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54 **Paper coating composition.**

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Description

This invention relates generally to a paper coating composition to be used for the production of coated papers and, more specifically, to an aqueous coating composition to be applied over the surface of a paper for improving its surface properties such as surface smoothness, gloss and printability. The present invention is also directed to a coated paper having a surface coated layer obtained from the above coating composition.

DE-A-3603392 discloses the use of polymers of acrylic acid or methacrylic acid as milling aids and dispersants for eg white pigments such as titanium dioxide and kaolin for producing aqueous pigment slurries for paper-making compositions.

One known coating composition includes a white pigment such as kaolin, a binder, a latex acid a dispersing agent. For the purpose of controlling the viscosity, fluidity and water retentivity of such a composition, it is also known to incorporate therein an additive such as sodium alginate or carboxymethyl-cellulose.

These known additives suffer from a drawback because, when they are used in an amount sufficient to obtain a desired water retentivity, the viscosity of the resulting composition becomes so high, with the simultaneous reduction of the fluidity, that it becomes impossible to effect a high speed coating. On the other hand, water retentivity of the coating composition fails to be sufficiently improved when the additives are used in an amount providing suitable viscosity and fluidity. Poor water-retentivity is disadvantageous because when the coating composition is brought into contact with a paper to be coated, water tends to be separated from the coating composition and penetrates into the paper together with a portion of the binder, so that the resulting coat becomes poor in smoothness, printability and the like surface properties. The present invention has been made from a consideration of the foregoing problems of the conventional paper coating compositions.

In accordance with one aspect of the present invention, there is provided an aqueous coating composition comprising:

(i) a white pigment;

(ii) a binder;

(iii) an additive which is at least one member selected from acrylic acid/methacrylic acid copolymers and copolymers of the following two monomers:

(a) an unsaturated acid of the formula:



wherein R¹ stands for hydrogen or a methyl group, and

(b) an unsaturated ester of the formula:



wherein R² stands for hydrogen or a methyl group and R³ stands for an alkyl group having 2-4 carbon atoms, said additive being present in an amount of 0.001-2 % based on the weight of said white pigment; and

(iv) a polyol.

In another aspect, the present invention provides a coated paper obtained by coating the above composition over the surface of a paper.

The present invention will now be described in detail below.

The paper coating composition according to the present invention is characterized by the inclusion of a specific additive, i.e. an acrylic acid/methacrylic acid copolymer and/or a copolymer of (a) acrylic acid or methacrylic acid and (b) an alkyl acrylate or alkyl methacrylate, together with a polyol. The alkyl group of the monomer (b), i.e. alkyl acrylate or methacrylate has 2-4 carbon atoms. The additive preferably has an average molecular weight of 5,000 to 500,000. It is important that the additive should be present in an amount of 0.001 to 2 %, preferably 0.01 to 1 % based on the weight of the white pigment. Too small an amount of the additive below 0.001 % by weight is insufficient for attaining the object of the present invention. On the other hand, when the amount of the additive exceeds 2 % by weight, the resulting coating composition becomes considerably high in viscosity or gellation of the composition occurs.

The acrylic acid/methacrylic acid copolymer preferably has a molar ratio of the former acid to the latter acid of 9:1 to 3:2, more preferably 4:1 to 13:7 and an average molecular weight of 10,000 to 100,000. The copolymer of the acid (a) and the ester (b) preferably has a molar ratio of the acid (a) to the ester (b) of in

the range of 19:1 to 1:1, more preferably 4:1 to 3:2, and an average molecular weight of 60,000 to 300,000.

The use of the specific copolymer additive has the effect of imparting excellent water-retentivity, viscosity and fluidity properties to the composition and these properties are further improved by the use in conjunction with the copolymer additive of the polyol, whereby the coating composition of the present invention can give coated paper having excellent properties such as printability and gloss.

Examples of suitable polyols include glycerin, alkylene glycols such as ethylene glycol and propylene glycol, and polyalkylene glycols such as polyethylene glycol and polypropylene glycol. The use of glycerin is particularly preferred. The polyol is preferably used in an amount of 1-20%, more preferably 5-15% based on the weight of the copolymer.

Any known white pigment conventionally used for a paper coating composition may be used in the present invention. Illustrative of suitable pigments are clay, calcium carbonate, kaolin, talc, titanium oxide, aluminum hydroxide, silica, zinc oxide, activated terra alba, acid terra alba, lake, diatomaceous earth, plastic pigments and mixture thereof. The content of the white pigment in the coating composition is generally 40-70% by weight.

