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(54) Titre : LATEX ACETATE DE POLYVINYLE
(54) Title: POLYVINYL ACETATE LATEX

(57) Abrégé/Abstract:
The present invention relates to a process for preparing an aqueous dispersion of a vinyl acetate polymer comprising the step of polymerizing vinyl acetate under emulsion polymerization conditions in the presence of a chain transfer agent which is a hypophosphite salt or X-R^1-SH, where R^1 is a C_1-C_4 alkyl group and X is sulfonate, hydroxyl, sulfate, phosphate, phosphonate, carboxylic acid or a salt thereof, or C_1-C_3-alkyl carboxylate. The process provides a way of lowering the viscosity of the vinyl acetate polymer at a given solids content.

Abstract

The present invention relates to a process for preparing an aqueous dispersion of a vinyl acetate polymer comprising the step of polymerizing vinyl acetate under emulsion polymerization conditions in the presence of a chain transfer agent which is a hypophosphite salt or X-R^1-SH, where R^1 is a C_1-C_4 alkyl group and X is sulfonate, hydroxyl, sulfate, phosphate, phosphonate, carboxylic acid or a salt thereof, or C_1-C_3-alkyl carboxylate. The process provides a way of lowering the viscosity of the vinyl acetate polymer at a given solids content.

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POLYVINYL ACETATE LATEX

Background of the Invention

The present invention relates to a polyvinyl acetate latex composition, more particularly, a relatively low viscosity polyvinyl acetate latex composition.

Historically, polyvinyl acetate containing latexes develop high in-process viscosities, which present great challenges to processing and manufacturing. Failure to reduce in-process viscosity often forces latex manufacturers to either use extreme agitation, which may present safety issues in a plant, or to reduce polymer solids, which adds unnecessary cost for shipping and handling. Furthermore, low solid content latexes limit the marketability of the latex. Accordingly, it would advantageous to develop polyvinyl acetate latexes with higher solids and/or lower viscosities.

Summary of the Invention

The present invention is a composition comprising vinyl acetate polymer particles dispersed in an aqueous phase, wherein the aqueous phase comprises 1) a chain transfer agent; and 2) a vinyl acetate oligomer; wherein the chain transfer agent is sodium hypophosphite or X-R^1-SH, where R^1 is a C_1-C_4 alkyl group and X is sulfonate, hydroxyl, sulfate, phosphate, phosphonate, carboxylic acid or a salt thereof, or C_1-C_3-alkyl carboxylate; and wherein the vinyl acetate oligomer has a weight average molecular weight (M_w) in the range of from 1000 to 7000 Daltons. The composition of the present invention provides vinyl acetate polymers with lower end-of-feed viscosities at a given solids content.

Detailed Description of the Invention

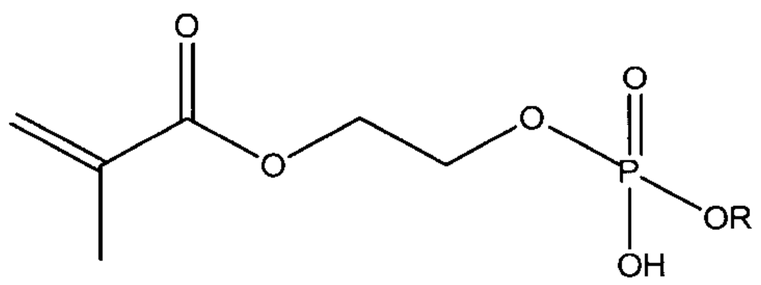
The present invention is a composition comprising vinyl acetate polymer particles dispersed in an aqueous phase, wherein the aqueous phase comprises 1) a chain transfer agent; and 2) a vinyl acetate oligomer; wherein the chain transfer agent is sodium hypophosphite or X-R^1-SH, where R^1 is a C_1-C_4 alkyl group and X is sulfonate, hydroxyl, sulfate, phosphate, phosphonate, carboxylic acid or a salt thereof, or C_1-C_3-alkyl carboxylate; and wherein the vinyl acetate oligomer has a weight average molecular weight (M_w) in the range of from 1000 to 7000 Daltons. The vinyl acetate polymer may be a homopolymer or a copolymer; therefore, the polymer may be prepared by homopolymerization or copolymerization in the presence of one or

more other monomers, such as acrylates and methacrylates including methyl methacrylate, butyl acrylate, ethyl acrylate, ethylhexyl acrylate, and ureido methacrylate; vinyl esters of a branched carboxylic acid monomer, including vinyl versatate; and phosphorus acid monomers such as phosphoethyl methacrylate (PEM), phosphopropyl methacrylate, CH_2=CH-CH_2-$(OCH_2CH_2)_n(O)_m$-P(O)$(OH)_2$, or a salt thereof, where n is from 1 to 5 and m is 0 or 1; and acrylamide monomers and sulfonic acid monomers and salts thereof and combinations thereof including acrylamide, 2-acrylamido-2-methylpropane sulfonic acid or a salt thereof, and vinyl sulfonic acid or a salt thereof.

