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⑤④ **Polymeric compositions useful as binders in coating colors and coating colors prepared therefrom.**

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Description

The present invention relates to a synthetic polymer composition useful as the binder component in coating colors and to coating colors containing these polymeric compositions.

In the production of paper, the paper surface is often coated with a composition (commonly referred to as a coating color) which imparts desirable properties such as printability to the paper. Conventionally, the coating color consists primarily of suspension of a pigment and/or filler such as clay in an aqueous medium containing a binder.

In one conventional method for applying the coating color, the coating is continuously transferred as a liquid film from an applicator roll to the paper surface, with any applied excess removed using suitable means such as blade or air-knife techniques. In the preparation of the highest quality paper, the paper is often coated sequentially with a coating color of one composition and thereafter with a coating color of a second composition. In general, in the preparation of the double coated paper, the two coating colors contain the same or similar binders but different filler materials.

For various reasons, paper producers have continuously strived to reduce the finished weight of the coated paper. One method by which this can be achieved is by reducing the amount of the coating color applied to the paper. Unfortunately, a reduction in the coat weight generally results in a drop of the finished paper properties, particularly in the print quality. To effectively coat the paper, at the desirable coat weight, the coating colors advantageously exhibit desirable physical properties, e.g., stability and rheological properties. These properties are particularly important in the preparation of quality paper grades such as those printed by gravure techniques.

Heretofore, a natural, high molecular weight material such as starch or protein has been used as the binder component of the coating color. Unfortunately, these natural materials are susceptible to attack by microorganisms and when employed alone give brittle coatings. Moreover, using a starch binder, the coated paper often does not possess the required print quality due to insufficient coat hold-out, i.e., excessive penetration of the coating into the paper.

It has heretofore been suggested to employ synthetic polymers as the binder in paper coatings. Many such synthetic polymer binders consist of two polymeric components with one copolymer being employed primarily to impart the desired binding strength and other properties to the coated paper and the second copolymer component being employed primarily to affect the rheological properties of the coating colors prepared therefrom. For example, U.S. Patent 3 694 394 discloses an aqueous coating composition comprising a blend of two latexes. The first latex is a film-forming polymer (copolymer A) that is insol-

uble and not swellable to any substantial extent in aqueous alkali and is a copolymer of styrene and/or methyl methacrylate, an ethylenically unsaturated carboxylic acid and butadiene. The second polymer (copolymer B) is substantially swellable and insoluble in aqueous alkali and is a cross-linked copolymer of butadiene, styrene and/or methyl methacrylate and an ethylenically unsaturated acid. However, the paper coated with these compositions does not possess the desired balancer of properties. USP 3 297 615 discloses a pigment coating composition comprising an adhesive derived from 75 to 95 percent ethylacrylate, 4 to 24 percent acrylonitrile and 1 to 3 percent methacrylic acid. The coating composition can further contain a supplemental adhesive such as starch or polyvinyl alcohol or a preservative such as a melamine-formaldehyde resin. German Patent 1 546 315 discloses a synthetic polymer binder comprising 60 to 85 percent of a first copolymer of butadiene, styrene and/or acrylonitrile and 5 to 40 percent of a second copolymer of acrylic or methacrylic acid, a monomer which forms a water-insoluble homopolymer (at least a portion of which is an ester of acrylic or methacrylic acid) and, optionally, acryl- or methacrylamide. Unfortunately, coating colors prepared from this binder are generally deficient, particularly using gravure printing techniques, due again to insufficient coat hold-out. In addition, using coating colors prepared from the described polymeric binders, difficulties are experienced in the preparation of a double coated paper. Specifically, an undesirable number of paper breaks and discontinuities on the coated paper are experienced using the coating colors prepared from these copolymer binders.

A similar synthetic polymeric binder except that the first copolymer is derived from an ester of acrylic or methacrylic acid, a vinyl ester or propionic acid, and optionally other copolymerizable monomers, is described by U.S. Patent No. 3 365 410. While coating colors prepared using these polymeric binders improve the print quality of paper prepared therefrom, a further improvement in the balance of the paper properties is required.

EP 57 857 describes the use of an aqueous dispersion of a copolymer derived from a C_4 - C_8 alkyl acrylate and an acrylic or methacrylic acid as the sole binder and thickener in a paper coating. A wide variety of optionally employed comonomers are also stated to be useful in the preparation of the binder/thickener copolymer. Although a number of conventional additives, including polymeric additives, can be employed in combination with the sole binder/thickener copolymer, there is no suggestion nor any reason to employ a binder copolymer with the specified copolymer.

In view of the aforementioned deficiencies of the synthetic polymer binders employed heretofore, it remains highly desirable to provide a polymeric composition which can effectively be employed as the binder in a paper coating color

to impart an improved balance of properties in the paper coated herewith.

Ex. 5 of DE-A 2 806 862 describes a composition comprising a butadiene/styrene copolymer and a rheology control copolymer prepared from 66 wt.% methacrylic acid, 28 wt.% ethyl acrylate and 6 wt.% acrylonitrile. 0.002 wt.% divinyl benzene, based on the total weight of the above monomers, is also present during the preparation of the rheology control copolymer. In the sentence bridging pp. 14 and 15 it is stated that water-soluble polymer or dispersions of water-insoluble polymers containing the rheology control copolymer may be used, among other things, for the surface treatment of paper. According to Claim 1 the rheology control copolymer can contain down to 30 wt.% of acid monomer.