As the binder, there may be used a latex or a solution of synthetic or natural high molecular weight polymers. Illustrative of suitable polymers to be used as the binder are styrene/butadiene copolymers, styrene/acryl copolymers, vinyl acetate/acryl copolymers, ethylene/vinyl acetate copolymers, butadiene/methyl methacrylate copolymers, vinyl acetate/butyl acrylate copolymers, styrene/maleic anhydride copolymers, isobutene/maleic anhydride copolymers, acrylic acid/methylmethacrylate copolymers, water-soluble starch, casein and soy bean protein. The content of the binder is preferably 3 to 30%, more preferably 7 to 20% based on the weight of the pigment.

The coating composition according to the present invention preferably also contains a dispersing agent such as sodium polyacrylate, sodium hexametaphosphate or sodium pyrophosphate.

The coating composition according to the present invention is suitably applied over one or both sides of a paper such as a wood-free paper, a ground wood paper or a paper board to give a coated paper. Coating may be effected in a manner known per se using, for example, a blade coater, a roll coater, an air knife coater or a short dwell coater.

The following examples will further illustrate the present invention.

Preparation of Coating Liquid:

Comparative Example 1

A coating liquid having the following composition was prepared:

<u>Ingredient</u>	<u>Amount (parts by weight)</u>
Pigment	
Clay	90
Heavy calcium carbonate	10
Binder	
Latex *1	10
Oxidized starch	7
Dispersant *2	0.1
Additive *3	0.1
Water	78

*1 Styrene/butadiene latex (L-1622 manufactured by Asahi Kasei Kogyo K.K.)

*2 Sodium polyacrylate (SDA-40N, manufactured by Somar Corporation)

*3 Methacrylic acid/ethyl acrylate copolymer
(manufactured by Rohm & Haas), referred to as
Copolymer A

Comparative Example 2

A coating liquid was obtained by replacing the additive of Comparative Example 1 with a methacrylic acid/butyl acrylate copolymer (manufactured by Rohm & Haas, referred to as Copolymer B).

Example 1

A coating liquid was obtained by replacing the additive of Comparative Example 1 with a mixture of 10 parts by weight of the methacrylic acid/ethyl acrylate copolymer (Copolymer A) with 1 part by weight of glycerin.

Example 2

A coating liquid was obtained by replacing the additive of Comparative Example 1 with a mixture of 10 parts by weight of the methacrylic acid/butyl acrylate copolymer (Copolymer B) with 1 part by weight of glycerin.

Example 3

A coating liquid was obtained by replacing the additive of Example 1 with a mixture of 10 parts by weight of an acrylic acid/methacrylic acid copolymer (Copolymer C, average molecular weight: 70,000) with 1 part by weight of glycerin.

Example 4

A coating liquid was obtained by replacing Copolymer C of Example 3 with an acrylic acid/methacrylic acid copolymer (Copolymer D, average molecular weight: 40,000).

Comparative Example 3

A coating liquid was obtained by replacing the additive of Comparative Example 1 with carboxymethyl-cellulose (CMC).

Comparative Example 4

A coating liquid was obtained by replacing the additive of Comparative Example 1 with sodium alginate.

Comparative Example 5

A coating liquid was obtained by replacing the additive of Comparative Example 1 with water.

Properties of Coating Liquids

The above coating liquids were tested for their viscosity, fluidity and water retentivity in the following manner:

(1) B-Type viscosity (mPaS):

Measured in accordance with TAPPI Standard T648 Su-72 at a revolution speed of 60 rpm.

(2) HS (High Share) viscosity (mPaS):

Measured with a High Share Viscosimeter (manufactured by d Seiki K. K.) at a revolution speed of 4000 rpm.

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(3) Fluidity:

Defined by the following equation (smaller, the better):

10 Fluidity = (viscosity of the coating composition) / (viscosity of the aqueous phase of the coating composition*)

15 (4) Water-retentivity:

Measured in accordance with the S&D Warren method (greater, the better).

The test results were as summarized in Table 1.

20 Production of Coated Paper:

Each of the above coating liquids was applied over one side of a paper having a basis weight of 60 g/m² and then dried to obtain a coated paper having a basis weight of 75 g/m².

25 Properties of the Coated Paper:

The thus obtained coated papers were tested for their gloss, brightness, smoothness and resistance to picking in the following manner:

30 (1) Gloss:

Measured in accordance with Japan Industrial Standard JIS P8142 (1965).

(2) Brightness:

35

Measured in accordance with Japan Industrial Standard JIS P8123 (1961).

(3) Smoothness:

40

Measured in accordance with Japan Industrial Standard JIS P8119 (1976).

