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(54) High solids paper coating composition.

(57) A paper coating compound containing from 65 to 75 weight percent solids, and having good rheology may be perpared from a carboxylated stryene-butadiene latex container from about 4 to 10 weight percent carboxylation which has good stability in the presence of multi-valent ions. Paper coated with such compounds have a good balance of properties including high gloss and pick strength.

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HIGH SOLIDS PAPER COMPOSITION

The present invention relates to paper coating compounds. More particularly, the present invention relates to high solids paper coating compounds having good rheology which provide coated paper with a good balance of properties; particularly good gloss and pick characteristics.

Carboxylated styrene-butadiene latices have been offered to the paper coating industry since at least as early as the early 1960's. Typical of the latices sold at that time was K-55E, sold by ARCO, a styrene-butadiene latex containing from 1 to 2% carboxylation.

U.S. Patent 3.399.080 issued August 27, 1968 to the Dow Chemical Company disclosed the use of a latex polymer comprising 2 to 10 weight percent of a carboxylic acid; 30 to 50 weight percent of a C_{4-9} conjugated diolefin and 48 to 68 weight percent of a monomer composition comprising 10 to 100 weight percent of an alkenyl mononuclear aromatic monomer and the balance acrylonitrile.

The above latices were used in medium solids paper coating compounds and were suitable for use in the paper coating process of the mid 1960's to mid 1970. The paper coating compounds of the present invention have a higher solids than the 60% solids level taught in the examples in U.S. Patent 3,399,080.

The next major advance in the art was U.S. Patent 4,154,899 issued May 15, 1979 to Potlatch Forest Inc. (the Hershey patent) which discloses high solids paper coatings having good rheology. Unfortunately, the compounds in the Hershey patent merely specify the use of carboxylated lates. Applicant has found that by using a specified carboxylated latex, improved pick and gloss properties may be obtained, while retaining suitable rheology characteristics.

United States Patent 3,985,932 issued October 12, 1979 to Moore and Munger discloses a high solids paper coating compound. An essential ingredient in the compound is a hard, high molecular weight tax. The present invention does not contemplate the use of such wax.

Chemical Abstract 97:111522u of Japanese Patent 82 66,195 discloses a high solids paper coating compound. The compound uses as a binder a latex comprising mixed ethylenically unsaturated carboxylic acids; butadiene; styrene and methyl methacrylate. The polymer composition of the present invention does not include alkyl (meth)acrylates.

The present invention seeks to provide a simple high solids paper coating compound which has a good rheology, good stability to multi-valent, preferably bi-valent, ions, and provides coated paper having a good balance of properties including high gloss and pick strength.

The present invention provides a paper coating composition having a solids content of from 65 to 75 weight percent and a viscosity as measured on a Hercules Hi Shear viscometer with an E bob and a 400,000 dynes cm·cm spring at 4400 rpm and 105° F of less than 80 centipoise, which comprises from 95 to 85 weight percent by dry weight of a composition comprising

100 to 40 weight percent of clay; and

0 to 60 weight percent of one or more members selected from the group consisting of calcium carbonate, aluminium trihydrate, titanium dioxide, and barium sulfate;

from 5 to 15 weight percent by dry weight of a latex which produces less than 0.5 weight percent coagulum on exposure to 10% $CaCl_2$ comprising an interpolymer of

from 55 to 65 weight percent of a C_{8-12} vinyl aromatic monomer which is unsubstituted or substituted by a C_{1-4} alkyl radial or a chlorine atom;

form 30 to 40 weight percent of a branched or straight chained C_{4-5} conjugated diolefin which is unsubstituted for substitttuted by a chlorine atom; and

from 4 to 10 weight percent of one or more C_{3-6} ehtylenically unsaturated carboxylic acids.

The present invention also provides paper coated with the above composition at a weight of 8 to 15 lb dry per 3300 ft^2 (ream) (9 to 17 g/m^2). Paper coated in accordance with the present invention has a good balance of properties including sheet gloss, ink holdout characteristics, brightness, with IGT binding strengths of at least 400 m/sec (#4 tack ink).

The paper coatings of the present invention comprise a major amount, from 95 to 85 weight percent of a pigment. The pigment may be all clay or the pigment may comprise from 100 to 40, preferably more than 70 weight percent clay and up to 60, preferably less than 30 weight percent of calcium carbonate. A preferred pigment composition comprises from 70 to 80 weight percent of clay and from 30 to 20 weight percent of calcium carbonate.