Accordingly, the present invention is such an improved polymeric composition useful as the binder component in a coating color. The polymeric composition is composed of two polymeric components, the improvement in said composition comprising the inclusion, as one of the two polymeric components, of a lightly cross-linked copolymer comprising, in polymerized form, an α,β -ethylenically, unsaturated carboxylic acid in an amount of 1 to less than 30 wt.%, an ester of an α,β -ethylenically unsaturated carboxylic acid and an unsaturated nitrile. The lightly cross-linked copolymer (hereinafter referred to as the «rheology control copolymer») is cross-linked sufficiently to improve the rheological and/or other properties of the polymeric composition and/or coating colors prepared therefrom, which is achieved by using a small amount of from 0.01 to 10 weight percent of a cross-linking monomer. The other copolymer (hereinafter referred to as the «binder copolymer») is generally a copolymer of a vinyl aromatic monomer, a conjugated diene and, optionally, other copolymerizable monomers or a copolymer of an ester of an α,β -ethylenically unsaturated carboxylic acid, a comonomer which forms a water-insoluble homopolymer and, optionally, one or more copolymerizable monomers.

In a preferred embodiment, the polymeric composition comprises from 60 to 90 weight parts of the binder copolymer and from 10 to 40 weight parts of the rheology control copolymer. The binder copolymer comprises, based on 100 weight parts, at least 60 weight parts in polymerized form, of a vinyl aromatic monomer and a conjugated diene, these monomers being employed in an amount such that the binder copolymer comprises from 10 to 90 weight percent of the vinyl aromatic monomer and from 10 to 90 weight percent of a conjugated diene, said weight percents being based on the total weight of the vinyl aromatic monomer and the conjugated diene. The binder copolymer can optionally comprise, in polymerized form, up to 20 weight parts of an α,β -ethylenically unsaturated carboxylic acid and up to 20 weight parts of other copolymerized monomers. The rheology control polymer comprises, based on 100 weight parts, in

polymerized form, from 40 to 90 weight parts of an ester of an α,β -ethylenically unsaturated carboxylic acid; from 1 to less than 30 parts of an α,β -ethylenically unsaturated carboxylic acid; from 0.5 to 30 weight parts of an ethylenically unsaturated nitrile and from 0.01 to 10 weight parts of a cross-linking monomer.

The coating colors containing a sufficiently cross-linked polymeric component possess rheological and/or other properties which cannot be obtained without the cross-linking. In addition, the flexibility imparted by the cross-linked structure allows ready adaptability of the polymeric binder composition to various formulations in the preparation of coating colors. Paper coated with the coating colors exhibit unexpectedly high binding strengths and excellent printability.

The polymeric compositions of the present invention are useful as the binder component in various compositions, particularly coating colors. They are particularly useful as the binder component in coating colors employed in the two step coating processes for preparing the highest quality paper used in rotogravure printing.

The polymeric composition of the present invention comprises two polymeric components, herein referred to as a binder copolymer and a rheological control polymer. The binder copolymer which primarily imparts the binding strengths and other properties to the coated paper is preferably derived from a vinyl aromatic monomer, a conjugated diene and, optionally, other monomers copolymerizable therewith. Representative vinyl aromatic monomers include styrene; α -alkyl styrenes such as α -methyl styrene and α -ethyl styrene; nuclear substituted, alkyl substituted styrenes such as vinyl toluene, *o*-ethyl styrene, 2,4-demethyl styrene, nuclear substituted halo-styrene such as chlorostyrene and 2,4-dichlorostyrene; styrene substituted with both a halo and an alkyl group such as 2,2-chloro-4-methyl styrene and combinations thereof. In general, styrene, or a combination of styrene with small amounts (i.e., less than 10 weight percent of the monovinylidene aromatic employed) of one or more other vinylidene aromatic monomers, particularly on α -alkylstyrene, are preferred. Most preferably, styrene is employed as the vinyl aromatic monomer. The conjugated diene is an alkadiene, preferably a 1,3-conjugated diene such as butadiene, isoprene, propylene, chloroprene and the like. The preferred conjugated diene is 1,3-butadiene.

Often, but optionally, the binder copolymer comprises one or more additional copolymerizable monomers. Such comonomers are employed to vary the properties of the resulting polymer and the specific comonomers and their amounts selected to obtain a copolymer having desirable properties. For example, to increase the binding strength of a coated paper, it is often desirable to employ an α,β -ethylenically unsaturated carboxylic acid such as acrylic, methacrylic, itaconic, fumaric or maleic acid in the preparation of the binder copolymer. Preferred of such acids are ita-

conic or acrylic acid or a combination thereof. Other comonomers which are often advantageously employed in the presence of such copolymer binder include unsaturated nitriles such as acrylonitrile and methylacrylonitrile, the halo-substituted olefins such as vinylidene chloride, esters of α,β -ethylenically unsaturated carboxylic acids, ethylenically unsaturated amides such as acrylamide and methylacrylamide, and the ethylenically unsaturated alcohols.

The relative proportions of the vinyl aromatic monomer, conjugated diene and other monomers, if employed in the preparation of the preferred binder copolymer, are dependent on a variety of factors including the specific vinyl aromatic monomer and conjugated diene employed and the desired properties of the binder copolymer. For example, the binder copolymer advantageously exhibits a second-order transition temperature, as defined by P.J. Flory in «Principles of Polymer Chemistry» published in 1953 by Cornell University Press, Ithaca, N.Y., p. 56 between -60° and $+40^\circ\text{C}$ and the monomers and their amounts selected accordingly. In general, the binder copolymer comprises at least 60, preferably at least 80, more preferably at least 90, weight percent of the vinylidene aromatic monomer and conjugated diene, said weight percents being based on the total weight of the first copolymer. In general, the vinyl aromatic monomer is employed in amounts from 10 to 90, preferably from 50 to 70, weight percent and the conjugated diene is employed in amounts from 10 to 90, preferably from 30 to 50, weight percent, said weight percents being based on the total amount of vinyl aromatic monomer and conjugated diene employed in the preparation of the binder copolymer. The α,β -ethylenically unsaturated carboxylic acids are employed in amounts from 0 to 20 weight percent, preferably from 1 to 5 weight percent, and the other copolymerizable monomers are employed in amounts from 0 to 20, more generally from 0 to 5, weight percent, said weight percents being based on the total weight of the binder copolymer. In general, the binder copolymer of the present invention is preferably derived from 50 to 70 weight percent of a vinyl aromatic monomer, particularly styrene, from 30 to 50 weight percent of a conjugated diene, particularly 1,3-butadiene, and from 1 to 5 weight percent of an α,β -ethylenically unsaturated carboxylic acid, particularly itaconic acid, acrylic acid or a combination thereof.

