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(54) Emulsion polymerisation.

(57) Aqueous polymer emulsions are used in paper coating prior to applying inks to the paper surface.
This invention provides an emulsion comprising a copolymer of vinyl alkanoate, alkylene and vinyl versatate. This emulsion, when used for coating paper subjected to offset lithographic printing, provides improved wet pick strength.

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EMULSION POLYMERISATION

Field of the Invention:

This invention relates to aqueous emulsions containing copolymers of vinyl acetate and ethylene in which vinyl acetate is the major component. Copolymers of the invention are utilised in paper coating compositions and demonstrate good rheology and dry pick strength with enhanced wet pick strength.

Background of the Invention:

Paper coating compositions usually comprise an aqueous polymer binder emulsion, a pigment and optionally other additives common in the technology. The present invention is specifically directed to novel emulsions based on copolymers comprising a vinyl C1 to C4 alkanoate component forming at least about 60% by weight of the copolymer, more usually at least about 70% by weight and an alkylene component, eg. ethylene. Vinyl acetate is an example of a vinyl ester of a C1 to C4 alkanoic acid to which the invention is generally directed. Coating compositions of the invention will contain a pigment, for example clay, which is compounded with the latex binder and used in coating a cellulosic web for example a paper or paperboard web. The characteristics of the latex binder component are significant in the ease of preparation of the paper coating composition, its application and on the qualities of the coated product.

The coating composition will be coated on to a paper substrate, dried and calendered. Usually the composition will be applied at a level to give a loading of about 18 to about 24 g/m^2 solids on one surface. The copolymer particles will bind those of the pigment filler to provide cohesive strength and contribute to the adhesion between the coating and paper substrate. The coating, which will usually have a thickness of about 3 microns to about 10 microns imparts gloss and whiteness to the paper and provides a suitable surface for receiving ink.

When the coating is subjected to successive printing operations, for example in offset lithography, the coating must provide acceptable wet and dry pick strengths. When the first colour is printed any pull by the tacky ink giving failure of the coating is termed 'dry pick'. Failure when the coated paper passes to the second inking stage, when ink is applied to prewetted areas, is termed 'wet pick'. Subsequent inking steps can also give rise to wet pick failure.

General description of the Invention:

The invention provides the use in paper coating of an aqueous copolymer emulsion having a solids content from about 20% to about 70% by weight and comprising

i) from about 60%, preferably from about 70%, to about 90% by weight of a vinyl C1 to C4 alkanoate,

ii) from about 5% to about 20% of a C1 to C4 alkylene monomer, and

iii) from about 5% to about 20% by weight, preferably from about 8% to about 15% by weight, of vinyl esters having the general formula $R_1R_2R_3$ $CCOOCHCH_2$ wherein R_1R_2 and R_3 are each alkyl groups having at least one carbon atom and $R_1 + R_2 + R_3$ is from 6 to 9.

This product has good rheology and dry pick strength and enhanced wet pick strength which is attributable to the presence of vinyl ester (iii) monomers. There is a general requirement in paper coating to improve these characteristics.

The invention extends to a pigmented paper coating composition comprising

i) to 100 parts of pigment and

ii) from about 3% to about 30% by dry weight of an aqueous emulsion as defined above.

In the emulsions prepared for use in paper coatings the polymerisation system will be substantially free of protective colloids. Colloidal materials may be added subsequently to the paper coating composition.

Although vinyl acetate is the preferred vinyl alkanoate monomer because of its availability, cost and known reactivity, other vinyl esters within the class defined are usable in particular vinyl formate, propionate, butyrate and isobutyrate.

The preferred alkylene is ethylene but other ethylenic hydrocarbons, for example propylene, butylene and isobutene are usable.

Optionally the copolymer may contain minor monomer components added to provide specific benefits, examples are sodium vinyl sulphonate, acrylic acid, methacrylic acid, acrylamide, hydroxy functional acrylates, vinyl silanes and vinyl halides. A favoured comonomer is a polyethylencially unsaturated compound selected from triallyl cyanurate, triallyl isocyanurate, diallyl maleate, diallyl fumarate, divinyl benzene and diallyl phthalate.

Methods for preparing the copolymer emulsions of the invention are well characterised in the literature. Polymer Synthesis (vols I and III) by Sandler & Karo (Academic Press 1974) and Preparative Methods of Polymer Chemistry (2nd Ed) by Sorenson and Campbell (Interscience 1968) provide preparative information. Methoden der Organischen Chemie (Houben-Wey) Band XIV published by George Thieme Verlag Stuttgart (1961) also provides preparative descriptions.

Preferably at least one surfactant used in the polymerisation process contains a C14 to C20 alkylene moiety and examples are an oleyl propanol amide sulphosuccinate obtainable from Witco of USA under the trade name Emcol K8300 and the potassium salt of the sulphonation product of oleic acid obtainable from Lankro Chemicals of Manchester England under the trade name Lankropol OPA.

