⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number: **0 237 643**
A2

⑫

EUROPEAN PATENT APPLICATION

㉑ Application number: 86117659.2

(51) Int. Cl.^{3}: **D 04 H 1/64**

㉒ Date of filing: 18.12.86

㉚ Priority: 24.12.85 US 813111

㊸ Date of publication of application:
23.09.87 Bulletin 87/39

(84) Designated Contracting States:
BE DE FR GB IT NL SE

(71) Applicant: AIR PRODUCTS AND CHEMICALS, INC.
P.O. Box 538
Allentown, Pennsylvania 18105(US)

(72) Inventor: Goldstein, Joel Erwin
524 Benner Road Apt. 101
Allentown PA 18104(US)

(72) Inventor: Pinschmidt, Robert Kratz
1033 Glenwood Street
Allentown PA 18104(US)

(72) Inventor: Lenney, William Edward
1382 Deerfield Drive
Allentown PA 18104(US)

(74) Representative: Kador & Partner
Corneliusstrasse 15
D-8000 München 5(DE)

(54) Formaldehyde-free vinyl acetate/ethylene/N-acryl-amidoglycolic acid copolymers useful as non-woven binders.

(57) A copolymer binder emulsion prepared by the copolymerization of vinyl acetate, 1 to 30 wt% ethylene and 0.5 to 15 wt% acrylamidoglycolic acid. Nonwoven fabrics bonded with such copolymers possess properties comparable to that obtained using N-methylolacrylamide-containing copolymers but without the emission of formaldehyde.

EP 0 237 643 A2

Croydon Printing Company Ltd.

FORMALDEHYDE-FREE VINYL ACETATE/ETHYLENE/AGA COPOLYMERS USEFUL AS NONWOVEN BINDERS

TECHNICAL FIELD

The present invention relates to binder compositions for nonwoven fabrics comprising copolymerized ethylene and vinyl acetate.

BACKGROUND OF THE INVENTION

Emulsion polymers prepared from vinyl acetate and ethylene provide wide application as binders in industry. Unfortunately, these binders experience unacceptable loss in strength in the presence of water and other solvents. In addition, they exhibit deficiencies in adhesion to the substrates on which they are used. These shortcomings have been reduced by the use of adhesion promoting or crosslinking comonomers and/or post-added crosslinkers.

The most successful of the many chemistries employed is aminoplast technology, especially N-methylolacrylamide (NMA) and urea-formaldehyde (U/F) condensates. While they are low in cost, compatible with aqueous emulsions, rapidly cured under acid catalysis and substrate reactive, they suffer from two deficiencies: the emission of low levels of formaldehyde, a suspect carcinogen; and inadequate adhesion to certain substrates, for example, metal, glass and synthetics such as mylar.

Many attempts have been made to overcome or minimize the first deficiency, especially after the potential carcinogenicity and irritant properties of formaldehyde became widely recognized.

To reduce the level of formaldehyde in emulsion products, the use of O-alkylated NMA's such as isobutoxymethacrylamide (IBMA) or the use of 1:1 molar ratios of NMA with acrylamide were introduced. These materials did not, however, eliminate the presence of formaldehyde.

Epoxide functional comonomers such as allyl glycidyl ether, glycidyl (meth)acrylate or their precursors have also been used. These materials suffer from high costs, limited shelf stability of the functionalized emulsion polymer and toxicity questions associated with epoxide materials.

Other approaches use esterification chemistry (carboxylic acid + alcohol to give an ester crosslink), but such approaches require a slow and expensive high temperature curing cycle. Post-addition of formaldehyde-free urea/glyoxal condensates including N,N'-dialkyl-4,5-dihydroxy imidazoles has been used in Japan for fabric treating, but such systems are less efficient than formaldehyde-containing analogs.

The use of amide/glutaraldehyde condensates, for example, the condensate with acrylamide, has been attempted. The combination of the reagents, however, gave a complex mixture of uncharacterizable products which did not perform well in textile crosslinking applications.