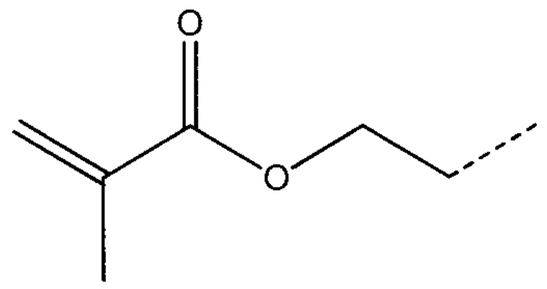
Preferably, the concentration of vinyl acetate is from 40, more preferably from 50, and most preferably from 60 weight percent, to preferably 95, and more preferably to 90 weight percent based on the weight of total monomers.

A low T_g alkyl acrylate such as butyl acrylate, ethyl acrylate, or ethylhexyl acrylate is preferably included as a comonomer at a concentration in the range of from 5, more preferably from 8, and most preferably to 10 weight percent, to 50, more preferably to 40, and most preferably to 35 weight percent, based on the weight of total monomers.

When a phosphorus acid monomer is used, it is preferably included at a concentration in the range of from 0.1, more preferably from 0.2 weight percent to preferably 5, more preferably to 3, and most preferably to 2 weight percent based on the weight of total monomers. A preferred phosphorus acid monomer is PEM, which is characterized by the following formula:



where R is H or



wherein the dotted line represents the point of attachment to the oxygen atom.

2-Acrylamido-2-methylpropane sulfonic acid or a salt thereof or vinyl sulfonic acid or a salt thereof, preferably 2-acrylamido-2-methylpropane sulfonic acid or a salt thereof, is preferably included as a comonomer at a concentration in the range of from 0.1, more preferably from 0.5 weight percent, to 5, more preferably to 3, and most preferably to 2 weight percent, based in the weight of total monomers.

Ureido methacrylate may also be included at a concentration in the range of from 0.1, more preferably from 0.2, and most preferably from 0.5 weight percent, to 5, more preferably to 3, and most preferably to 2 weight percent, based on the weight of total monomers.

Examples of preferred chain transfer agents include sodium and potassium hypophosphite salts; sodium and potassium salts of β-mercaptoethansulfonate; γ-mercaptopropionic acid and sodium and potassium salts thereof; and β-mercaptoethanol.

The chain transfer agent (CTA) is preferably used at a concentration of from 0.01, more preferably from 0.02, and most preferably from 0.05 weight percent, to preferably 2, more preferably to 1, and most preferably to 0.5 weight percent, based on the total weight of monomers or water, since the solids content of the latex is targeted at 50 weight percent.

As used herein, the term "vinyl acetate oligomer" refers to a water soluble product of the vinyl acetate polymerization (or copolymerization) reaction that includes chemically bound CTA. Some amount of vinyl acetate oligomer that is not chemically bound to CTA may also be present. The vinyl acetate oligomer can be identified and quantified in the aqueous phase of the dispersion and measured as follows. The water soluble oligomer and the CTA can be conveniently isolated by way of centrifugation (e.g., 100,000 rpm for 25 minutes). A portion of the supernatant can then be transferred to a petrie dish and the water can be removed at room temperature *in vacuo*. Solids are measured and typically found to be in the range of 1 to 10 weight percent, based on the weight of the aqueous phase. Another portion of the supernatant is transferred to an NMR tube whereupon quantitative proton or ^{31}P NMR spectroscopy is carried out to identify the percent oligomer in the supernatant solids, which is generally in the range of 5 to 25 weight percent of total supernatant solids. Thus, the concentration of oligomer in the aqueous phase is preferably from 0.05 to 2.5 weight percent; more preferably, the concentration of oligomer in the serum phase is from 0.1 to 1 weight percent, based on the weight of the

aqueous phase of the dispersion. Standard ^{1}H and gradient diffusion experiments can be used to selectively detect oligomers as described by Beshah et al. in *Macromolecules* **2001**, *46*, 2216-27. 2D NMR spectroscopic techniques are also advantageously used to identify end group species that arise from the CTA, as described by Beshah in *Makromol. Chem.* **1993**, *194*, 3311-3321. The amount of CTA in the serum phase after polymerization is generally in the range in 0.002 weight percent to 1 weight percent, based on the weight of water. Unreacted sodium hypophosphite, for example, can be identified by ^{31}P NMR spectroscopy at about 6.2 ppm (using orthophosphoric acid as an internal standard)