The paper coating composition comprises a pigment, for example clays, hydrated silica clays, and other conventional ingredients. The clays used include Kaolin group clays and hydrated silica clays, specific clays are disclosed in "Kaolin Clays and their Industrial Uses" by J. M. Huber Corp. (1949) New York chapters 10 to 16.

Other pigments, for example calcium carbonate, titanium dioxide, blanc fixe, lithopone and zinc sulphide may be used in addition to clay. In general the paper coating composition will comprise

Component	Parts by weight
Pigment	100
dispersing agent eg. sodium pyrophosphate	0.1 to 0.5
latex (on solids basis)	3 to 30
Cobinder eg. starch or casein	0 to 25
Defoamer, eg. a hydrocarbon oil	0 to 0.2
Water to provide desired solids level.	

The coating compositions produced with the aid of the latexes of the invention will be applied to fibrous paper webs using conventional means for example trailing blade coaters, air knife coaters and roll coaters.

Literature

The applicants are aware of the following disclosures relating to polymer emulsions.

EPA 0295727 (Shell) describes polymer emulsions containing vinyl acetate, ethylene and versatates (Veova 9) for use in paint compositions to give non tacky surfaces which are alkali resistant. These benefits are demonstrated in comparison with Veova 10. The description suggests the emulsions are usable in paper coating and other fields, but there is no disclosure of the wet pick benefit identified in the present application.

EPA 0172354 (Air Products) describes vinyl alkanoate/Ethylene emulsions for paper coating which provide enhanced dry pick strength and gloss. The additional monomers are unsaturated acids/esters and dicyclopenta-dienyl acrylate. Vinyl versatates are quoted as examples of the alkanoates but there is no suggestion to use them as a third monomer with VA/E. VA/E is stated to lack sufficient wet pick resistance for offset printing.

GB 1144316 (Dunlop) describes alkali-soluble polymer emulsions formed from quaternary alpha carbon carboxylic, vinyl carboxylate and unsaturated carboxylic monomers. pH and viscosity stability derive from the tertiary monomer.

Test Methods:

i) Dry pick strength values (cm/sec) were measured using a coating composition on Reeds Aircoat woodfree paper using an IGT Dynamic Pick Tester (AÇ2 Model) with 25 Kg load and low viscosity ink. The

composition tested contained:

Pigment SPS clay*	to 100 parts	
Emulsion under test	24 parts of 50% solids emulsion	
Water retention aid**	Finnfix FF5	0.5 parts
Dispersant***	Dispex N40	0.3 parts
Sodium hydroxide		0.15 parts
Water to give 45% solids		

* obtainable from English China Clay of St Austell England.
** Obtainable from Finn Forest Chemicals of Cheam, England.
*** Allied Colloids of Bradford, England.

ii) The wet pick strength was measured with the apparatus of the dry pick method. 0.3 mls of ink was applied to each roller and distributed for 15 minutes. A test strip of paper coated with the test composition to a level of 20g/m^2 (solids) was placed in the device. The inked roller was contacted with the test strip and adjusted to a printing force of 35 Kgf. A drop of tap water was placed on the test strip immediately in the path of the roller so ink is applied over a layer of water spread by progress of the roller.

The degree of resistance to pick is judged at a qualitative level i.e. good - fair - bad.

Specific description of the invention:

Examples of the invention will now be given to illustrate but not limit the invention.

In the examples several functional monomers and surfactants were used and these are represented by abbreviations and letters in the table of results in order to simplify the presentations.

Functional monomers: A172 is vinyl tris trimethoxy silane obtainable from Union Carbide of USA.
DAM is diallyl maleate.
EHM is ethyl hydrogen maleate
SVS is sodium vinyl sulphonate

Surfactants: A is sodium nonylphenol 20 EO sulphate obtainable from Lankro Chemicals of Manchester England as Perlankrol RN75.
B is sodium oleyl propanol amide sulphosuccinate obtainable from Witco of USA as Emcol K8300.
C is sodium dodecyl benzene sulphonate obtainable from Lankro Chemicals as Arylan SC15.
D is disodium salt of an ethoxylated alcohol half ester of sulphosuccinic acid obtainable from Cyanamid of Wayne New Jersey USA as Aerosol A102.

Example I

A surfactant solution (initial charge) comprising 37% aq. solution of Emcol K8300 (74.2g), 30% aq solution of Aerosol A102 (53.2g) and ammonium persulphate (4.3g) dissolved in deionised water (999g) was prepared and charged to a 4 litre pressure vessel. The contents are heated to 68° C. At 68° C the reactor was purged twice with nitrogen, once with ethylene and pressurised with ethylene to 450 lbs/sqin gauge with stirring. The temperature was adjusted to 76° C while 10% of the liquid monomer phase was pumped to the reactor.