U.S. 4,289,676 discloses binder copolymers containing at least 85 wt%

(a) a mixture of from 40-60 parts by weight of styrene and/or acrylonitrile and from 60-40 parts by weight of butadiene or

(b) esters of acrylic acid and/or methacrylic acid with alkanols of 1-8 carbon atoms, and/or vinyl esters of acetic acid or propionic acid and/or vinyl chloride, and optionally up to 40 wt% based on total monomers (b), of acrylonitrile, styrene or butadiene,

from 0 to 5 wt% of alpha,beta-monoolefinically unsaturated monocarboxylic acids and/or dicarboxylic acids of 3 to 5 carbon atoms and/or their amides, and

3 to 10 wt% N-acrylamidoglycolic acid and/or N-methacrylamidoglycolic acid.

SUMMARY OF THE INVENTION

The present invention provides an aqueous dispersion of vinyl acetate-ethylene copolymers of 35 to 65 wt% solids which are useful as nonwoven binders. The aqueous dispersion, or emulsion, comprises a copolymer consisting essentially of vinyl acetate, 1 to 30 wt% ethylene and 0.5 to 15 wt% of an N-acrylamidoglycolic acid (AGA).

The copolymer emulsions of the invention can be applied to a nonwoven web of fibers to provide a nonwoven bonded substrate by curing the AGA-containing vinyl acetate/ethylene copolymers under acid catalysis and heating. The strength of the bonded products in solvents is comparable to that obtained using current technology but formaldehyde is not emitted.

In comparing bonded nonwovens using a "formaldehyde-free" binder, the copolymer of the present invention demonstrates surprisingly good block resistance.

The copolymers can also be used as a binder adhesive or coating on any substrate, especially those with hydroxyl, carboxylic, primary or secondary amide surface groups. The copolymers should be able to interact with oxirane (epoxide) containing polymers and should be suitable as an adhesive for those substrates.

DETAILED DESCRIPTION OF THE INVENTION

There is provided an aqueous emulsion comprising an aqueous medium having colloidally dispersed therein a copolymer consisting essentially of vinyl acetate, 1 to 30 wt% ethylene and 0.5 to 15 wt% N-acrylamidoglycolic acid (AGA) and/or N-methacrylamidoglycolic acid (MethAGA). Whenever "AGA" is used it is to be understood that "MethAGA" is also contemplated. The preferred copolymers consist essentially of vinyl acetate and 6 to 18 wt% ethylene, especially 10 to 12 wt%, with preferably 2 to 10 wt% AGA. Such copolymer emulsions which are useful as nonwoven binders would have Brookfield viscosities ranging from 10 to 2600 cps, preferably 400-1000 cps. The copolymers would have a Tg between -20 and 32°C, preferably -5 to 25°C.

The vinyl acetate/ethylene/AGA copolymers may optionally include one or more additional ethylenically unsaturated copolymerizable monomers. Exemplary of such comonomers, which may be present at up to 10 wt%, are C_3-C_{10} alkenoic and alkenedioic acids, such as acrylic acid, methacrylic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid and itaconic acid and their monoesters and diesters with C_1-C_{18} alkanols, such as methanol, ethanol, propanol, butanol and 2-ethylhexanol; carboxyethyl acrylate; vinyl halides such as vinyl chloride; and nitrogen-containing monoolefinically unsaturated monomers, particularly nitriles, amides, N-methylolamides, lower alkanoic acid esters of N-methylolamides, lower alkyl ethers of N-methylolamides and allylcarbamates, such as acrylonitrile, acrylamide, methacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-methylolallylcarbamate, and N-methylol lower alkyl ethers or N-methylol lower alkanoic acid esters of N-methylolacrylamide, N-methylolmethacrylamide and N-methylolallylcarbamate. If such additional ethylenically unsaturated comonomer is used, about 2 to 5 wt% is preferred. A particularly preferred comonomer for increasing the water resistance of the copolymer is one of the alkenoic acids, namely crotonic acid at up to 3 wt%, preferably 0.5 to 1.5 wt%.

Contemplated as the functional, or operative, equivalent of vinyl acetate in the copolymer emulsions, are vinyl esters of C_1-C_{18} alkanoic acids, such as vinyl formate, vinyl proprionate, vinyl laurate and the like.

AGA is employed in the preparation of the aqueous copolymer emulsion by emulsion polymerization in amounts which yield a copolymer that is 0.5 to 15 wt%, preferably 2 to 10 wt% AGA. AGA and a process for its preparation are known from British Patent No. 1,103,916. It can be purchased from Societe Francaise Hoechst (American Hoechst is the distributor in the U.S.).

