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(71) Applicant: **VINAMUL LTD.**
Mill Lane
Carshalton, Surrey SM5 2JU(GB)

(72) Inventor: **Dr. Siddiqui, Adnan**
51 Marchmont Road
South Wallington, Surrey SM6 9NT(GB)
Inventor: **Dr. McLennan, Alistair John**
11 Bluebell Close
Hackbridge, Surrey SM6 7HL(GB)

(74) Representative: **Hagemann, Heinrich, Dr. rer. nat., Dipl.-Chem. et al**
Patentanwälte
HAGEMANN & KEHL
Postfach 86 03 29
D-81630 München (DE)

(54) **Binding Composition.**

(57) Binding composition for non-woven fibrous materials, comprising a copolymer emulsion in which at least 30 % by weight of the monomer content is vinyl C1 to C4 alkanoate, 0.5% to 3% by weight of N-(n-butoxymethyl) acrylamide as a post polymerisation cross-linking agent and 0.5 % to 5% by weight of acrylamide. The combination of N-(n-butoxymethyl) acrylamide with acrylamide leads to low formaldehyde content together with good physical characteristics.

Rank Xerox (UK) Business Services
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Field of the invention

This invention relates to compositions based on copolymer emulsions which are used to bind together non-woven fibrous materials. More particularly, this invention relates to non-woven materials bonded with a binder composition comprising a copolymer emulsion and N-(n-butoxymethyl) acrylamide (NBMA) as a post polymerisation cross-linking agent.

Background of the invention

Non-woven fibrous material comprises a consolidated mass of fibres which may be laid down by mechanical, chemical, pneumatical, electrical or vacuum means and deposited in a desired flat shape, for example as webs, mats or sheets, or in a three dimensional form. The fibres may be natural or synthetic or a combination. In general the fibres to be used will be selected to suit the desired end use of the non-woven product. Thus fibres may be derived from wood, i.e. cellulose, or may be cotton, glass, asbestos, rayon, wool, viscose, etc. The fibres may be deposited in a random manner, or may be positioned or aligned along particular axes. The non-woven product may contain layers of fibres oriented in a cross-layered manner to provide a uniform strength across the product.

Usually, it is necessary to submit the product to a binding step to ensure the product maintains its physical integrity.

One route to binding the product is to introduce a binding composition during or after formation of the product. In general, there is no restriction on the means of application of the binding composition and this may be by, e.g. dipping, soaking or spraying. Subsequent treatment, usually by the application of heat, dries the binding composition and gives structural integrity to the product.

Bound non-woven fibre products are useful e.g. as curtains, in furniture, as drapes, filters, packaging, wiping cloths, fabric interlining for clothes, and industrial sealing material such as gaskets. A particular market is in the use of non-woven padding as absorbents in, e.g. babies nappies (diapers), female sanitary products etc.

It is well known to use copolymer emulsions as binding compositions for non-woven fibrous materials. A particularly suitable base for binding compositions is copolymer emulsions obtained by polymerising unsaturated monomers in an emulsion system. Suitable copolymer emulsions may be obtained by means of processes performed at ambient pressure or under elevated pressure, e.g. up to 120 bars. Copolymer emulsion compositions suitable for this purpose will usually contain a monomer capable of cross-linking in a post-polymerisation step. Thus the copolymer emulsion will be applied to the non-woven product and first subjected to heating to remove water. Then in a further heating step the cross-linkable monomer cross-links to provide a three dimensional copolymer network with strength sufficient to provide structural integrity.

The cross-linkable monomer used is required to have an appropriate cross-linking efficiency as well as appropriate wet, dry and solvent strengths. Additionally, there has been a general desire to reduce the formaldehyde content in non-woven products, in particular those designed for human contact, e.g. babies nappies. Formaldehyde may be generated by the cross-linking reaction and may also be present in the fibrous components of the non-woven product.

Description of prior art

US 4,449,978, discloses a non-woven product comprising a non-woven web of fibres bonded together with a binder which comprises an interpolymer of vinyl acetate / ethylene / N-methylol acrylamide / acrylamide containing 5 to 40% by weight of ethylene, 1.75% to 3.5% by weight of N-methylol acrylamide (NMA) and 1.25% to 8.25% by weight of acrylamide.