Generally, the clay used in paper coating compounds have an average particle size of less than 5 microns. Most preferably, the clay has a size of less than about 2 microns. When calcium carbonate is used in the coating compounds of the present invention, the average particle size should be less than 2 microns.

The latex binder used in accordance with the present invention comprises

from 55 to 65, preferably 58 to 62 weight percent of a C_{8-12} vinyl aromatic monomer which is unsubstituted or substituted by a C_{1-4} alkyl radical or a chlorine atom;
from 30 to 40, preferably from 32 to 36 weight percent of a branched or straight chained C_{4-6} conjugated diolefin which is unsubstituted or substituted by a chlorine atom; and
from 4 to 10, preferably 5 to 7 weight percent of one or more C_{3-6} ehtylenically unsaturated carboxylic acids.

If desired the polymer may optionally contain a minor amount, less than 5, preferably less than 2 weight percent of an additional functional monomer selected from the group consisting of amides of a C_{3-6} ethylenically unsaturated carboxylic acids which amides are unsubstituted or substituted at the nitrogen atom by up to two radials selected from the group consisting of C_{1-4} alkyl and hydroxyalkyl radicals, and C_{3-6} ethylenically unsaturated aldehydes.

Suitable C_{8-13} vinyl aromatic monomers include styrene and alpha methyl styrene. Useful C_{4-6} conjugated diolefins include butadiene, isoprene and chloroprene. Suitable C_{3-6} ethylenically unsaturated carboxylic include both mono- and di-carboxylic acids; such as acrylic, methacrylic, fumaric and itaconic acids and mixtures thereof. Particularly useful results are obtained when the polymer contains mixed mono- and di-carboxylic acids. If mixed mono- and di-carboxylic acid monomers are used they may be used in a weight ratio of 10:1 to 1:10. Peferably the weight ratio of mono- to di-carboxylic acid monomer is from about 2:1 to 8:1, most preferably from about 4:1 to 6:1.

In preparing the polymer, conventional techniques are used. Generally the latex will contain from 45 to 55 weight percent solids. Preferably, the polymer is prepared in the presence of from 0.5 to 2, most preferably about 1 part by weight of a chain transfer agent. Preferred chain transfer agents are the C_{8-12} alkyl mercaptans. Chloroform and bromoform are also suitable chain transfer agents.

The polymers of the present invention have a high stability of multi-valent ions, particularly calcium ions. In the presence of 10% $CaCl_2$ solution for 14 days there should be only a trace (less than 0.5%) of coagulum.

In preparing the coating compound a dispersant may be added to the pigments. If necessary, a thickener and/or opacifying agent(s) may be added to the coating compound and dilution made with water to the required solids contact. Useful dispersants and thickeners are listed in trade catalogues such as McCutcheon's Functional Materials (either the North American edition or the International edition), published annually by McCutcheon's Division, The Manufacturing Confectioner Publishing Co. The selection of any specific functional material will depend on the specific properties desired in the coating.

If thickeners are used, their use should be kept to a minimum. The compound at a solids content of from 65 to 70 weight percent should have a viscosity of less than 80, preferably from 20 to 70 centipoise, as measured on a Hercules Hi Shear viscometer with an E bob, a 400,000 dyne cm/cm spring at 4400 rpm at 105° F.

Paper may be coated with the coating compounds of the present invention using conventional techniques and where required calendered under appropriate conditions. The resulting paper should have a dry pick of at least 400 m/sec.

The following examples are intended to illustrate the invention and not to limit, etc. In the examples, unless otherwise stated, parts are in parts by dry weight.

Example 1

A base latex was prepared by emulsion polymerization of approximately 60 parts stryene, 33 parts butadiene, 7 parts of mixture of acrylic and itaconic acid in the presence of 1 part of a chain transfer agent. The latex had a 50 weight percent solids level after stripping.

For comparison purposes, a commercially available carboxylated styrene-butadiene latex sold under the trademark POLYSAR having a carboxylic acid monomer content of about 2.5 weight percent and a styrene content of about 63 weight percent was used as a control in the experiments.

A base compound was prepared comprising

Clay	70
$CaCl_3$	30
Latex	12
Starch	2
Water to about -	65% solids

The viscosity of the compound was measured with a Hercules Hi Shear viscometer with an E bob, a 400,000 dyne cm cm spring at 4400 rpm and 105° F.

The coating compound was coated on paper at a dry weight of 9.5 lb per ream and calendered to simulate mill conditions. The coated paper was conditioned overnight at 73° F and 50% relative humidity.

The papers were then tested for sheet gloss, brightness (Diano S-4) and IGT Dry Pick (Model AIC2) at 4 m sec increasing velocity at 35 kgf using a #4 tack rated ink.