Alternatively, but less preferably, the binder copolymer is derived from an ester of an α,β -ethylenically unsaturated carboxylic acid and a comonomer which forms a water-insoluble homopolymer. Representative esters are the esters of acrylic and/or methacrylic acids with alcohols having from 1 to 8 carbon atoms including ethyl acrylate, n-butylacrylate, i-butylacrylate, 2-ethylhexylacrylate and the like. Esters of acrylic acid with alcohols having from 4 to 8 carbon atoms are preferred. Representative comonomers which form a water-insoluble homopolymer in-

clude generally the vinyl aromatic monomers, particularly styrene; the unsaturated nitriles, particularly acrylonitrile; the vinyl esters of a monocarboxylic acid, particularly vinyl acetate or vinyl propionate; the halo-olefins such as vinyl chloride or vinylidene chloride; or a combination thereof. The preferred of such comonomers are the vinyl esters, particularly vinyl acetate and vinyl propionate. In general, the binder copolymer will comprise from 10 to 90, preferably from 35 to 60, weight percent of the ester of an unsaturated carboxylic acid and from 10 to 90, preferably from 35 to 60, weight percent of the vinyl acetate, and optionally, up to 10 weight percent of a further comonomer, said weight percents being based on the total weight of the binder copolymer. Although such further comonomer can be a comonomer which forms a water-insoluble homopolymer, it is more advantageously an α,β -ethylenically unsaturated carboxylic acid, preferably an acid having from 3 to 5 carbon atoms, including acrylic, methacrylic, crotonic, maleic, fumaric or itaconic acid and their amides, monoalkylamides, dialkylamides, N-methylolamides and esters of the N-methylolamides, including the half amides and half esters of the di-carboxylic acids; or a more strongly acidic comonomer such as vinyl sulfonic acid and p-toluene sulfonic acid. Preferred of such comonomers are the α,β -ethylenically unsaturated acids, particularly those acids having from 3 to 5 carbon atoms. These acids are preferably employed in amounts from 0.1 to 5 weight percent based on the total weight of the binding copolymer.

The rheology control polymeric component comprises a lightly cross-linked copolymer of an α,β -ethylenically unsaturated acid, an ester of an α,β -ethylenically unsaturated carboxylic acid and an unsaturated nitrile.

The esters of the α,β -ethylenically unsaturated acids advantageously employed in the present invention are those esters of a carboxylic acid having from 3 to 5 carbon atoms such as acrylic, methacrylic, maleic, fumaric or itaconic acids (preferably acrylic or methacrylic acids) with alcohols having from 2 to 10 carbon atoms, preferably 2 to 4 carbon atoms. Exemplary examples of such esters are ethyl acrylate, propyl acrylate, butyl acrylate, propylmethacrylate and the like.

The unsaturated carboxylic acids advantageously employed herein are those carboxylic acids which contain from 3 to 10 carbon atoms. Representative of such acids are acrylic, methacrylic, crotonic, itaconic, fumaric and ethacrylic acids.

Representative of ethylenically unsaturated nitriles include acrylonitrile, methacrylonitrile, maleic nitrile and cinnamionitrile.

In general, a cross-linking monomer, i.e., a copolymerizable monomer which when included in the polymerization recipe introduces cross-linkages into the resulting polymer, is employed to lightly cross-link the rheology control copolymer. Representative cross-linking monomers include the ethylenically unsaturated monomers which

contain two or more non-conjugated terminal ethylenic groups. Examples of such monomers are the polyvinyl aromatics such as divinylbenzene, divinyl toluene, divinyl xylene and trivinylbenzene; the allyl or butenyl acrylates and/or methacrylates such as allyl methacrylate, ethylene glycol dimethylacrylate and the like. Preferred cross-linking monomers contain from 4 to 15 carbon atoms, with allyl acrylate and allyl methacrylate being most preferred.

The specific monomeric components and the relative proportions of each, including the cross-linking monomer and its amounts, most advantageously employed in preparing the rheology control polymer are dependent on a variety of factors including the composition of the binder copolymer employed and the desired properties of the coating color prepared therefrom. For example, if the binder copolymer is a copolymer of an ester of an unsaturated acid and a vinyl ester of an unsaturated carboxylic acid, the desired polymeric properties of the copolymers can often be obtained using a lightly cross-linked polymer derived from the ester of an unsaturated carboxylic acid, preferably from 40 to 90 weight percent of an ester of acrylic acid with an alcohol having from 1 to 8 carbon atoms; the unsaturated carboxylic acid, preferably from 5 to less than 30 weight percent of acrylic and/or methacrylic acid; and an unsaturated nitrile, preferably from 0.5 to 25 weight percent of acrylonitrile, said weight percents being based on the total weight of the rheology control polymer. The cross-linking monomer is advantageously incorporated using from 0.05 to 5 weight percent of a cross-linking monomer, preferably from 0.05 to 2 weight percent of allyl acrylate or methacrylate. In addition, small amounts (i.e., less than 10 weight percent) of a vinyl ester of a monocarboxylic acid can optionally be employed.

Alternatively, when the binder copolymer is a copolymer derived primarily from a vinyl aromatic monomer and a conjugated diene, to obtain the most desirable properties, the lightly cross-linked rheology control copolymer is advantageously derived from 40 to 90 weight percent of the ester of an unsaturated carboxylic acid, preferably from 45 to 75 weight percent of ethyl acrylate and/or ethyl methacrylate; from 1 to 30 less than weight percent of an unsaturated carboxylic acid, preferably from 5 to 25 weight percent acrylic and/or methacrylic acid; from 0.5 to 30 weight percent of an unsaturated nitrile, preferably from 5 to 25 weight percent of acrylonitrile or mixtures of acrylonitrile with maleic nitrile or methacrylonitrile; and 0.01 to 10 weight percent of a cross-linking monomer, preferably from 0.05 to 5 weight percent of allyl acrylate and/or allyl methacrylate, wherein said weight percents are based on the total weight of the rheology control copolymer.