WO 92/08835 (Unilever) discloses a binding composition for non-woven fibrous materials comprising a copolymer emulsion based on vinyl alkanoate and using N-(n-butoxymethyl) acrylamide (NBMA) as a post polymerisation cross-linking agent to reduce formaldehyde emission. However, the more NBMA is added, the more formaldehyde is produced during the cross-linking reaction and the more residual formaldehyde is present in fabrics. In order to minimize both the formaldehyde production during the cross-linking reaction and the residual formaldehyde present in fabrics, there is a need for a binding composition as described in WO 92/08835 wherein the NBMA content is below 3% by weight. An other advantage of such a composition would be a significant cost reduction since NBMA is a quite expensive product.

However, using NBMA as a post polymerisation cross-linking agent gives rise to some problems when the amount of NBMA (in % by weight of the total monomer content) is low, i.e. below 3%. More particularly, the runnability of the process, more specifically the roller stability, is poor. In other respects, the wet, dry and solvent strengths prove to drop dramatically.

Therefore, there is a need for a NBMA-containing binding composition for non-woven fibrous materials which maintains good runnability as well as good wet, dry and solvent strengths whereas the NBMA content is below 3% by weight.

General description of the invention

It is a first object of the present invention to provide a binding composition for non-woven fibrous materials, comprising a copolymer emulsion in which at least 30% by weight of the monomer content is vinyl C1 to C4 alkanoate, 0.5% to 3% by weight of N-(n-butoxymethyl) acrylamide as a post polymerisation cross-linking agent and 0.5% to 5% by weight of acrylamide.

Preferably not more than 90% by weight, more preferably between 60 and 80% by weight, of the monomer content is C1 to C4 alkanoate, with the preferred material being vinyl acetate.

The copolymer emulsion may include a C2 to C4 alkylene monomer, e.g. ethylene, typically in an amount of from 5% to 40% by weight of total monomer.

Another possible comonomer is selected from the alkyl (C2 to C10) (meth) acrylate class e.g., butylacrylate or 2 ethyl hexyl acrylate, which will preferably be present in an amount of from about 10% to about 60% by weight of total monomer.

A further class of possible functional comonomer is carboxyl group-containing monomers, e.g. acrylic acid, methacrylic acid, crotonic acid, itaconic acid, etc.

Sodium vinyl sulphonate is a further example of a functional monomer that may be included. Preferably between 0.2% to 1% by weight of total monomer is added.

One or more surfactants (non-ionic and anionic) may be included as appropriate.

The copolymer emulsion can be prepared using generally conventional techniques which are well known and characterised in the literature. Polymer synthesis (volumes I & II) by Sandler & Karo (Academic Press 1974) and Preparative Methods of Polymer Chemistry (2nd Edition) by Sorensen & Campbell (Interscience 1968) provide preparative information. Methoden der Organischen Chemie (Houben-Weyl) Band XIV published by Georg Thieme Verlag Stuttgart (1961) also provides preparative descriptions.

Any suitable initiator system can be used, but it is preferred not to use formosul (sodium formaldehyde sulphoxylate) as this produces formaldehyde. It is preferred to use either a thermal polymerisation, with no reducing agent, e.g. using ammonium or alkali metal persulphates, or redox initiation, with a persulphate, hydrogen peroxide or an organic peroxide as the oxidising agent and with the reducing agent typically being ascorbic acid or sodium metabisulphite.

The binding composition of the invention can be used for binding non-woven fibrous materials in generally conventional manner, e.g. by dipping, soaking, or spraying or by use of rollers and a bath.

It is therefore a second object of the present invention to provide a process of binding a non-woven fibrous material, comprising impregnating the material with a binding composition in accordance with the invention; drying the copolymer emulsion; and subjecting the impregnated material to thermal treatment to provide cross-linking.

It is a third object of the present invention to provide a non-woven fibrous material comprising a mass of fibres bound together by use of a binding composition in accordance with the invention.