(4) Resistance to Picking:

45 Dry pick and wet pick were measured using a printability tester (RI tester manufactured by Akira Seisakusho K.K.) and evaluated in terms of 5-level rating (greater, the better).

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*: The composition is first separated into a liquid (aqueous) phase and a solid phase by centrifugation. Then, the viscosity of the liquid phase is measured.

The test results are summarized in Table 1.

Table 1

Coating Liquid	Additive	Properties of Coating Liquid			Properties of Coated Paper					
		B-type viscosity (mPas)	HS viscosity (mPas)	Fluidity (sec)	Water-retentivity (sec)	Gloss	Brightness	Smoothness (sec)	Dry pick	Wet pick
Comp.1	Copolymer A	2050	63	220	24.0	52.7	71.0	35.0	3.8	4.0
Comp.2	Copolymer B	1900	63	198	25.0	52.7	71.0	36.0	3.8	4.1
Ex. 1	Copolymer A & glycerin	1800	60	172	25.7	52.6	71.3	36.6	4.5	4.3
Ex. 2	Copolymer B & glycerin	1750	61	168	25.8	53.2	71.0	37.0	4.5	4.4
Ex. 3	Copolymer C & glycerin	2850	62	158	26.2	54.0	70.8	43.0	4.0	4.2
Ex. 4	Copolymer D & glycerin	2620	60	162	26.0	54.0	70.8	42.8	4.0	4.2
Comp.3	CMC	2850	70	350	23.6	46.5	71.1	36.0	3.8	4.0
Comp.4	sodium alginate	2900	66	240	22.5	48.0	71.2	36.0	4.0	4.0
Comp.5	-	1140	52	1558	20.7	50.7	71.0	32.6	3.5	4.0

Claims

1. An aqueous coating composition comprising:
 (i) a white pigment;
 5 (ii) a binder; and characterized in that the additive (iii)
 (iii) an additive; is at least one member selected from acrylic acid/methacrylic acid copolymers and
 copolymers of the following two monomers:
 (a) an unsaturated acid of the formula:
 10
$$\text{CH}_2 = \text{CR}^1\text{COOH}$$

 wherein R^1 stands for hydrogen or a methyl group, and
 (b) an unsaturated ester of the formula:
 15
$$\text{CH}_2 = \text{CR}^2\text{COOR}^3$$

 wherein R^2 stands for hydrogen or a methyl group and R^3 stands for an alkyl group having 2-4
 carbon atoms, said additive being present in an amount of 0.001-2 % based on the weight of said
 white pigment; and in that the composition further comprises:
 20 (iv) a polyol.
2. A coating composition according to claim 1, wherein said additive is a copolymer of the acid (a) and
 the ester (b) with a molar ratio of the acid (a) to the ester (b) being in the range of 19:1 to 1:1.
- 25 3. A coating composition according to claim 1, wherein said additive is a copolymer of acrylic acid and
 methacrylic acid with a molar ratio of the former acid to the latter acid being 9:1 to 6:4.
4. A coating composition according to any preceding claim, wherein said additive has an average
 molecular weight of 5,000 to 500,000.
 30
5. A coating composition according to claim 4 when appendant to claim 2, wherein said copolymer of the
 acid (a) and the ester (b) has an average molecular weight of 60,000 to 300,000.
- 35 6. A coating composition according to claim 4 when appendant to claim 3, wherein wherein said acrylic
 acid/methacrylic acid copolymer has an average molecular weight of 10,000 to 100,000.
7. A coating composition according to any preceding claim, wherein the content of said additive is 0.01-1
 % based on the weight of said pigment.
- 40 8. A coating composition according to any preceding claim, wherein said white pigment is at least one
 member selected from clay, calcium carbonate, kaolin, talc, titanium oxide, aluminum hydroxide, silica,
 zinc oxide, activated terra alba, acid terra alba, lake, diatomaceous earth and plastic pigments.
9. A coating composition according to any preceding claim, wherein said binder is at least one member
 45 selected from styrene/butadiene copolymers, styrene/acryl copolymers, vinyl acetate/acryl copolymers,
 ethylene/vinyl acetate copolymers, butadiene/methyl methacrylate copolymers, vinyl acetate/butyl ac-
 rylate copolymers, styrene/maleic anhydride copolymers, isobutene/maleic anhydride copolymers,
 acrylic acid/methylmethacrylate copolymers, water-soluble starch, casein and soy bean protein.
- 50 10. A coating composition according to any preceding claim, wherein the content of said binder is 3 to 30
 % based on the weight of said pigment.
11. A coating composition according to any preceding claim, further comprising a dispersing agent.
- 55 12. A coating composition according to any preceding claim, wherein said polyol is a member selected
 from ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol and glycerin.