Most preferably, the rheology control copolymer comprises, in polymerized form, from 50 to 70 weight percent ethyl acrylate, from 10 to 20 weight percent methacrylic acid, from 10 to 20

weight percent acrylonitrile and from 0.05 to 2 weight percent of a cross-linking monomer, particularly allyl methacrylate.

The binder copolymer and rheology control copolymer are prepared separately using continuous, semi-continuous or batch emulsion polymerization techniques. Such techniques are well-known in the art and reference is made thereto for the purposes of this invention. In general, the polymeric components are prepared by dispersing the desired monomers in an aqueous polymerization medium which typically contains an emulsifying agent and other conventionally employed polymerization aids, e.g., chain transfer agent and chelating agent.

Free radical initiation means which are advantageously employed include UV light and conventional chemical initiators such as peroxygens, e.g., hydrogen peroxide and cumene hydroperoxide; persulfates, e.g., potassium persulfate, sodium persulfate and ammonium persulfate; organic azo compounds such as azobisisobutyronitrile; redox initiators such as peroxide in combination with a sulfite or thiosulfate reducing agent; and the like. Typically, such initiators are employed in amounts which generally range from 0.01 to 5 weight percent based on the total weight of the monomers being polymerized.

In preparing the copolymers, surfactants advantageously employed are anionic and nonionic surfactants conventionally employed heretofore in emulsion polymerizations. Representative anionic surfactants useful herein include the alkyl aryl sulfonates such as sodium dodecyl benzene sulfonate, alkyl phenoxy polyethylene sulfonates and phosphates, sodium lauryl sulfate, potassium lauryl sulfonate and the like. Representative nonionic surfactants useful herein include the reaction product of an alkylene oxide with alkylated phenols or long chain, e.g., from 6 to 20 carbon atoms, fatty alcohols, fatty acids, alkyl mercaptans and primary amines; mono esters, e.g., the reaction product of polyethylene glycol with a long chain carboxylic acid with polyglycol esters of a polyhydric alcohol. The surfactants are employed in an amount which effectively stabilizes the dispersion during polymerization. In general, such amount will vary from 0.1 to 5 weight percent based on the total weight of the monomers employed. To assist in controlling the molecular weight of the resulting polymers, a chain transfer agent is often, but optionally included in the aqueous polymerization medium. In general, chain transfer agents which have conventionally been employed heretofore in emulsion polymerization processes can be employed in the practice of the present invention. Representative of such chain transfer agents include the mercaptans such as n-dodecyl mercaptan cyclohexene, bromoform, carbon tetrabromide, carbon tetrachloride and the like. When employed, the chain transfer agents are generally advantageously employed in amounts from 0.05 to 5 weight percent based on the total weight of the monomers.

Polymerization is advantageously conducted at as low a temperature sufficient to polymerize the monomers at a practical rate. In general, the polymerization is conducted at temperatures from 40–100°C, preferably from 60–90°C, for periods sufficient to convert desired amounts of monomer to the desired polymer (generally the conversion of at least 90 percent of the monomer to polymer) which conventionally takes from 1–6 hours. The polymer dispersions may be prepared over a wide range of concentrations, with the resulting aqueous dispersions advantageously ranging from 20 to 60 weight percent solids.

The polymeric composition of the present invention is prepared by admixing the desired amounts of the binder copolymer with the rheology control copolymer. The relative concentrations of the binder copolymer and the rheology control copolymer are selected on the basis of the desired properties of the polymeric composition and the coating color prepared therefrom. In general, the binder copolymer is employed in amounts from 50 to 97, preferably 60 to 90, more preferably 70 to 90, weight percent and the rheology control copolymer is used in amounts from 3 to 50, preferably 10 to 40, more preferably 10 to 30, weight percent, said weight percents being based on the total weight of the two copolymers.

The method by which the two polymers are admixed is not particularly critical to the practice of the present invention. In general, the two polymer dispersions will be compatible with one another, especially if any carboxyl groups contained in either or both copolymer are not neutralized or only partially neutralized prior to admixture. The admixture of the two polymer dispersions is readily achieved by mixing the dispersion of the first binder copolymer, as prepared, with the dispersion of the rheology control copolymer, as prepared, using mild agitation.

In the preparation of coating colors using the polymeric compositions of this invention as the binder component, the polymeric composition of the present invention is commonly admixed with other, optionally employed adjuncts, such as fillers and/or pigments including clay and, optionally chalk, or calcium carbonate, and, if desired, other adjuncts such as dispersing agents, lubricants or the like. Although such adjuncts can be mixed with either copolymer prior to their subsequent admixture in general, an aqueous dispersion of the pigment and/or filler is prepared and the two copolymers are added thereto, with agitation shortly before use. Prior to the application of a coating color containing the polymeric composition of the present invention to a paper surface, the carboxylic groups are advantageously neutralized by adding a basic material such as sodium or potassium hydroxide or ammonia, preferably sodium hydroxide. The alkali is added in an amount sufficient to give the aqueous dispersion containing the polymer a pH from 8 to 9.5. The resulting coating color can be applied to raw papers using any of the known methods.

The following example is set forth to illustrate

the invention and should not be construed to limit its scope. In the examples, all parts and percentages are by weight unless otherwise indicated.

Example

Preparation of the Binder Copolymer

To a suitably sized polymerization flask equipped with agitation means, heating and cooling means, thermometer, and addition funnel, is added 60 parts water, 0.1 parts of an anionic surfactant, 0.8 parts of a free-radical initiator and 3 parts of a chain transfer agent. The vessel is purged with nitrogen and heated to 90°C. Over a 4 hour period, 57 parts of styrene, 39 parts of butadiene, 1 part of itaconic and 3 parts of acrylic acid are added cocurrently with an aqueous stream comprising additional surfactant and free-radical initiator. The vessel is maintained at 90°C during this addition and for an additional 2 hours. At this time, the polymerization is stopped. The resulting emulsion contains 50 percent solids and the particle size of the resulting styrene/butadiene/itaconic acid/acrylic acid copolymer is found to be approximately 180 nm.