Detailed description of the invention

The invention will be further illustrated by way of illustration in the following Examples.

Test methods

i) Viscosity

This was measured in centipoise using a Brookfield viscometer (ERV type) at 25 ° C with spindle 2 at 20 rpm.

ii) Tensile strength

This was measured for dry wet and solvent (acetone) treated samples, on a Lloyd or Instron tensometer. The emulsions were diluted to 20% and impregnated on Whatman's No.4 filter paper and viscose web of weight 15 g/m2. The impregnated paper or viscose web was dried at 60 ° C and then cured at 165 ° C on a rotary iron for 12 seconds. The cross linking reaction was catalysed by citric acid (1% w/w on polymer solids). Strips of impregnated substrate (200 x 50 x 0.2mm) were stretched at a speed of 100mm/minute. The breaking load F (in Kg) and strain E (in %) at break were measured.

iii) Formaldehyde content

Formaldehyde reacts with acidified chromotropic acid solution to form a purple coloured monocationic chromogen. The absorbance of the coloured solution is measured using a spectrophotometer at 570 nm and is proportional to the amount of formaldehyde in the solution.

To assess the formaldehyde content from impregnated substrate, a 2g sample of impregnated substrate was immersed in deionised water (50 ml)for 1 hour at 40 ° C and then filtered. 1.0ml of the extract was diluted with 2.7ml of deionised water. 0.3ml of a 1% w/v of chromotropic acid solution and 6.0ml of concentrated sulphuric acid were added. The solution was cooled and the 570nm absorption was measured.

The formaldehyde content of the emulsion was assessed by drying the emulsion in a stream of carrier gas (air or nitrogen). Thus, a 1g sample of emulsion was placed in a test tube, in an oven set at 120 ° C for 90 minutes. A carrier gas was used over the sample to carry the vapours to water traps situated outside the oven. The solutions from the water trap were analysed for formaldehyde in an analogous manner to that described above using chromotropic acid.

iv) Runnability

To check the roller stability of the latex, the latex sample was diluted to 20%. The diluted latex sample was placed in a machine to test the roller stability of emulsions. The pressure between the two rollers was set to 4 bar and the revolving speed of the rollers to around 80 rpm and the test run at room temperature (25 ° C). Qualitatively, the latex was judged to be good if there was no build of solid polymers on the roller after one hour.

Example 1

The monomer composition of this example was:

	% by weight
Vinyl acetate (VA)	66.5
Ethylene (E)	30.0
Acrylic Acid (AA)	0.5
N-butoxymethylacrylamide (NBMA)	1.5
Acrylamide (AMD)	1.0
Sodium vinyl sulphonate (SVS)	0.5

An initial aqueous phase, consisting of deionised water, (800 g), Empimin OT (37.5 g), formic acid (0.3 g), ascorbic acid (0.4 g), ferric chloride (0.9 g of a 1% solution), was charged to a 4 litre stainless steel reactor. The reactor was sealed, purged twice with nitrogen and once with ethylene. The reactor was pressurized with ethylene to 870 psi and then heated to between 32-34 ° C. A monomer mixture consisting of vinyl acetate (60g), acrylic acid (0.45 g), and NBMA (1.35 g) was added followed by the aqueous phase addition of deionised water (21.0 g), Empimin OT (1.87 g), synperonic NP30 (1.28 g), SVS (1.8 g of a 25% solution), AMD (1.8g of a 50% solution) and ammonia (0.45g).