Weight average molecular weight (M_w) of the oligomers was determined by first measuring the diffusion coefficient of the aqueous phase by NMR spectroscopy as described by C.S. Johnson in *Prog. NMR Spectrosc.* **1999**, *34*, 203. The M_w was then measured using polystyrene standards as described by Weibin et al. in *Macromolecules* , **2012** 45 (24), 9595–9603. Preferably, the M_w of the oligomer (with or without chemically bound CTA) is from 1500, more preferably from 2000 Daltons, to 6000, more preferably to 5500, and most preferably to 4000 Daltons.

It has been discovered that the aqueous dispersion of the vinyl acetate polymer (the PVA latex), preferably the vinyl acetate copolymer, exhibits a lower viscosity in the aqueous phase than comparable aqueous dispersions of vinyl acetate polymers that are not prepared using these CTAs. It has been found that hypophosphites and water-soluble alkyl mercaptans, when used as CTAs in the polymerization reaction, reduce the weight average molecular weight (M_w) of water-soluble polymers and the percentage of high molecular oligomers in the aqueous phase, accounting for a reduced in-process latex viscosity at constant solids content (or an increased solids content at comparable viscosity) measured against a variety of PVA latexes that do not use CTAs within the specified class. Lowering the viscosity in a latex formulation without lowering solids content provides for a more efficient use of water in a latex formulation.

The PVA latex is useful as a binder for coatings compositions, adhesives, or construction materials. For coating compositions, the latex can combined with one or more ingredients selected from the group consisting of pigments such as TiO_2, dispersants, defoamers, surfactants, solvents, additional binders, thickeners, extenders, coalescents, biocides, and colorants.

Abbreviations

Abbreviation	Name
BA	Butyl Acrylate
VA	Vinyl Acetate
AMPS	2-Acrylamido-2-methylpropane sulfonic acid
PEM	Phosphoethyl Methacrylate
t-BHP	*t*-Butyl Hydroperoxide
IAA	Isoascorbic Acid
UMA	Ureido Methacrylate
EA	Ethyl Acrylate
MMA	Methyl Methacrylate
MAA	Methacrylic Acid
NaPS	Sodium Persulfate
PS	Particle Size

Examples

In the following examples, the average particle size was measured using dynamic light scattering at 90° on a Brookhaven 90Plus Particle Size Analyzer. The viscosity was measured on either a Brookfield DV-II Pro Viscometer or a Brookfield LVTD Viscometer.

Comparative Example 1 – Preparation of PVA Copolymer without any CTA

The monomer emulsion was prepared by first mixing DI water (2258 g), PEM (60% active, 230.85 g), NaOH (50%, 151 g), Disponil FES-77 surfactant (185.37 g), TERGITOL™ 15-S-40 surfactant (169.2 g), and dodecylbenzene sulfonate (22.5% aq., 220.35 g) followed by BA (1370.63 g), VA (9810.90 g) and Lubrizol AMPS 2405 (259.7 g).

A 5-gal (19-L) reactor equipped with a mechanical stirrer, nitrogen gas blanket, thermometer, condenser, heating mantel, and temperature controller was charged with DI water (9386.8 g) and heated to 71 °C under N_2. To this flask were added Disponil FES-32 surfactant (250.08 g), TERGITOL™ 15-S-40 surfactant (169.2 g), and a solution of $FeSO_4$ heptahydrate (0.36 g) in

water (20 g). Co-feed catalyst solution *t*-BHP (37.1 g) in water (222.6 g) and co-feed activator solution IAA (51.08 g) and sodium acetate (35.67 g) in water (482.18 g) were fed to the flask at a rate of 1.44 g/min, and 2.96 g/min, respectively. Two minutes later, monomer emulsion was fed to the flask at a rate of 64.78 g/min. Ten minutes later, the monomer emulsion feed rate was increased to 129.55 g/min and the reaction temperature was controlled at 71 °C. After the monomer emulsion addition was complete, the monomer emulsion vessel was rinsed with DI water (160 g), and the co-feed solutions were continued for an additional 60 min until completion. After the co-feed solutions were complete, a solution of *t*-BHP (12.36 g) in water (74.21 g) and a solution of sodium bisulfite (15.38 g) in water (161.56 g) were fed separately to the flask at 1.44 g/min and 2.95 g/min, respectively, to reduce the residual monomer. After completion of all feeds, the flask was cooled to room temperature. When the flask was cooled to 50 °C, NH_3 (52.46 g, 28% aq.) was added to the flask at 10.49 g/min over 5 min, then cooled to 40 °C, whereupon a solution of KATHON™ LX bactericide (24.74 g, 1.5%) in water (60 g) was added at a rate of16.95 g/min over 5 min. After cooled to room temperature, the contents were filtered to remove gel. The filtered dispersion was found to have a solids content of 44.0% and a pH of 6.