The AGA units in the vinyl acetate/ethylene copolymers can also advantageously be introduced by reacting emulsion copolymers which contain, as copolymerized units, vinyl acetate and ethylene, and which also contain from 0.3 to 8 wt% of acrylamide and/or methacrylamide as copolymerized units, with glyoxylic acid in, for example, an equivalent or excess amount based on the copolymerized acrylamide or methacrylamide (though a less than equivalent amount of glyoxylic acid may also be used). Further, the copolymers according to the invention, can be prepared by polymerizing the monomer mixture containing acrylamide or methacrylamide in aqueous emulsion in the presence of glyoxylic acid under otherwise conventional conditions.

Methods for preparing vinyl acetate/ethylene copolymer emulsions are well known in the art and any of the customary procedures, together with the incorporation of an ethylene pressure, can be used, such as those emulsion polymerization techniques described in such chemistry texts as POLYMER SYNTHESIS, Vol. I and II, by Stanley R. Sandler and Wolf Karo, Academic Press, New York and London (1974), and PREPARATIVE METHODS OF POLYMER CHEMISTRY, Second Edition, by Wayne R. Sorenson and Tod W. Campbell, Interscience Publishers (John Wiley & Sons), New York (1968).

In general, suitable vinyl acetate/ethylene copolymer emulsions can be prepared by the copolymerization of the monomers in the presence of suitable emulsifying agents, i.e. protective colloids and surfactants, in an aqueous medium under pressures generally not exceeding about 100 atm and in the presence of a redox system which is added incrementally, the aqueous system being maintained by a suitable buffering agent at a pH of about 2 to 6. The process first involves a homogenization in which the vinyl acetate suspended in water is thoroughly agitated in the presence of ethylene under the working pressure to effect solution of the ethylene in the vinyl acetate while the reaction medium is gradually heated to a polymerization temperature. The homogenization period is followed by a polymerization period during which the redox system is added incrementally.

The crosslinking monomer AGA may be added all at once with the vinyl acetate and ethylene or incrementally over the course of the polymerization reaction, with the latter being preferred. Advantageously a portion of the AGA is added during the beginning of the polymerization reaction, not added at all during the middle period and again added during the last part of the polymerization reaction.

Minor amounts, e.g. 0.01 to 0.25 wt%, of a polyolefinic comonomer such as triallyl cyanurate, diallyl maleate and the like can be added to increase the molecular weight of the polymer. Sodium vinyl sulfanate can be added to increase mechanical stability of the emulsion and reduce grits.

The emulsifying agents which can be used in the polymerization recipe include ionic and nonionic surfactants, preferably the anionic types which are well known to those skilled in the polymerization art. Suitable nonionic emulsifying agents include polyoxyethylene condensates and the preferred anionic emulsifying agents include aryl alkyl sulfonates. Other emulsifying agents include protective colloids, such as polyvinyl alcohol and the cellulose materials such as methyl cellulose, hydroxyethyl cellulose, hydroxypropylmethyl cellulose and the like.

The concentration range of the total amount of the emulsifying agents useful is from 0.5 to 10%, preferably 4 to 5%, based on emulsion solids.

Various free-radical forming sources can be used in carrying out the polymerization of the monomers, such as peroxide compounds. Combination-type systems employing both reducing agents and oxidizing agents, i.e. a redox system, are especially preferred. Suitable reducing agents include bisulfites, sulfoxylates, alkali metal bisulfite-ketone adducts, or other compounds having reducing properties such as ascorbic acid, erythorbic acid and other reducing sugars. The oxidizing agents include hydrogen peroxide, organic peroxides such as t-butyl hydroperoxide and the like, persulfates, such as ammonium or potassium persulfate and the like. Specific redox systems which can be used include hydrogen peroxide and zinc formaldehyde sulfoxylate; hydrogen peroxide and erythorbic acid, hydrogen peroxide, ammonium persulfate or potassium persulfate with sodium metabisulfite, sodium bisulfite, ferrous sulfate, zinc formaldehyde sulfoxylate or sodium formaldehyde sulfoxylate; and t-butyl hydroperoxide with sodium bisulfite-acetone adduct. Other free radical forming systems that are well known in the art can also be used to polymerize the monomers. Obviously, for a completely formaldehyde-free binder emulsion the redox system would comprise a reducing agent that does not liberate formaldehyde; i.e. ascorbic or erthythorbic acid, a bisulfite or especially an alkali metal bisulfite-ketone adduct.