10% of the solution of the initiators, ammonium persulphate [(10.8g) in water (184 g)] and ascorbic acid [(3.6g) in water (184.0g)] was added to the reactor. Once the exotherm had subsided monomers, VA (1137.0 g), AA (8.55 g), NBMA (25.5g) and the remainder of the aqueous phase monomers [deionised water (399.0g), Empimin OT (35.63g), Synperonic NP30 (24.42g), SVS (34.2g of a 25% solution), AMP (34.2g of a 50% solution) and ammonia (8.55g)] were added at a constant rate for six hours, whilst the remaining initiators were added over a period of seven hours with the last hour at 2.5 times the normal constant rate. One hour into the continuous additions, the temperature of polymerisation was brought to 50-52 ° C and kept there for the rest of the additions. One and a half hours into the process, the pressure of the reactor, using ethylene was maintained for two and a half hours at 870 psi. Once all the additions were completed the reactor was cooled at around 30-32 ° C and the addition of tertiary butyl hydroperoxyde (3.6g) in deionised water (41.g) and of sodium metabisulphite (2.16g) in deionised water (41.0g) were started. At the end of the additions the reactor was cooled to below 30 ° C. The emulsion was discharged from the reactor and filtered using 250 mesh. The latex had a solids content of 49.0% and a viscosity of 100 centipoise.

Empimin OT used in the examples is a 60% active solution of sodium di-octyl sulphosuccinate obtainable from Surfachem Ltd., Leeds, U.K..

Synperonic NP30 (70% active) used in the examples is nonyl phenol, nonionic containing 30 ethylene oxide units, obtainable from Cargo Fleet Chemicals U.K..

Example 2

The monomer composition of this example was:

	% by weight
Vinyl acetate (VA)	76.4
Ethylene (E)	20.6
Acrylic Acid (AA)	0.5
N-butoxymethyl acrylamide (NBMA)	1.5
Acrylamide (AMD)	1.0

A solution of 103g of Synperonic NP30, (70% active), and 4.0g of Perlankrol PA (in 750.5g of deionised water), and a monomer mixture consisting of 67g of vinyl acetate and 0.45g of acrylic acid were charged to a 4 litre stainless steel reactor. The temperature was raised to 30 ° C, then the reactor was purged twice with nitrogen and once with ethylene. The reactor was charged with ethylene to a pressure of 50 bar, and then heated to a temperature of 75 ° C. At this temperature 15% of a solution of sodium persulphate (9.0g in 275g of water) was added to the reactor. A monomer mixture consisting of 1306g of vinyl acetate, 30.0g of NBMA and 8.6g of acrylic acid was added at a constant rate over 4 hours. A solution of 18.0g of acrylamide and 2.3g of ammonia , in 264g of water, was added over 4 hours and the remaining sodium persulphate solution was added over 4 hours 30 minutes. Ethylene was charged to the reactor during the first three hours of these additions to maintain the pressure at 62 bar. The temperature was maintained at 75 ° C throughout the slow additions and for a further 30 minutes. The temperature was reduced to 50 ° C and solutions of t-butylhydroperoxide, (3.6g in 70g of water), and sodium metabisulphite, (2.4g in 70g of water), were added over 30 minutes while cooling to 30 ° C. A solution of 1.8g of Kathon LXE in 48.2g of water was added. The emulsion was discharged from the reactor and filtered through 250 mesh nylon to remove coagulum. The resultant latex has a solids content of 56.45% and a viscosity of 312 centipoise.

Perlankrol PA used in the examples is (92% active) anionic based on sulphated nonyl phenol with 3-4 ethylene oxide units, obtainable from Lankro Chemicals Ltd., U.K..

Kathon LXE is obtainable from Rohm and Haas.

Example 3

The monomer composition of this example was:

	% by weight
Vinyl acetate (VA)	66.0
Veova 9	30.0
Acrylic Acid (AA)	0.5
NBMA	2.0
Acrylamide (AMD)	1.0
Sodium vinyl sulphonate (SVS)	0.5

Veova 9 is a vinyl ester of versatic 9, a carboxylic acid, and is obtainable from Shell Chemicals Ltd. U.K..

The process is very similar to that described above, in example 1, except that here the reaction was carried out on a conventional open reactor.

