional groups.

5. The adhesive of claim 1 wherein said amine is an alkanolamine.

6. The adhesive of claim 1 wherein said alkanolamine is dimethylethanolamine or diethylethanolamine.

7. The adhesive of claim 1 wherein said acrylic latex functionality consists essentially of hydroxyl and carboxyl groups.

8. The adhesive of claim 1 comprising

   10 to 30 parts acrylic latex,

   70 to 85 parts polyurethane dispersion,

   0.2 to 1.0 parts tertiary amine, and

   1 to 3 parts melamine formaldehyde resin.

9. The adhesive of claim 1 comprising

20 parts acrylic latex,

77 parts polyurethane dispersion,

0.6 parts tertiary amine, and

1.5 parts melamine formsldehyde resin.

10. A method of preparing laminated substrates of substrate-thermoset adhesive-substrate comprising

combining an acrylic latex having reactive functional groups and a polyurethane dispersion with a tertiary amine blocking agent so that the pH is greater than 7,

adding said combination to a melamine formaldehyde resin having reactive imino functionality,

forming a waterborne liquid adhesive having shelf stability of 4 months at ambient temperature and 2 months at elevated temperature,

dispensing said adhesive on to a release liner forming an adhesive film,

drying said film,

removing said release liner,

inserting said film between two substrates

heating said substrates and film,

volatilizing said amine,

forming crosslinked thermoset polymer, and

adhering both substrates together.

11. The method of Claim 10 wherein said acrylic latex is a carboxyl functional latex.

12. The method of Claim 11 wherein said adhered laminated substrates are resistant to delamination at 240°F (116°C) with a 250 gram weight load.

13. The method of Claim 10 wherein said resin comprises more than 1.0 parts by weight methoxy methyl imino melamine formaldehyde resin.

14. The method of Claim 10 wherein said substrates comprise a porous substrate and a non-porous substrate.

15. The method of Claim 10 wherein during said heating step said amine volatilizes and said pH drops below 16 forming acid groups capable of catalyzing the reaction between carboxyl groups and imino groups.

16. The method of Claim 10 wherein said amine is an alkanolamine.

17. The method of Claim 16 wherein said alkanolamine is dimethylethanolamine or diethylethanolamine.

18. The method of Claim 10 wherein said amine has a vapor pressure of 1 mm to 4 mm at 20°C.

19. The method of Claim 10 wherein the sole functionality of said latex is carboxyl and hydroxyl functionality.

20. The laminate made by the method of Claim 10.

21. The method of claim 10 wherein said elevated temperature is greater than 210°F (99°C).

22. The method of claim 10 wherein said mixture comprises 10 to 30 parts acrylic latex, 70 to 85 parts polyurethane dispersion, 0.2 to 1.0 parts tertiary amine, and 1 to 13 parts melamine formaldehyde resin.

23. The method of claim 22 comprising 20 parts acrylic latex, 77 parts polyurethane dispersion, 0.6 parts tertiary amine, and 1.5 parts melamine formaldehyde resin.

24. A method of laminating two substrates comprising combining a functional acrylic latex and a polyurethane dispersion with a tertiary amine, reaching pH greater than 8, adding said combination to melamine formaldehyde resin, forming a water borne liquid adhesive, dispensing said adhesive onto a first substrate, drying said coated substrate, rolling said coated substrate, transporting said roll to a place of manufacture, unrolling said substrate, applying said substrate to a second substrate so that the coated surface of said first substrate is adjacent to said second substrate, heating said substrates under pressure, curing said adhesive, removing said substrates having cured thermoset adhesive there between and said laminate being resistant to delamination at 240°F (116°C).

25. The method of Claim 24 wherein said acrylic latex functionaltiy is solely carboxyl and hydroxyl functionality.

26. The method of claim 24 comprisng a porous substrate and a non-porous substrate.

27. The method of claim 24 wherein during said heating step said amine volatilizes, said pH drops below 7 forming acid groups capable of catalyzing the reaction between carboxyl groups and imino groups on said melamine resin.

28. The method of claim 24 wherein said tertiary amine comprises alkanolamine.

29. The method of claim 24 wherein said alkanolamine comprises dimethylethanolamine or diethylethanolamine.

30. The method of claim 24 wherein said amine vapor pressure at 20°C is 1 mm to 4 mm.

31. The method of claim 24 wherein said mixture comprises

10 to 30 parts acrylic latex,

70 to 85 parts polyurethane dispersion,

0.2 to1.0 parts tertiary amine, and

1 to 3 parts melamine formaldehyde resin.

32. The method of claim 31 wherein said mixture comprises:

20 parts acrylic latex,

77 parts polyurethane dispersion,

1.5 parts melamine formaldehyde resin,

and 0.6 parts tertiary amine.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/06088

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL :524/236, 247, 501, 507, 512; 156; 191,246, 306.9, 331.31 427/177
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/236, 247, 501, 507, 512; 156 /191,246, 306.9, 331.31; 427/177

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2,586,587 A (WENDT) 19 February 1952 (19-02-52), see entire document.	10-23
Y	US 4,948,829 A (MITSUJI et al) 14 August 1990 (14-08-90), see entire document.	1-32
Y,P	US 5,631,341 A (MORISHIMA et al) 20 May 1997 (20-05-97), see entire document.	10-32
Y	JP 58-147315 A (SUMITOMO CHEMICAL KK) 02 September 1983 (02-09-83), see entire document.	23-32

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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INTERNATIONAL SEARCH REPORT

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