The oxidizing agent is generally employed in an amount of 0.01 to 1%, preferably 0.05 to 0.5% based on the weight of the vinyl acetate introduced into the polymerization system. The reducing agent is ordinarily added in the necessary equivalent amount.

The reaction temperature can be controlled by the rate of redox addition and by the rate of heat dissipation via a reaction vessel water jacket. Generally, it is advantageous to maintain a mean temperature of about 50°C during the polymerization of the monomers and to avoid temperatures much in excess of 80°C. Although temperatures as low as 0°C can be used, economically the lower temperature limit is about 30°C.

The reaction time will depend upon variables such as the temperature, the free radical forming source and the desired extent of polymerization. It is generally desirable to continue with the reaction until less than 0.5% of the vinyl acetate remains unreacted.

In carrying out the polymerization, an amount of the vinyl acetate is initially charged to the polymerization vessel and saturated with ethylene. At least about 25% of the total vinyl acetate to be polymerized is initially charged and the remainder of the vinyl acetate is added incrementally during the polymerization. Preferably all the vinyl acetate is charged initially with no additional incremental supply.

When reference is made to incremental addition, whether a vinyl acetate or redox system or any other ingredient, intermittent additions are contemplated. Such additions are also referred to as "delay" additions.

The quantity of ethylene entering into the copolymer is influenced by the pressure, the agitation and the viscosity of the polymerization medium. Thus, to increase the ethylene content of the copolymer higher pressures, greater agitation and a low viscosity are employed.

The process of forming the vinyl acetate-ethylene copolymer emulsion generally comprises the preparation of an aqueous solution containing the emulsifying system and, optionally, the buffering system. This aqueous solution and the initial or total charge of the vinyl acetate are added to the polymerization vessel and ethylene pressure is applied to the desired value. The pressurized ethylene source can be shut off from the reactor so that the ethylene pressure decays as it is polymerized or it can be kept open to maintain the ethylene pressure throughout the reaction, i.e. make-up ethylene. As previously mentioned, the mixture is thoroughly agitated to dissolve ethylene in the vinyl acetate and in the water phase. Conveniently, the charge is brought to polymerization temperature during this agitation period. The polymerization is then initiated by introducing initial amounts of the oxidant, the reductant having been added with the initial charge. After the polymerization has started, the oxidant and reductant are incrementally added as required to continue polymerization. Any other copolymerizable monomer and the remaining vinyl acetate and/or AGA, if any, may be added as separate delays.

As mentioned, the reaction is generally continued until the residual vinyl acetate content is below about 0.5%. The completed reaction product is then allowed to cool to about room temperature while sealed to the atmosphere.

Vinyl acetate/ethylene/AGA copolymer emulsions of relatively high solids content can be directly produced having a solids content of 35 to 60% or more.

The vinyl acetate-ethylene copolymer binders of the invention can be used to prepare nonwoven products, or fabrics, by a variety of methods known in the art which, in general, involve the impregnation of a loosely assembled mass of fibers with the binder emulsion, followed by a moderate heating to dry the mass. In the case of the present invention, this moderate heating also serves to cure the binder by forming a crosslinked interpolymer. Before the binder is applied, it is, of course, mixed with a suitable catalyst for the crosslinking monomer AGA. For example, an acid catalyst such as mineral acids, e.g. hydrogen chloride, or organic acids, e.g. oxalic acid, or acid salts such as ammonium chloride, are suitably used as known in the art. The amount of catalyst is generally from 0.5 to 2% of the total polymer.

The starting fiber layer or mass can be formed by any one of the conventional techniques for depositing or arranging fibers in a web or layer. These techniques include carding, garnetting, air-laying, wet laying and the like. Individual webs or thin layers formed by one or more of these techniques can also be laminated to provide a thicker layer for conversion into a fabric. Typically, the fibers extend in a plurality of diverse directions in general alignment with the major plane of the fabric, overlapping, intersecting and supporting one another to form an open, porous structure.