The initial waterphase, consisting of deionised water (250g), Empimin OT (10.4g), formic acid (0.03g), Ascorbic acid (0.1g), Ferric chloride (0.25g of a 1% solution), was charged to a 1 litre glass reactor. The reactor was purged with nitrogen and a slow purge continued during the reaction. The reactor was heated to between 32-34 ° C. A monomer mixture consisting of vinyl acetate (16.5g), acrylic acid (0.12g), NBMA (0.51g), and Veova 9 (7.5g) was added followed by the aqueous phase monomer addition of deionised water (4.5g), Empimin OT (0.52g), synperonic NP30 (0.36g), sodium vinyl sulphonate (0.8g), acrylamide

(0.25g), and ammonia (0.17g).
10% of the solution of the initiators, ammonium persulphate [(3.0g) in water (48.4g)] and ascorbic acid [-(0.9g) in water (48.4g)] was added to the reactor.

Once the exotherm had subsided monomers [vinyl acetate (313.5g), acrylic acid (2.38g), NBMA (9.69g), Veova 9 (142.5g) and the remaining aqueous phase monomers [deionised water (85.6g), Empimin OT (9.88g), synperonic NP30 (6.78g), sodium vinyl sulphonate (15.83g) acrylamide (4.75g) and ammonia (3.3g)] were added at a constant rate for four hours, whilst the remaining initiators were added over a period of five hours with the last half hour at two and a half times the normal constant rate. One hour into the continuous additions, the temperature of polymerisation was brought to 50-52°C and kept there for the rest of the additions. Once all the additions were completed, the reactor was cooled to around 30-32°C, and the additions of tertiary butyl hydroperoxide (1.0g) in deionised water (11.3g) and of sodium metabisulphite (0.6g) in deionised water (11.3g) were started. At the end of the additions the reactor was cooled to below 30°C. the emulsion was discharged from the reactor and filtered using 250 mesh. The emulsion had a solids content of 51.85% and viscosity of 330 centipoise, as measured by the method described previously.

Example 4

The manufacturing process is exactly the same as for example 3 except that instead of using 2% NBMA, in this example 1.5% of NBMA was used, vinyl acetate being increased to 66.5%. The latex properties were solids content 51.85%, and viscosity of 500 centipoise.

Example 5

The manufacturing process is again the same as for example 3, except that the acrylamide level was increased to 1.5%, whilst the NBMA content was at 1.5%.

Example 6 (Comparative Example)

The manufacturing process for this product is given below.

The monomer composition of this example was:

	% by weight
Vinyl acetate (VA)	72.0
Ethylene (E)	25.0
Acrylic Acid (AA)	0.5
NBMA	2.0
Sodium vinyl sulphonate (SVS)	0.5

The product was prepared in a 50 gallon reactor.

The initial waterphase, consisting of deionised water (60.0Kg), Empimin OT (3.7kg), formic acid (0.03kg), Ascorbic acid (0.035Kg), Ferric chloride (0.006Kg of a 1% solution), was charged to a 50 gallon stainless steel reactor. The reactor was sealed purged twice with nitrogen and once with ethylene. The reactor was pressurized with ethylene to 870 psi and then heated to between 32-34°C. A monomer mixture consisting of vinyl acetate (6.4Kg), acrylic acid (0.045Kg), and NBMA (0.17Kg), was added followed by the aqueous phase monomer addition of deionised water (2.0Kg), Empimin OT (0.18Kg), synperonic NP30 (0.12Kg), sodium vinyl sulphonate (0.17Kg), and ammonia (0.02Kg).

10% solution of the initiators, ammonium persulphate [(1.6Kg) in water (18.0Kg)] and ascorbic acid [-(0.35Kg) in water (18.0Kg)] was added to the reactor. Once the exotherm had subsided monomers [vinyl acetate (121.6Kg), acrylic acid (0.84Kg), NBMA (3.32Kg), and the remaining aqueous phase monomers [deionised water (40.0Kg), Empimin OT (3.51Kg), synperonic NP30 (0.37Kg), sodium vinyl sulphonate (3.34Kg), and ammonia (0.418Kg)] were added at a constant rate for six hours, whilst the remaining initiators were added over a period of seven hours with the last half hour at two and a half times the normal constant rate. One hour into the continuous additions, the temperature of polymerisation was brought to 50-52°C and kept there for the rest of the additions. About one and a half hours into the process, the pressure of the reactor was maintained for two and a half hours at 870 psi, using ethylene. Once all the additions were completed, the reactor was cooled and at around 30-32°C the additions of tertiary butyl hydroperoxide (0.35Kg) in deionised water (4.0Kg) and of sodium metabisulphite (0.21Kg) in deionised water (4.0Kg) were started. At the end of the additions the reactor was cooled to below 30 ° C. The emulsion was discharged from the reactor and filtered using 250 mesh. The latex had a solids content of 49.0% and viscosity of 100 centipoise, as measured by the method described previously.