Preparation of the Rheology Control Polymer

To a suitably sized polymerization vessel similar to that used in the preparation of the first copolymer is added 188 parts of water, 0.02 parts of a chelating agent and 0.5 parts of an anionic surfactant. The vessel is then heated to 80°C. A first monomer feed stream comprising 60 parts ethylacrylate, 15 parts acrylonitrile, 25 parts methacrylic acid and 0.05 parts of allylmethacrylate are added to the mildly stirred aqueous polymerization mixture for a period of about 4 hours. Coincident with the addition of the monomers, an additional 50 parts water, 2.0 parts of anionic surfactant, 0.2 parts of sodium hydroxide, and 0.7 parts of a free-radical initiator is added to the polymerization medium. The temperature of the vessel is maintained at 80°C during the addition of the monomer and polymerization aids and for an additional 2 hours. At the end of this period, the flask is then cooled to ambient temperatures and the subsequent emulsion subjected to steam distillation to remove the unconverted monomer. The resulting emulsion contains about 30 percent solids.

Preparation of Coating Color

A polymeric blend is prepared by admixing, with mild agitation, 84 parts, on a dry basis, of the emulsion containing the binder copolymer with 16 parts, on a dry basis, of the emulsion containing the rheology control copolymer to form a blend of 46 weight percent solids.

A pre-coat, paper coating composition is prepared by adding 5 parts of this blend to 100 parts of calcium carbonate dispersed in an aqueous solution of 0.1 parts sodium polyacrylate and 0.2 parts sodium metaphosphate using vigorous agitation. The pH of the resulting admixture is then adjusted to 8.5 by the addition of caustic soda. The resulting pre-coat has 62 percent solids with

a viscosity of 900 mPa.s measured using a Brookfield® viscometer, type No. RVT, using Spindle No. 5 at 100 rpm and 25°C.

An identical top-coat paper coating composition is prepared except that 100 parts of Dinkie® A clay is used in place of the calcium carbonate. The resulting top-coat has 58 percent solids with a viscosity of 1600 mPa.s measured using a Brookfield viscometer, type No. RVT, using Spindle No. 5 at 100 rpm and 15°C.

A base paper of 36 grams per square meter (g/m²) is coated with the pre-coat composition at a speed of 600 m/min and at 10 g/m² coat weight with 6 percent moisture using a conventional blade coating technique. The pre-coated paper is then dried and subsequently coated with the top-coat composition at a speed of 600 m/min and at 10 g/m² coat weight with 6 percent moisture using a conventional blade coating technique. Excellent runability characteristics were observed. The binding strength of the coated paper is found to be 48 cm/sec when measured using conventional IGT test equipment with a pendulum drive, with the result being reported in centimeters per second to the first pick of the coated paper using a low viscosity oil at a printing pressure of 350 newtons per square centimeter. The printability of the coated paper is found to be above 45 mm when measured using a testing device, for measuring printability of paper printed using rotogravure printing techniques, which has been adapted to a pendulum drive IGI tester, Type 2A, with the results being reported in millimeters (mm) to twenty missing dots using a printing pressure of 250 newtons/cm².

Comparative Example

A double coated paper is prepared using the same coating techniques by coating the base paper with identical pre-coat and top-coat compositions except prepared with a polymeric binder composition of a first polymer of an acrylate and vinyl acetate and a second copolymer of an acrylate, carboxylic acid and an amide. The double coated paper exhibits a binding strength of only 24 cm/sec and approximately the same printability as the double coated paper using the pre-coat and top-coat composition prepared using the polymeric binder of the present invention.

As shown by this Example, the polymeric compositions of the present invention are exceptional binders for paper coatings. Specifically, the paper coatings prepared using the polymeric compositions of the present invention impart unexpectedly high binding strengths in combination with excellent printability characteristics.

Claims

1. A polymeric composition useful as the binder component in a coating color, the polymeric composition comprising a copolymer binder and a rheology control copolymer, characterized in that the rheology control copolymer comprises an α,β -ethylenically unsaturated carboxylic acid

in an amount of 1 to less than 30 wt.%, an ester of an α,β -ethylenically unsaturated carboxylic acid, an unsaturated nitrile, from 0.01 to 10 weight percent of a cross-linking monomer and, optionally up to 10 weight percent of a vinyl ester of a monocarboxylic acid, said weight percent being based on the total weight of the rheology control polymer.

2. The polymeric composition of Claim 1 wherein the binder copolymer is a copolymer of a vinyl aromatic monomer, a conjugated diene and, optionally, other copolymerizable monomers or a copolymer of an ester of an α,β -ethylenically unsaturated carboxylic acid, a comonomer which forms a water-insoluble homopolymer and, optionally, other comonomers.

3. The polymeric composition of Claim 2 wherein the composition comprises from 50 to 97 weight percent of the binder copolymer and from 3 to 50 weight percent of the rheology control copolymer, these weight percents being based on the total amount of the rheology control copolymer and the binder copolymer.

4. The polymeric composition of Claim 3 wherein the polymeric composition comprises from 60 to 90 weight parts of a binder copolymer comprising, based on 100 weight parts, at least 60 weight parts, in polymerized form, of a vinyl aromatic monomer and a conjugated diene, the vinyl aromatic monomer and conjugated diene being employed in amounts such that the vinyl aromatic monomer comprises from 10 to 90 weight percent and the conjugated diene comprises from 10 to 90 weight percent of the total weight of the vinyl aromatic monomer and conjugated diene employed and from 10 to 40 weight parts of a rheology control copolymer comprising, based on 100 weight parts, in polymerized form from 40 to 90 weight parts of an ester of an α,β -ethylenically unsaturated carboxylic acid, from 1 to less than 30 weight part of an α,β -ethylenically unsaturated carboxylic acid, from 0.5 to 30 weight parts of an ethylenically unsaturated nitrile and from 0.01 to 10 weight parts of a cross-linking monomer.