When reference is made to "cellulose" fibers, those fibers containing predominantly $C_6H_{10}O_5$ groupings are meant. Thus, examples of the fibers to be used in the starting layer are the natural cellulose fibers such as wood pulp, cotton and hemp and the synthetic cellulose fibers such as rayon, and regenerated cellulose. Often the fiber starting layer contains at least 50% cellulose fibers, whether they be natural or synthetic, or a combination thereof. Often the fibers in the starting layer may comprise natural fiber such as wool, jute; artificial fibers such as cellulose acetate; synthetic fibers such as polyamides, nylon, polyesters, acrylics, polyolefins, i.e. polyethylene, polyvinyl chloride, polyurethane, and the like, alone or in combination with one another.

The fibrous starting layer is subjected to at least one of several types of bonding operations to anchor the individual fibers together to form a self-sustaining web. Some of the better known methods of bonding are overall impregnation or printing the web with intermittent or continuous straight or wavy lines for areas of binder extending generally transversely or diagonally across the web and additionally, if desired, along the web.

The amount of copolymer binder, calculated on a dry basis, applied to the fibrous starting web is that amount which is at least sufficient to bind the fibers together to form a self-sustaining web and suitably ranges from about 3 to about 100% or more by weight of the starting web, preferably from about 10 to about 50 wt% of the starting web. The impregnated web is then dried and cured. Thus the nonwoven products are suitably dried by passing them through an air oven or the like and then through a curing oven. Typical conditions to achieve optimal crosslinking are sufficient time and temperature such as drying at 150-200°F (66-93°C) for 4-6 minutes, followed by curing at 300-310°F (149-154°C) for 3-5 minutes or more. However, other time-temperature relationships can be employed as is well known in the art, shorter times and higher temperature or longer times at lower temperature being used.

An emulsion copolymer prepared with an alkali metal bisulfite-ketone adduct, sodium meta-bisulfite, ascorbic acid or erythorbic acid as the reducing agent and containing AGA as the crosslinking monomer is 100% formaldehyde-free. There are no formaldehyde donors or emitters present. N-methylolacrylamide, being prepared from acrylamide and formaldehyde in an equilibrating, reversible reaction will always contain some formaldehyde and will continue to generate some until all the NMA has been either used or lost its formaldehyde. AGA is not prepared using formaldehyde, but rather glyoxylic acid, and though its preparation is by a reversible process, this would release glyoxylic acid and not formaldehyde.

EXAMPLE 1

This example demonstrates the preparation of a vinyl acetate/ethylene/AGA copolymer emulsion.

A one gallon reactor was charged with 136.9g vinyl acetate, 19.1g Igepal CO-887 surfactant, 13.3g Igepal CO-630 surfactant, 13.3g Pluronic F-68 surfactant, 13.3g Pluronic L-64 surfactant, 1142.7g of a 2% aqueous solution of Natrosol 250 LR hydroxyethyl cellulose, 5.5g sodium acetate, 0.05g ferric ammonium sulfate and 3.1g acetic acid. It was purged for 40 minutes with nitrogen. The kettle was heated to 48°C, agitated at 800 rpm, pressurized with ethylene to 450 pounds and charged with 15.2g of 7% aqueous solution of sodium acetone bisulfite (SAB). The reaction was initiated by adding 3% aqueous solution of t-butyl hydroperoxide (TBHP) at 0.6 ml/min. Upon initiation the rate of addition was switched to automatic and 1228g vinyl acetate was added at 7.3 ml/min. and 493g of monomer solution (55.0g AGA in 495g deionized water) was added at 2.7 ml/min. Ten minutes after initiation, a 7% aqueous solution of SAB was added at 0.3 ml/min. The reactor temperature was maintained at 49°C and the pressure at 450 pounds. After three hours, the vinyl acetate and AGA feeds were complete but the reducing agent and oxidizing agent feeds continued for an additional seventy minutes. Thereupon, the reaction was cooled, degassed and treated with 5g of a 10% aqueous solution of TBHP and 4.6g of a 50% aqueous solution of Colloid 585 defoamer. Solids: 46%; Viscosity: 652 cps.

Example 2

This example is a repeat of Example 1 in which the initial charge to the reactor contained 4.0g acetic acid and the monomer solution comprised 110g AGA in 440g deionized water. Solids 45.4%; Viscosity 232 cps.