Example 7 (Comparative Example)

The monomer composition of this example was:

	% by weight
Vinyl acetate (VA)	76.5
Ethylene (E)	20.5
Acrylic Acid (AA)	0.5
NBMA	1.5
Sodium vinyl sulphonate (SVS)	1.0

A solution of 10.5kg of Synperionic NP30, (70% active), and 0.40kg of Perlankrol PA (in 98kg of deionised water) and a monomer mixture consisting of 7.0kg of vinyl acetate and 0.056kg of acrylic acid were charged to a 50 gallon reactor. The reactor was purged three times with nitrogen and once with ethylene. The reactor was charged with ethylene, (12.5kg), to a pressure of 40 bar, then 15% of a solution of sodium persulphate, (0.92kg in 19kg of water), was added to the reactor. The temperature was raised to 70 ° C, and then allowed to exotherm to 75 ° C. At this temperature a monomer mixture consisting of 135kg of vinyl acetate, 3.0kg of NBMA and 0.88kg of acrylic acid was added at a constant rate over 5 hours. A solution of 7.4kg of sodium vinyl sulphonate, (25%), and 0.25g of ammonia in 10.0kg of water was added over 5 hours and the remaining sodium persulphate solution was added over 5 hours 30 minutes. After 30 minutes a further 24.5kg of ethylene was charged to the reactor over 3.5 hours maintaining the pressure at less than 60 bar. The temperature was maintained at 75 ° C throughout the slow additions and for a further 30 minutes. The temperature was reduced to 50 ° C and solutions of 0.37kg of t-butylhydroperoxide plus 0.09kg of ammonia in 6.0kg of water and sodium metabisulphite, (0.24kg in 6.0kg of water), were added over 30 minutes while cooling to 30 ° C. A solution of 1.86kg of citric acid in 2.0kg of water and a solution of Kathon LXE, (0.12kg in 0.5kg of water), were added. The emulsion was discharged from the reactor and filtered through 250 mesh nylon to remove coagulum. The resultant latex had a solids content of 55.80%, viscosity of 78 centipoise.

Example 8 (Comparative Example)

The manufacturing process for this product is given below.
The monomer composition of this example was:

	% by weight
Vinyl acetate (VA)	65.5
Ethylene (E)	30.0
Acrylic Acid (AA)	0.5
N-methylolacrylamide (NMA)	4.0

The initial waterphase, consisting of deionised water (800g), Empimin OT (37.5g), formic acid (0.3g), formosul (0.4g), Ferric chloride (0.9g of a 1% solution), was charged to a 4 litre stainless steel reactor. The reactor was sealed purged twice with nitrogen and once with ethylene. The reactor was pressurized with ethylene to 870 psi and then heated to between 32-34 ° C. A monomer mixture consisting of vinyl acetate (60g), acrylic acid (0.45g), was added followed by the aqueous phase monomer addition of deionised water (21.0g), Empimin OT (1.87g), synperonic NP30 (1.28g), NMA (7.5g), and ammonia (0.45g). 10% of the solution of the initiators, ammonium persulphate [(10.8g) in water (184g)] and formosul [(3.4g) in water (184.0g)] was added to the reactor. Once the exotherm had subsided monomers [vinyl acetate (1119.0g), acrylic acid (8.55g)], and the remaining aqueous phase monomers [deionised water (356.0g), Empimin OT (35.63g), synperonic NP30 (24.42g), NMA (142.5g) and ammonia (8.55g)] were added at a constant rate for six hours, whilst the remaining initiators were added over a period of seven hours with the last half hour at two and a half times the normal constant rate. One hour into the continuous additions, the temperature of polymerisation was brought to 50-52 °C and kept there for the rest of the additions. About one and a half hours into the process, the pressure of the reactor was maintained for two and half hours at 870 psi, using ethylene. Once all the additions were completed, the reactor was cooled and at around 30-32 °C the additions of tertiary butyl hydroperoxide (3.6g) in deionised water (41.0g) and of sodium metabisulphite (2.16g) in deionised water (41.0g) were started. At the end of the additions the reactor was cooled to below 30 °C. The emulsion was discharged from the reactor and filtered using 250 mesh. The latex had a solids content of 50.0% and viscosity of 800 centipoise, as measured by the method described previously.