5. The polymeric composition of Claim 4 wherein the binder copolymer further comprises up to 20 weight percent of an α,β -ethylenically unsaturated carboxylic acid.

6. The polymeric composition of Claim 4 wherein the binder copolymer is composed based on 100 weight parts, in polymerized form, of from 50 to 70 weight parts of a vinyl aromatic monomer, from 30 to 50 weight parts of a conjugated diene and from 1 to 5 weight parts of an α,β -ethylenically unsaturated carboxylic acid.

7. The composition of Claim 6 wherein the vinyl aromatic monomer is styrene, the conjugated diene is 1,3-butadiene and the unsaturated carboxylic acid is itaconic and/or acrylic acid.

8. The polymeric composition of Claim 7 wherein the rheology control copolymer is composed, based on 100 weight parts, in polymerized form, of from 45 to 75 weight parts of ethyl acrylate and/or ethyl methacrylate, from 5 to 25 weight parts of acrylic acid and/or methacrylic

acid, from 5 to 25 weight parts of acrylonitrile and from 0.05 to 5 weight parts of allyl methacrylate and/or allyl acrylate.

9. The polymeric composition of Claim 3 wherein the binder copolymer is derived from 35 to 60 weight percent of an ester of acrylic and/or methacrylic acid with an alcohol having from 1 to 8 carbon atoms, from 35 to 60 weight percent of a vinyl acetate and/or vinyl propionate, and, optionally, up to 10 weight percent of a copolymerizable monomer, said weight percents being based on the total weight of the binder copolymer.

10. The polymeric composition of Claim 9 wherein the rheology control copolymer is derived from 40 to 90 weight percent of an ester of acrylic acid with an alcohol having from 1 to 8 carbon atoms, from 5 to less than 30 weight percent of acrylic and/or methacrylic acid, from 0.5 to 25 weight percent of acrylonitrile and up to 10 weight percent of a vinyl ester of a monocarboxylic acid and from 0.05 to 5 weight percent of a cross-linking monomer, said weight percent being based on the total weight of the rheology control polymer.

11. A paper coating comprising a suspension of a pigment and/or filler in an aqueous medium and containing, as the binder component, the polymeric composition of Claim 3.

12. A paper coating comprising a suspension of a pigment and/or filler in an aqueous medium and containing, as the binder component, the polymeric composition of Claim 4.

13. The paper coating of Claim 11 wherein the polymeric composition comprises from 60 to 90 weight parts of a binder copolymer derived from 35 to 60 weight percent of an ester of acrylic and/or methacrylic acid with an alcohol having from 1 to 8 carbon atoms, from 35 to 60 weight percent of a vinyl acetate and/or vinyl propionate, and, optionally, up to 10 weight percent of a copolymerizable monomer, said weight percents being based on the total weight of the binder copolymer, and from 10 to 40 weight parts of a rheology control copolymer derived from 40 to 90 weight percent of an ester of acrylic acid with an alcohol having from 1 to 8 carbon atoms, from 5 to less than 30 weight percent of acrylic and/or methacrylic acid, from 0.5 to 25 weight percent of acrylonitrile, up to 10 weight percent of a vinyl ester of a monocarboxylic acid and from 0.05 to 2 weight percent of a cross-linking monomer, said weight percents being based on the total weight of the rheology control polymer.

Revendications

1. Composition polymère utile en tant que liant dans un bain de couche, la composition polymère comprenant un liant copolymère et un copolymère de contrôle de rhéologie, caractérisée en ce que le copolymère de contrôle rhéologie comprend un acide carboxylique à insaturation α,β -éthylénique en une quantité de 1 à moins de 30% en poids, un ester d'un acide carboxylique à

insaturation α,β -éthylénique, un nitrile insaturé, de 0,01 à 10% en poids d'un monomère de réticulation, et éventuellement, jusqu'à 10% en poids d'un ester vinylique d'un acide monocarboxylique, lesdits pourcentages pondéraux étant rapportés au poids total du polymère de contrôle de rhéologie.

2. Composition polymère conforme à la revendication 1, dans laquelle le liant copolymère est un copolymère d'un monomère aromatique vinylique, d'un diène conjugué, et éventuellement d'autres monomères copolymérisables, ou un copolymère d'un ester d'un acide carboxylique à insaturation α,β -éthylénique, d'un comonomère qui forme un homopolymère insoluble dans l'eau, et éventuellement d'autres comonomères.

3. Composition polymère conforme à la revendication 2, dans laquelle la composition comprend de 50 à 97% en poids du liant copolymère et de 3 à 50% en poids du copolymère de contrôle de rhéologie, ces pourcentages pondéraux étant rapportés à la quantité totale du copolymère de contrôle de rhéologie et du liant copolymère.

4. Composition polymère conforme à la revendication 3, dans laquelle la composition polymère comprend de 60 à 90 parties en poids d'un liant copolymère comprenant, rapportées à 100 parties en poids, au moins 60 parties en poids, sous forme polymérisée, d'un monomère aromatique vinylique et d'un diène conjugué, le monomère aromatique vinylique et le diène conjugué, le monomère aromatique vinylique et le diène conjugué étant utilisés en des quantités telles que le monomère aromatique vinylique constitué de 10 à 90% en poids, et le diène conjugué, de 10 à 90% en poids, du poids total du monomère aromatique vinylique et du diène conjugué utilisés, et de 10 à 40 parties en poids d'un copolymère de contrôle de rhéologie comprenant, rapportées à 100 parties en poids, sous forme polymérisée, de 40 à 90 parties en poids d'un ester d'un acide carboxylique à insaturation α,β -éthylénique, de 1 à moins de 30 parties en poids d'un acide carboxylique à insaturation α,β -éthylénique, de 0,5 à 30 parties en poids d'un nitrile à insaturation éthylénique, et de 0,01 à 10 parties en poids d'un monomère de réticulation.