The continuous addition of persulphate solution (5.3g in 300g of deionised water) was begun and the reaction mass was held at 76° C for 45 minutes. At the end of this period, the continuous addition of the remainder (90%) of the monomer phase was started. The persulphate solution was added over 6.5 hours and the monomer phase over 5.0 hours. The pressure was maintained at 450 lbs/sq in gauge until the desired quantity of ethylene had been reacted, this was after four hours from start of continuous persulphate additon.

After completion of the addition of monomer, the reaction mass was held at 80° C for 45 mins, at the end of which the addition of persulphate solution was stopped. The contents of the reactor was cooled to 40° C, followed by pumping of finishing off stage (4.6g of each in 70g of deionised water) to the reactor, in

separate streams, over 30 minutes.

The contents of the reactor were then cooled to 25° C and discharged to a degassing tank.

Ammonia solution was used to adjust the pH of the emulsion latex to 8. The emulsion had a solids content of 51.6% by wt.

FORMULA	
Initial Charge:	Parts per hundred monomer
distilled water	64.06
Emcol K8300	4.75
Aerosol A102	3.41
Ammonium Persulphate	0.28
Liquid monomers:	
Vinyl Acetate (VA)	74.95
Veova 9** (VV9)	9.93
Silane A172	0.49
Diallylmaleate	0.19
Ethylene (E)	14.41
Distilled Water	0.19
Ammonium Persulphate	0.34
Distilled Water	4.48
TBH	0.30
Distilled Water	4.48
Sodium Metabisulphite	0.30
	182.56

** VeoVa 9 is vinyl ester of versatic acid in which $R_1 + R_2 + R_3 = 7$ and is obtainable from Shell Chemicals of Chester England.

The result of the dry and wet pick tests on a coating composition containing the resulting emulsion are given in Table I.

Examples II to XII

Additional examples were performed using the process steps of Example I but varying the quantities of the base monomers, i.e. vinyl acetate, VeoVa 9 and ethylene, the functional monomers and the stabilising surfactants. These emulsions were also tested for wet and dry pick strengths.

The emulsion products had solids contents comparable to that obtained in Example I.

The applicants have found the addition of a vinyl ester of the class exemplified by VeoVa 9 to a vinyl acetate/ethylene emulsion polymer system improves the wet pick resistance of a paper coating composition.

TABLE I

EXPT	MONOMERS							PICK STRENGTH			
	COPOLYMERS			FUNCTIONAL MONOMERS				SURFACTANTS		DRY	WET
	VA	VV9	E	A172	DAM	EHM	SVS				
I	79	15	4	**	**	**		A	B	190	Good
II	77	15	6	**	**	**		A	B	400	Good
III*	83	15	0	**	**	**		A	B	140	Good/Fair
IV	70	20	8	**	**		**	A	B	100	Good/Fair
V*	85	10	4	**				C	B	154	Poor
VI	76	10	13	**				D	B	145	Good/Fair
VII	82	10	6	**	**	**		A	B	231	Good
VIII	82	10	6	**	**	**		D	B	204	Good
IX	81	10	7	**	**	**		D	B	159	Good
X*	78	5	15	**				D	B	136	Poor
XI*	82	5	12	**	**			D	B	183	Poor
XII	81	0	17	**	**	**		A	B	NM	Poor

* Comparative Example
** functional monomer present
NM - not measured

Claims

1. The use in paper coating of an aqueous copolymer emulsion having a solids content from about 20% to about 70% by weight and comprising

i) from about 60% to about 90% by weight of a vinyl C1 to C4 alkanoate,

ii) from about 5% to about 20% of a C1 to C4 alkylene monomer, and

iii) from about 5% to about 20% by weight, preferably from about 8% to about 15% by weight, of vinyl esters having the general formula $R_1R_2R_3$ $CCOOCHCH_2$ wherein R_1R_2 and R_3 are each alkyl groups having at least one carbon atom and $R_1 + R_2 + R_3$ is from 6 to 9.

2. A pigmented paper coating composition comprising

i) to 100 parts by weight of pigment, and

ii) from about 3 parts to about 30 parts by dry weight of an aqueous emulsion as defined in claim 1.

3. A pigmented paper coating composition as claimed in claim 2 further comprising:
from about 0.1 to about 0.5 parts of dispersing agent,
from 0 to about 2.5 parts of cobinder,
from 0 to about 0.2 parts of defoamer, and water to appropriate level.

4. A process of offset lithographic printing of paper wherein the paper is coated with the composition of claim 2 prior to printing.

5. A process as claimed in claim 4 wherein the composition is applied at a level to give about 18 g/m^2 to about 24 g/m^2 dry solids.

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EUROPEAN SEARCH REPORT

Application Number

EP 90 30 0790

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)
X	US-A-4 657 821 (SHIGERU URA et al.) * Claims; examples *	1-5	D 21 H 19/60
X	US-A-3 477 871 (VAN WESTRENEN) * Claims; examples; column 4, lines 7-19; column 6, line 22 - column 7, line 27 *	1-5	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

D 21 H 19/60
C 09 D 131/02

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	09-05-1990	FOUQUIER J.P.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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