Example 3

This example shows the use of triallylcyanurate and sodium vinyl sulfonate in the preparation of a vinyl acetate/ethylene/AGA/acrylamide copolymer emulsion.

A one-gallon reactor was charged with 1364.8g vinyl acetate, 7.6g Igepal CO887 surfactant, 33.9g Siponate DS-10 surfactant, 1.6g triallylcyanurate, 27.0g sodium vinyl sulfonate (25% in H_2O), 1142.7g of a 2% aqueous solution of Natrosol 250 LR hydroxyethyl cellulose, 5.5g sodium acetate, 0.05g ferric ammonium sulfate and 0.5g phosphoric acid. It was purged for 40 minutes with nitrogen. The kettle was heated to 48°C, agitated at 800 rpm, pressurized with ethylene to 340 pounds and charged with 30.4g of a 3.5% aqueous solution of SAB. The reaction was initiated by adding 1.5% aqueous solution of TBHP at 0.2 ml/min. Upon initiation the rate of addition was switched to automatic to maintain a 5°C exotherm and 493g of monomer solution (55.0g AGA and 17.5g acrylamide in 477.5g deionized water) was added at 2.0 ml/min. Ten minutes after initiation, a 3.5% aqueous solution of SAB was added at 0.3 ml/min. The reactor temperature was maintained at 49°C and the pressure at 340 pounds. After four hours, the AGA feed was complete but the SAB and TBHP feeds continued for an additional five minutes. Thereupon, the reaction was cooled, degassed and treated with 5g of 10% aqueous solution of TBHP and 4.6g of 50% aqueous solution of Colloid 585 defoamer. Solids: 43.4%; Viscosity: 200 cps.

Example 4

This example shows the preparation of a vinyl acetate/ethylene/AGA/acrylamide copolymer emulsion following a procedure similar to Example 3.

A one-gallon reactor was charged with 1364.8g vinyl acetate, 15.2g Rewopol NOS 25 surfactant, 33.9g Siponate DS-10 surfactant, 1.6g triallylcyanurate, 27.0g sodium vinyl sulfonate (25% in H_2O), 1142.7g of a 2% aqueous solution of Natrosol 250 LR hydroxyethyl cellulose, 5.5g sodium acetate, 0.05g ferric ammonium sulfate and 0.5g phosphoric acid. It was purged for 40 minutes with nitrogen. The kettle was heated to 48°C, agitated at 800 rpm, pressurized with ethylene to 340 pounds and charged with 30.4g of a 0.7% aqueous solution of sodium acetone bisulfite

(SAB). The reaction was initiated by adding 1.5% aqueous solution of t-butyl hydroperoxide (TBHP) at 0.2 ml/min. Upon initiation the rate of addition was switched to automatic to maintain a 2°C exotherm and 525g of monomer solution (55.0g AGA and 17.5g acrylamide in 477.5g deionized water) was added at 2.2 ml/min. Ten minutes after initiation, a 0.7% aqueous solution of SAB was added at 0.3 ml/min. The reactor temperature was maintained at 49°C and the pressure at 340 pounds. After two hours, the AGA feed was stopped and the reaction maintained at a 2°C exotherm. At the four hour mark the AGA delay was restarted and 45 minutes later the SAB solution was changed to a 3.5% aqueous solution of SAB and the TBHP solution switched to 1.5% aqueous solution of TBHP. At the six hour mark, the AGA feed was complete but the SAB and TBHP feeds continued for an additional five minutes. Thereupon, the reaction was cooled, degassed and treated with 5g of 10% aqueous solution of TBHP and 4.6g of 50% aqueous solution of Colloid 585 defoamer. Solids: 41.0%; Viscosity: 80 cps.

Example 5

This example was the same as Example 3 except 17.0g crotonic acid was added to the premix. Solids: 43.0%; Viscosity: 660 cps.

Table 1 presents the comparative performance data of the five copolymer emulsions of Examples 1-5 with prior art vinyl acetate/ethylene copolymers containing N-methylolacrylamide (NMA), isobutoxymethacrylamide (IBMA) and an equimolar ratio of N-methylolacrylamide and acrylamide (AM) in Examples 6-8, respectively. It can be seen from the performance data that the vinyl acetate/ethylene/AGA emulsion copolymers according to the invention exhibited dry and wet tensile strengths and solvent resistance comparable to the prior art vinyl acetate/ethylene/crosslinker copolymers with the added advantage of not emitting formaldehyde.