Example 9 (comparative Example)

The monomer composition of this example was:

	% by weight
Vinyl acetate (VA)	76.5
Ethylene (E)	20.0
Crotonic Acid (AA)	0.5
N-methylolacrylamide (NMA)	3.0

A solution of 103g of Synperonic NP30 (70% active), 1.36g of ferric ion solution and 0.7g of formic acid in 750g of deionised water and a monomer mixture consisting of 67g of vinyl acetate and 0.45g of crotonic acid were charged to a 4 litre stainless steel reactor. The temperature was raised to 30 °C, then the reactor was purged twice with nitrogen and once with ethylene. The reactor was charged with ethylene to a pressure of 57 bar. A monomer mixture consisting of 1274g of vinyl acetate and 8.45g of crotonic acid and a solution of 120g of NMA (45% aq.), and 5.0g of ammonia in 205g of water were added at a constant rate over 5 hours. Initiator solutions comprising 7.2g of ammonium persulphate in 300g of water and 2.2g of formosul in 300g of water were added at double rate for 20 minutes, normal rate for 4 hours 20 minutes and double rate for 1 hour to give a total addition time of 5 hours 40 minutes. The temperature was slowly raised to 60 °C during the first 3 hours of additions and maintained until the monomer addition was complete, then it was raised to 70 °C until the initiator additions were complete. The temperature was reduced to 50 °C and solutions of t-butylhydroperoxyde (3.6g in 35g of water) and sodium metabisulphite (3.6g in 35g of water) were added over 30 minutes while cooling to 30 °C. The emulsion was discharged from the reactor and filtered through 250 mesh nylon to remove coagulum. The resultant latex had a solids content of 49.7% and a viscosity of 470 centipoise.

Example 10

The monomer composition of this example was:

	% by weight
Vinyl acetate (VA)	49.8
Butyl acrylate	46.0
Acrylic Acid (AA)	1.0
N-methylolacrylamide (NMA)	3.2

Deionised water (109g) and ferric chloride (1.25g of a 0.1% solution) were placed in an open glass reactor vessel (1 litre), and purged with nitrogen to betweeen 20-22 °C. A slow nitrogen purge was continued through out the reaction.

10% of a solution consisting of synperonic NP30 (10.71g), Gafec RE610 (0.5g), sodium hydroxide solution (0.32g of 10% aqueous solution), NMA (16.66g) and deionised water (75g) was added followed by vinyl acetate (12.5g), butyl acrylate (11.5g), methacrylic acid (0.25g). To this mixture were added 10% of the solutions of ammunium persulphate (2.5g) in water (31.2g), and ascorbic acid (0.9g) in water (31.2g). At maximun exotherm, continuous additions of vinyl acetate (112.5g), butyl acrylate (103.5g) and methacrylic acid (2.25g) were started in conjunction with the aqueous solution containing NMA, and the initiators, to last two hours. The temperature of the reaction was taken to between 40-51 °C. At the end of the additions, the temperature of reaction was held at 50 ° C for a further five minutes. On bringing the temperature to 45 ° C, tertiary butylhydroperoxide (0.25g) in water (0.8g) and sodium metabisulphite (0.25g) in water (0.8g) were added. The reaction was allowed to exotherm to 50 ° C, and then held at 50 ° C for a further 15 minutes. The reaction was cooled to below 30 ° C and pH adjusted to between 4-5 using ammonia [(1.25g of a 0.88 concentration) in water (1.25g)]. This resulted a latex having a solids content of 35% and a viscosity of 200 centipoise.