5. Composition polymère conforme à la revendication 4, dans laquelle le liant copolymère comprend en outre jusqu'à 20% en poids d'un acide carboxylique à insaturation α,β -éthylénique.

6. Composition polymère conforme à la revendication 4, dans laquelle le liant copolymère se compose de, rapportées à 100 parties en poids, sous forme polymérisée, de 50 à 70 parties en poids d'un monomère aromatique vinylique, de 30 à 50 parties en poids d'un diène conjugué, et de 1 à 5 parties en poids d'un acide carboxylique à insaturation α,β -éthylénique.

7. Composition conforme à la revendication 6, dans laquelle le monomère aromatique vinylique est le styrène, le diène conjugué est le 1,3-butadiène, et l'acide carboxylique insaturé est l'acide itaconique et/ou l'acide acrylique.

8. Composition polymère conforme à la reven-

dication 7, dans laquelle le copolymère de contrôle de rhéologie se compose de, rapportées à 100 parties en poids, sous forme polymérisée, de 45 à 75 parties en poids d'acrylate d'éthyle et/ou de méthacrylate d'éthyle, de 5 à 25 parties en poids d'acide acrylique et/ou d'acide méthacrylique, de 5 à 25 parties en poids d'acrylonitrile, et de 0,05 à 5 parties en poids de méthacrylate d'allyle et/ou d'acrylate d'allyle.

9. Composition polymère conforme à la revendication 3, dans laquelle le liant copolymère provient de 35 à 60% en poids d'un ester de l'acide acrylique et/ou de l'acide méthacrylique avec un alcool ayant de 1 à 8 atomes de carbone, de 35 à 60% en poids d'acétate de vinyle et/ou de propionate de vinyle, et éventuellement jusqu'à 10% en poids d'un monomère copolymérisable, lesdits pourcentages pondéraux étant rapportés au poids total du liant copolymère.

10. Composition polymère conforme à la revendication 9, dans laquelle le copolymère de contrôle de rhéologie provient de 40 à 90% en poids d'un ester de l'acide acrylique avec un alcool ayant de 1 à 8 atomes de carbone, de 5 à moins de 30% en poids d'acide acrylique et/ou d'acide méthacrylique, de 0,5 à 25% en poids d'acrylonitrile, et jusqu'à 10% en poids d'un ester vinylique d'un acide monocarboxylique, et de 0,05 à 5% en poids d'un monomère de réticulation, lesdits pourcentages pondéraux étant rapportés au poids total du polymère de contrôle de rhéologie.

11. Enduit pour papier, comprenant une suspension d'un pigment et/ou d'une charge en milieu aqueux, et contenant, en tant que liant, une composition polymère conforme à la revendication 3.

12. Enduit pour papier, comprenant une suspension d'un pigment et/ou d'une charge en milieu aqueux, et contenant, en tant que liant, une composition polymère conforme à la revendication 4.

13. Enduit pour papier conforme à la revendication 11, dans lequel la composition polymère comprend de 60 à 90 parties en poids d'un liant copolymère provenant de 35 à 60% en poids d'un ester de l'acide acrylique et/ou de l'acide méthacrylique avec un alcool ayant de 1 à 8 atomes de carbone, de 35 à 60% en poids d'acétate de vinyle et/ou de propionate de vinyle, et éventuellement, jusqu'à 10% en poids d'un monomère copolymérisable, lesdits pourcentages pondéraux étant rapportés au poids total du liant copolymère, et de 10 à 40 parties en poids d'un copolymère de contrôle de rhéologie provenant de 40 à 90% en poids d'un ester de l'acide acrylique avec un alcool ayant de 1 à 8 atomes de carbone, de 5 à moins de 30% en poids d'acide acrylique et/ou d'acide méthacrylique, de 0,5 à 25% en poids d'acrylonitrile, jusqu'à 10% en poids d'un ester vinylique d'un acide monocarboxylique, et de 0,05 à 2% en poids d'un monomère de réticulation, lesdits pourcentages pondéraux étant rapportés au poids total du polymère de contrôle de rhéologie.

Patentansprüche

1. Als Binder in Beschichtungsmassen verwendete Polymerzusammensetzungen, bestehend aus einem Copolymer-Binder und einem die Rheologie beeinflussenden Copolymer, dadurch gekennzeichnet, dass das die Rheologie beeinflussende Copolymer eine α,β -ethylenisch ungesättigte Carbonsäure in einer Menge von weniger als 30 Gew.-%, einen Ester einer α,β -ethylenisch ungesättigten Carbonsäure, ein ungesättigtes Nitril, 0,01 bis 10 Gew.-% eines vernetzenden Monomers und gegebenenfalls bis zu 10 Gew.-% eines Vinylesters einer Monocarbonsäure umfasst, wobei die Prozentangaben bezogen sind auf das Gesamtgewicht des die Rheologie beeinflussenden Polymers.

2. Polymerzusammensetzung nach Anspruch 1, dadurch gekennzeichnet, dass das Bindercopolymer ein Copolymer eines vinylaromatischen Monomers, eines konjugierten Diens und ggf. anderer copolymerisierbarer Monomere oder ein Copolymer eines Esters einer α,β -ethylenisch ungesättigten Carbonsäure, eines Comonomers, das ein wasserunlösliches Homopolymer bildet, und ggf. anderer Comonomere ist.

3. Polymerzusammensetzung nach Anspruch 2, dadurch gekennzeichnet, dass die Zusammensetzung 50 bis 97 Gew.-% Bindercopolymer und 3 bis 50 Gew.-% des die Rheologie beeinflussenden Copolymers enthält, wobei die Gew.-%-Angaben bezogen sind auf die Gesamtmenge von die Rheologie beeinflussendem Copolymer und Bindercopolymer.

4. Polymerzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, dass die Polymerzusammensetzung 60 bis 90 Gew.-% Teile Bindercopolymer, bestehend aus mindestens 60 Gew.-%-Teilen eines vinylaromatischen Monomeren und eines konjugierten Diens enthält in polymerisierter Form, bezogen auf 100 Gew.-%-Teile, wobei das vinylaromatische Monomer und das konjugierte Dien in solchen Mengen angewendet werden, dass das vinylaromatische Monomer 10 bis 90 Gew.-% und das konjugierte Dien 10 bis 90 Gew.-% des Gesamtgewichts des vinylaromatischen Monomers und des konjugierten Diens umfassen, und 10 bis 40 Gew.-% Teile eines die Rheologie beeinflussenden Copolymers, bestehend aus 40 bis 90 Gew.-%-Teilen eines Esters einer α,β -ethylenisch ungesättigten Carbonsäure, 1 bis weniger als 30 Gew.-%-Teile einer α,β -ethylenisch ungesättigten Carbonsäure, 0,5 bis 30 Gew.-%-Teile eines ethylenisch ungesättigten Nitrils und 0,01 bis 10 Gew.-%-Teile eines vernetzenden Monomers enthält in polymerisierter Form, bezogen auf 100 Gew.-%-Teile.

5. Polymerzusammensetzung nach Anspruch 4, dadurch gekennzeichnet, dass das Bindercopolymer weiterhin bis zu 20 Gew.-% einer α,β -ethylenisch ungesättigten Carbonsäure enthält.

6. Polymerzusammensetzung nach Anspruch 4, dadurch gekennzeichnet, dass das Bindercopolymer sich bezogen auf 100 Gew.-%-Teile aus 50 bis 70 Gew.-%-Teilen eines vinylaromatischen Mono-

mers aus 30 bis 50 Gew.-Teilen eines konjugierten Diens und aus 1 bis 5 Gew.-Teilen einer α,β -ethylenisch ungesättigten Carbonsäure in polymerisierter Form zusammensetzt.

7. Zusammensetzung nach Anspruch 6, dadurch gekennzeichnet, dass das vinylaromatische Monomer Styrol ist, das konjugierte Dien 1,3-Butadien ist und die ungesättigte Carbonsäure Itacon- und/oder Acrylsäure ist.

8. Polymerzusammensetzung nach Anspruch 7, dadurch gekennzeichnet, dass das die Rheologie beeinflussende Copolymer in polymerisierter Form, bezogen auf 100 Gew.-Teile zusammengesetzt ist aus 45 bis 75 Gew.-Teilen Ethylacrylat und/oder Ethylmethacrylat, 5 bis 25 Gew.-Teilen Acrylsäure und/oder Methacrylsäure, 5 bis 25 Gew.-Teilen Acrylnitril und 0,05 bis 5 Gew.-Teilen Allylmethacrylat und/oder Allylacrylat.

9. Polymerzusammensetzung nach Anspruch 3, dadurch gekennzeichnet, dass das Bindercopolymer erhalten wird aus 35 bis 60 Gew.-% eines Esters der Acryl- und/oder Methacrylsäure mit einem Alkohol mit 1 bis 8 Kohlenstoffatomen, aus 35 bis 60 Gew.-% von Vinylacetat und/oder Vinylpropionat und ggf. bis zu 10 Gew.-% eines copolymerisierbaren Monomers, wobei die Gew.-%-Angaben bezogen sind auf das Gesamtgewicht des Bindercopolymers.

10. Polymerzusammensetzung nach Anspruch 9, dadurch gekennzeichnet, dass das die Rheologie beeinflussende Copolymer erhalten wird aus 40 bis 90 Gew.-% eines Esters der Acrylsäure mit einem Alkohol mit 1 bis 8 Kohlenstoffatomen, 5 bis weniger als 30 Gew.-% Acryl- und/oder Methacrylsäure, 0,5 bis 25 Gew.-% Acrylnitril und bis zu 10 Gew.-% eines Vinylesters einer Monocar-

bonsäure und 0,05 bis 5 Gew.-% eines vernetzenden Monomers, wobei die %-Angaben bezogen sind auf das Gesamtgewicht des die Rheologie beeinflussenden Polymers.

11. Papierbeschichtung bestehend aus einer Suspension eines Pigmentes und/oder Füllmittels in einem wässrigen Medium und enthaltend als Binderkomponente die Polymerzusammensetzung nach Anspruch 3.

12. Papierbeschichtung, enthaltend eine Suspension eines Pigments und/oder Füllmittels in einem wässrigen Medium und enthaltend als Binderkomponente die Polymerzusammensetzung nach Anspruch 4.

13. Papierbeschichtung nach Anspruch 11, dadurch gekennzeichnet, dass die Polymerzusammensetzung aus 60 bis 90 Gew.-Teilen eines Bindercopolymers, das aus 35 bis 60 Gew.-% eines Esters der Acryl- und/oder Methacrylsäure mit einem Alkohol mit 1 bis 8 Kohlenstoffatomen, 35 bis 60 Gew.-% eines Vinylacetats und/oder Vinylpropionats und ggf. bis zu 10 Gew.-% eines copolymerisierbaren Monomers erhalten wird, wobei die Gew.-%-Angaben bezogen sind auf das Gesamtgewicht des Bindercopolymers, und 10 bis 40 Gew.-Teilen eines die Rheologie beeinflussenden Copolymers besteht, das aus 40 bis 90 Gew.-% eines Esters der Acrylsäure mit einem Alkohol mit 1 bis 8 Kohlenstoffatomen, 5 bis weniger als 30 Gew.-% Acryl- und/oder Methacrylsäure, 0,5 bis 25 Gew.-% Acrylnitril, bis zu 10 Gew.-% eines Vinylesters einer Monocarbonsäure und 0,05 bis 2 Gew.-% eines vernetzenden Monomers erhalten wurde, wobei die Gew.-%-Angaben bezogen sind auf das Gesamtgewicht des die Rheologie beeinflussenden Polymers.

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