The copolymers were applied as binder emulsions on Whatman paper at 10% binder solids. Phosphoric acid to pH 2.5 was added as a curing catalyst and the impregnated paper was dried and cured at 150°C for 3 minutes.

TABLE 1

Example	Crosslinking Monomer (wt%)	Tensile Strength* Dry	Wet	Perchloro	MEK
1	AGA (3)	16.0	5.7	--	4.3
2	AGA (6)	14.6	6.1	--	5.1
3	AGA (3)	15.5	6.0	--	5.1
4	AGA (3)	16.0	6.7	--	5.9
5	AGA (3)	17.0	6.6	--	6.1
6	NMA (5)	15.1	7.7	8.9	8.0
7	IBMA (5)	16.4	5.0	4.6	--
8	NMA/AM (2.5/2)	12.6	6.0	5.9	6.2

* PLI (pounds per linear inch)

The high temperature cure used to crosslink the copolymers according to the invention causes the amide nitrogen of one AGA molecule to add to the carbon which is alpha to both the amide nitrogen and the carboxylic acid functionality of another AGA unit with loss of water. These conditions also allow a hydroxyl group of cellulose to add to the carbon alpha to both the amide nitrogen and the carboxylic acid functionality of an AGA unit with loss of water. This second reaction binds the polymer to the cellulosic substrate, thereby strengthening the resulting network and preventing adhesive failure of the binder in water.

Polymers containing AGA perform well as nonwoven binders because the mechanics are present for the aminoplast technology, especially as the carboxylic acid group will stabilize the iminium intermediate, facilitating its formation and allowing it to exist long enough to find a nucleophile. This can include another AGA moiety or any other active hydrogen source such as a hydroxyl group from another monomer or from the cellulosic substrate. The key advantage is that the AGA does not contain or release formaldehyde during curing as it is not prepared using formaldehyde.

STATEMENT OF INDUSTRIAL APPLICATION

The invention provides vinyl acetate/ethylene/AGA copolymer emulsion binders useful for the preparation of nonwoven products.

CLAIMS

1. A copolymer emulsion for bonding nonwovens comprising an aqueous medium having colloidally dispersed therein a copolymer consisting essentially of vinyl acetate, 1 to 30 wt% ethylene and 0.5 to 15 wt% of an N-acrylamidoglycolic acid.

2. The emulsion of Claim 1 in which the copolymer contains 6 to 18 wt% ethylene.

3. The emulsion of Claim 1 in which the copolymer contains 2 to 10 wt% of an N-acrylamidoglycolic acid.

4. The emulsion of Claim 1 in which the copolymer contains N-acrylamidoglycolic acid.

5. The emulsion of Claim 1 in which the copolymer contains N-methacrylamidoglycolic acid.

6. The emulsion of Claim 1 in which the copolymer also contains up to 10 wt% of a C_3-C_{10} alkenoic acid comonomer.

7. The emulsion of Claim 1 in which the copolymer contains up to 3 wt% crotonic acid.

8. The emulsion of Claim 1 in which the copolymer contains 0.5-1.5 wt% crotonic acid.

9. A copolymer emulsion for bonding nonwovens comprising an aqueous medium having colloidally dispersed therein a copolymer consisting essentially of vinyl acetate, 6-18 wt% ethylene and 2-10 wt% N-acrylamidoglycolic acid.

10. The emulsion of Claim 9 in which the copolymer is 10-12 wt% ethylene.

11. The emulsion of Claim 9 in which the copolymer also contains 0.5-1.5 wt% crotonic acid.

12. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 1 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

13. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 2 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

14. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 3 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

15. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 4 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

16. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 5 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

17. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the

emulsion of Claim 6 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

18. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 7 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

19. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 8 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

20. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 9 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

21. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 10 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.

22. A nonwoven product comprising a nonwoven web of fibers bonded together with the vinyl acetate-ethylene copolymer deposited from the emulsion of Claim 11 at a binder add-on sufficient to bond the fibers together to form a self-sustaining web.