The results are reported in Table I.

		Control Latex	Experimental Latex
Hercules Apparent Viscosity (centipoise)		22	18
Gloss - calender nips	0	28	30
	4	70.4	72.0
Print Gloss		85.5	86.8
Brightness		84.8	84.5
IGT Dry Pick (#4 ink 4 m.sec 35kgf)		343	402

This shows that paper coating compounds prepared in accordance with the present invention have lower high shear viscosity and provide equivalent or better print gloss and improved dry pick over the prior art.

Example 2

The control and experimental latex of Example 1 were compounded as follows:

Clay	60
Calcium Carbonate	40
Latex	13
Starch	3
Lubricant	1

The compounds were diluted with water to a solids level of 63, 67 and 70 weight percent.

The latex was tested as in Example 1. Paper was coated on a laboratory coater at 9.5 lb (dry) per ream. The paper was calendered and tested as in Example 1. The results are set forth in Table II.

TABLE II

	Control Latex			Experimental Latex		
Compound Solids %	63	67	70	63	67	70
Hercules Viscosity	19	43	Break	17	38	70
Centipoise at 4400 rpm		(4000rpm)				
Sheet Gloss at 75° F	65	69	--	65	69	74
Print Gloss	77	81	--	80	83	87
Brightness	82.4	81.9	--	84.1	84.5	85.5
IGT Dry Pick (#4 ink 4 m sec 35 kgf)	600	580	--	625	600	575
Note: Test results on paper coated at 70% solids with the control latex were not taken as the paper could not be coated under conventional coating conditions. This shows the improvement in high shear rheology, print gloss and dry pick obtain ble in accordance with the present invention.						

Example 3

The experimental latex of Example 1 was tested for calcium ion stability.

A sample of the latex was titrated with a 10% $CaCl_2$ solution and then filtered. There was no detectable coagulum. For the control latex of Example 1, latex coagulum of 15% was obtained with a 10% $CaCl_2$ solution.

Claims

1. A paper coating composition having a solids content of from 65 to 75 weight percent and a viscosity as measured on a Hercules Hi Shear viscometer with an E bob and a 400,000 dynes cm/cm spring at 4400 rpm and 105° F of less than 80 centipoise, which comprises from 95 to 85 weight percent by dry weight of a composition comprising

100 to 40 weight percent of clay; and

0 to 60 weight percent of one or more members selected from the group consisting of calcium carbonate, aluminum trihydrate, titanium dioxide, and barium sulfate;

from 5 to 15 weight percent by dry weight of a latex which produces less than 0.5 weight percent coagulum on exposure to 10% $CaCl_2$ comprising an interpplymer of

from 55 to 65 weight percent of a C_{8-12} vinyl aromatic monomer which is unsubstituted or substituted by a C_{1-4} alkyl radical or a chlorine atom;

from 30 to 40 weight percent of a branched or straight chained C_{4-6} conjugated diolefin which is unsubstituted or substituted by a chlorine atom; and

from 4 to 10 weight percent of one or more C_{3-6} ethylenically unsaturated carboxylic acids.

2. A paper coating composition according to Claim 1 having a solids content of 65 to 70 weight percent and a viscosity as measured with a Hercules Hi Shear viscometer with an E bob and a 400,000 spring at 4400 rpm and 105° F from 20 to 70 centipoise.

3. A paper coating composition according to Claim 2 wherein said polymer contains both mono- and di-carboxylic acids in a weight ratio of mono- to di-carboxylic acid from 4:1 to 6:1.

4. A paper coating composition according to Claim 3 wherein said polymer comprises

from 58 to 62 weight percent of styrene;

from 32 to 36 weight percent of butadiene; and

from 5 to 7 weight percent of one or more carboxylic acids selected

from the group consisting of acrylic acid, methacrylic acid, itaconic acid and fumaric acid.

5. A paper coating composition according to Claim 4 wherein said coating composition comprises from 70 to 80 weight percent clay having an average particle size of less than 2 microns and 30 to 20 weight percent of calcium carbonate having an average particle size of less than 2 microns and 5 to 15 weigh percent of said polymer.

6. A paper coated with from 8 to 15 lb per 3300 ft^2 of a coating according to Claim 4 and having an IGT pick as measured with a #4 ink of not less than 450 m/sec.

7. A paper coated with from 8 to 15 lb clay per 3300 ft^2 of a coating according to Claim 5 and having an IGT pick as measured with a #4 ink of not less than 450 m/sec.