13. A coating composition according to any preceding claim, wherein said polyol is used in an amount of 1-20 % based on the weight of said copolymer.
14. A coating composition according to claim 13, wherein said polyol is used in an amount of 5-15% based on the weight of said copolymer.
15. A coated paper obtained by a method comprising coating a composition according to any preceding claim over the surface of a paper, and drying the resulting coated layer.

10 **Patentansprüche**

1. Wässrige Beschichtungszusammensetzung, mit:

- (i) einem weißen Pigment;
 (ii) einem Binder; und
 (iii) einem Zusatz, dadurch gekennzeichnet, daß der Zusatz
 (iii) mindestens ein Teil ist, welcher aus acrylischen Säure/methacrylischen Säure Copolymeren und Copolymeren aus den folgenden zwei Monomeren ausgewählt wird:
 a) einer ungesättigten Säure der Formel:



worin R¹ für Sauerstoff oder eine Methylgruppe steht, und

b) einem ungesättigten Ester der Formel:



worin R² für Wasserstoff oder eine Methylgruppe steht und R³ für eine Alkylgruppe mit 2-4 Kohlenstoffatomen steht, wobei der Zusatz in einer Menge von 0.001-2%, basierend auf dem Gewicht des weißen Pigments, vorliegt, und daß die Zusammensetzung weiterhin umfaßt:

(iv) ein Polyol.

2. Beschichtungszusammensetzung nach Anspruch 1, worin der Zusatz ein Copolymer der Säure (a) und des Esters (b) mit einem Mol-Verhältnis der Säure (a) zum Ester (b) im Bereich von 19:1 bis 1:1 ist.
3. Beschichtungszusammensetzung nach Anspruch 1, worin der Zusatz ein Copolymer von acrylischer Säure und methacrylischer Säure mit einem Mol-Verhältnis der ersteren Säure zu der letzteren Säure von 9:1 bis 6:4 ist.
4. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, worin der Zusatz ein durchschnittliches Molekulargewicht von 5,000 bis 500,000 hat.
5. Beschichtungszusammensetzung nach Anspruch 4, wenn abhängig von Anspruch 2, worin das Copolymer der Säure (a) und des Esters (b) ein durchschnittliches Molekulargewicht von 60,000 bis 300,000 hat.
6. Beschichtungszusammensetzung nach Anspruch 4, wenn abhängig von Anspruch 3, worin das acrylische Säure/methacrylische Säure Copolymer ein durchschnittliches Molekulargewicht von 10,000 bis 100,000 hat.
7. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, worin der Gehalt des Zusatzes 0.01-1%, basierend auf dem Gewicht des Pigments, beträgt.
8. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, worin das weiße Pigment mindestens ein Teil ist, welcher aus Ton, Calcium-Carbonat, Kaolin, Talk, Titanoxid, Aluminiumhydroxid, Kieselerde, Zinkoxid, aktivierter Terra Alba, saurer Terra Alba, Pigmentfarbe, Diatomeenerde und Kunststoffpigmenten ausgewählt wird.

- 5 9. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, worin der Binder mindestens ein Teil ist, welcher aus Styrol/Butadien Copolymeren, Styren/Acryl Copolymeren, Vinyl Acetat/Acryl Copolymeren, Ethylen/Vinyl Acetat Copolymeren, Butadien/Methyl Methacrylat Copolymeren, Vinyl Acetat/Butyl Acrylat Copolymeren, Styrol/Malein Anhydrid Copolymeren, Isobuten/Malein Anhydrid Copolymeren, Acrylischen Säure/Methacrylatischen Copolymeren, wasser-löslicher Stärke, Casein und Soja-Bohnen Protein ausgewählt wird.
- 10 10. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, worin der Inhalt des Binders 3 bis 30%, basierend auf dem Gewicht des Pigments, beträgt.
- 11 11. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, welche weiterhin ein Dispergierungsmittel umfaßt.
- 15 12. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, worin das Polyol ein Teil ist, welches aus Ethylen Glycol, Propylen Glycol, Polyethylen Glycol, Polypropylen Glycol und Glycerin ausgewählt wird.
- 20 13. Beschichtungszusammensetzung nach einem der vorhergehenden Ansprüche, worin das Polyol in einer Menge von 1-20%, basierend auf dem Gewicht des Copolymers, verwendet wird.
14. Beschichtungszusammensetzung nach Anspruch 13, worin das Polyol in einer Menge von 5-15%, basierend auf dem Gewicht des Copolymers, verwendet wird.
- 25 15. Beschichtetes Papier, erzielt durch ein Verfahren, welches die Beschichtung einer Zusammensetzung gemäß einem der vorhergehenden Ansprüche über die Oberfläche eines Papiers und die Trocknung der resultierenden beschichteten Schicht umfaßt.