Gafec RE610 is a phosphate ester obtainable from GAF Ltd., U.K.

The formaldehyde content, in the emulsion and on paper, was measured as herein-above described and the results are summarized in Table 1 wherein the formaldehyde content is in parts per million (ppm).

Table 1

	Formaldehyde in emulsion (ppm)	Formaldehyde in paper (ppm)
Example 1	90	2
Example 2	118	1
Example 3	160	26
Example 4	137	6
Example 5	149	not measured
Example 6	307	10
Example 7	298	5
Example 8	700	200
Example 9	1233	69
Example 10	1189	92

It is clear from Table 1 that the addition of acrylamide into the formulation dramatically reduces the levels of formaldehyde contents in the emulsion and the reduction is even more noticeable in the final product.

The runnability, i.e. the roller stability has been assessed, according to the method herein-above described, for examples 1,2 6,7,8 and 9.

The results are summarized in Table 2.

Table 2

	Roller stability
Example 1	Very good (2 hours)
Example 2	Fair (30 Minutes)
Example 6	Fair (30 Minutes)
Example 7	Poor (15 minutes)
Example 8	Good (1 Hour)
Example 9	Good (1 Hour)

It has been found that on replacing NMA with NBMA, roller stability suffers and, to improve the runnability, 0.5% of sodium vinyl sulphonate needed to be added (in Example 6) to improve the runnability, as according to the teaching of WO 92/08835. It can be seen that, for example 2, no sodium vinyl sulphonate has been added, nevertheless the roller stability is fair. It can also be noticed by comparing Examples 1 and 6 that, with the same amount of SVS being added, the roller stability is dramatically improved by the combination of NBMA and acrylamide.

Therefore, if a very good roller stability is required it is enough to add a very little amount of SVS, preferably between 0.2% and 1% of total monomer.

The tensile strengths F (wet, wet dry and in solvent) (in kg) and the elongation E (in %), have also been assessed for Examples 1, 2, 6, 7, 8, 9. The results are summarized in Table 3.

Table 3

Example	1	2	6	7	8	9
F dry	0.53	0.51	0.51	0.47	0.56	0.63
E dry	34.6	29.0	32.5	30.0	35.1	29.0
F wet	0.22	0.28	0.22	0.25	0.27	0.32
E wet	47.6	16.0	29.0	21.0	40.1	17.0
F in Solvent	0.11	0.15	0.10	0.09	0.13	0.19
E in Solvent	9.0	7.0	8.1	6.0	10.0	7.0

The comparison of Examples 6 and 7 with Examples 8 and 9 shows that the replacement of NMA with NBMA leads to a drop in dry, wet and solvent tensile strengths. The addition of acrylamide appears to restore the tensile strengths.

Claims

1. Binding composition for non-woven fibrous materials, comprising a copolymer emulsion in which at least 30 % by weight of the monomer content is vinyl C1 to C4 alkanoate, 0.5% to 3% by weight of N-(n-butoxymethyl) acrylamide as a post polymerisation cross-linking agent and 0.5 % to 5% by weight of acrylamide.

2. Binding composition according to claim 1 wherein sodium vinyl sulphonate is added in an amount of between 0.2% to 1% by weight of total monomer.

3. Process of binding a non-woven fibrous material, comprising impregnating the material with a binding composition in accordance with claim 1; drying the copolymer emulsion; and subjecting the impregnated material to thermal treatment to provide cross-linking.

4. Non-woven fibrous material comprising a mass of fibres bound together by use of a binding composition according to claim 1 or 2.

European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 94 10 1495

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
D,A	WO-A-92 08835 (UNILEVER PLC) 29 May 1992 * whole document * ---	1-4	D04H1/64
A	FR-A-2 185 708 (MONSANTO COMPANY) * whole document * -----	1-4	

TECHNICAL FIELDS SEARCHED (Int.Cl.5)
D04H

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	3 May 1994	V Beurden-Hopkins, S

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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