Revendications

- 30 1. Composé aqueux de revêtement comportant:
- (i) un pigment blanc;
- (ii) un liant; et
- (iii) un additif; caractérisé en ce que ledit additif est un élément au minimum sélectionné à partir de copolymères d'acide acrylique/acide méthacrylique et de copolymères des deux monomères suivants:
- 35 a) un acide non-saturé selon la formule:
- $$\text{CH}^2 = \text{CR}^1\text{COOH}$$
- 40 dont R¹ représente l'hydrogène ou un groupe méthyle, et
- (b) un ester saturé selon la formule:
- $$\text{CH}_2 = \text{CR}^2\text{COOR}^3$$
- 45 dont R² représente l'hydrogène ou un groupe méthyle, et R³ représente un groupe alcoyle ayant 2-4 atomes de carbone, ledit additif étant prévu à raison d'un montant de 0,001% à 2% par poids dudit pigment blanc; et en ce que le composé comporte en outre;
- (iv) un polyol.
- 50 2. Composé de revêtement selon la revendication 1, dont ledit additif est un copolymère de l'acide (a) et de l'ester (b) ayant un rapport molaire d'acide (a) et d'ester (b) dans l'ordre de 19:1 à 1:1.
3. Composé de revêtement selon la revendication 1, dont ledit additif est un copolymère d'acide acrylique et d'acide méthacrylique ayant un rapport molaire du premier au deuxième acide dans l'ordre de 9:1 à 6:4.
- 55 4. Composé de revêtement selon l'une quelconque des revendications précédentes, dont ledit additif présente un poids moléculaire moyen de 5.000 à 500.000 .

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5. Composé de revêtement selon la revendication 4 en conjonction avec la revendication 2, dont ledit additif d'acide (a) et l'ester (b) présente un poids moléculaire moyen de 60.000 à 300.000 .
- 5 6. Composé de revêtement selon la revendication 4 en conjonction avec la revendication 3, dont ledit copolymère d'acide acrylique/acide méthacrylique présente un poids moléculaire moyen de 10.000 à 100.000
7. Composé de revêtement selon l'une quelconque des revendications précédentes, dont la teneur dudit additif est de 0,01-1,0% basée sur le poids dudit pigment.
- 10 8. Composé de revêtement selon l'une quelconque des revendications précédentes, dont ledit pigment blanc est au minimum sélectionné à partir d'argile, de carbonate de chaux, kaolin, talc, d'oxyde de titane, d'hydroxyde d'aluminium, de silice, d'oxyde de Zinc, de terra alba activée, terra alba acide, colorant, diatomite et de pigments de matières plastiques.
- 15 9. Composé de revêtement selon l'une quelconque des revendications précédentes, dont le liant est au minimum sélectionné à partir de copolymères de styrène/butadiène, styrène/acrylique, acétate/acrylique, éthylène/acétate vinylique, butadiène/méthacrylate méthylique acétate/acrylate butylique, styrène/anhydride maléique, isobutène/anhydride maléique, acide acrylique/méthacrylate méthylique, d'amidon soluble dans l'eau, de caséine et protéine de graine de soja.
- 20 10. Composé de revêtement selon l'une quelconque des revendications précédentes, dont la teneur dudit liant est de 3% à 30% basé sur le poids dudit pigment.
- 25 11. Composé de revêtement selon l'une quelconque des revendications précédentes, comportant également un agent dispersant.
12. Composé de revêtement selon l'une quelconque des revendications précédentes, dont ledit polyol est un élément sélectionné à partir de glycol éthylénique, glycol propylène, glycol polyéthylène, glycol polypropylène et de glycérine.
- 30 13. Composé de revêtement selon l'une quelconque des revendications précédentes, dont le polyol est prévu à raison de 1% à 20% basé sur le poids dudit copolymère.
- 35 14. Composé de revêtement selon la revendication 13, dont ledit polyol est prévu à raison de 5% à 15% basé sur le poids dudit copolymère.
- 40 15. Papier revêtu obtenu par une méthode comportant l'application d'un composé de revêtement selon l'une quelconque des revendications précédentes sur la surface du papier, suivie du séchage de la couche de revêtement ainsi obtenue.
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