Example 1 – Preparation of PVA Copolymer with Sodium Hypophosphite CTA

The monomer emulsion was prepared by first mixing DI water (2258 g), a sodium hypophosphite solution (26.5 g, 45% aq), phosphoethyl methacrylate (60% active, 230.85 g), NaOH (50%, 151 g), Disponil FES-77 surfactant (185.37 g), TERGITOL™ 15-S-40 surfactant (169.2 g), and dodecylbenzene sulfonate (22.5% aq., 220.35 g) followed by BA (1255.21 g), VA (9810.90 g) and Lubrizol AMPS 2405 (259.7 g).

A 5-gal (19-L) reactor equipped with a mechanical stirrer, nitrogen gas blanket, thermometer, condenser, heating mantel and temperature controller was charged with deionized water (9160 g) and heated to 71 °C while purged with N_2. To this flask were added Disponil FES-32 surfactant (250.08 g), TERGITOL™ 15-S-40 surfactant (169.2 g), and a solution of $FeSO_4$ heptahydrate (0.36 g) in water (20 g). Co-feed catalyst solution *t*-BHP (37.1 g) in water (449 g) and a co-feed solution of IAA (51.08 g) and sodium acetate (35.67 g) in water (482.18 g) were fed to the flask at a rate of 2.7 g/min, and 2.96 g/min, respectively. Two minutes later, monomer emulsion was fed to the flask at a rate of 64.78 g/min. Ten minutes later, the monomer emulsion feed rate was

increased to 129.55 g/min and the reaction temperature was controlled at 71 °C. 60 min after the start of the monomer emulsion feed, UMA (50% active, 230.84 g) was added to the monomer emulsion. After the monomer emulsion addition was complete, the monomer emulsion vessel was rinsed with DI water (160 g), and the co-feed solutions were continued for an additional 60 min until completion. After the co-feed solutions were complete, a solution of *t*-BHP (12.36 g) in water (74.21 g) and a solution of sodium bisulfite (15.38 g) in water (161.56 g) were fed separately to the flask at 1.44 g/min and 2.95 g/min, respectively, to reduce the residual monomer. After completion of all feeds, the flask was cooled to room temperature. When the flask was cooled to 50 °C, NH_3 (52.46 g, 28% aq.) was added to the flask at 10.49 g/min over 5 min. The reactor was cooled to 40 °C, whereupon a solution of KATHON™ LX bactericide (24.74 g, 1.5%) in water (60 g) was added at a rate of 16.95 g/min over 5 min. After the reactor was cooled to room temperature, the contents were filtered to remove gel. The filtered dispersion was found to have a solids content of 44.3% and a pH of 6.

Example 2 – Preparation of PVA Copolymer with Sodium Hypophosphite CTA

The monomer emulsion was prepared by first mixing DI water (2258 g), a sodium hypophosphite solution (26.5 g, 45% aq), PEM (60% active, 230.85 g), NaOH (50%, 151 g), Disponil FES-77 surfactant (185.37 g), TERGITOL™ 15-S-40 surfactant (169.2 g), and dodecylbenzene sulfonate (22.5% aq., 220.35 g) followed by BA (1255.21 g), VA (9810.90 g) and Lubrizol AMPS 2405 (259.7 g).

A 5-gal (19-L) reactor equipped with a mechanical stirrer, nitrogen gas blanket, thermometer, condenser, heating mantel and temperature controller was charged with deionized water (8100 g) and heated to 71 °C while purged with N_2. To this flask were added Disponil FES-32 surfactant (250.08 g), TERGITOL™ 15-S-40 surfactant (169.2 g), and a solution of $FeSO_4$ heptahydrate (0.36 g) in water (20 g). Co-feed catalyst solution *t*-BHP (37.1 g) in water (449 g) and co-feed solution of IAA (51.08 g) and sodium acetate (35.67 g) in water (482.18 g) were fed to the flask at a rate of 2.7 g/min, and 2.96 g/min, respectively. Two minutes later, the monomer emulsion was fed to the flask at a rate of 64.78 g/min. Ten minutes later, the monomer emulsion feed rate was increased to 129.55 g/min and the reaction temperature was controlled at 71 °C. After the monomer emulsion addition was complete, the monomer emulsion vessel was rinsed with DI water (160 g), and the co-feed solutions were continued for an additional 60 min until

completion. After the co-feed solutions were complete, a solution of *t*-BHP (12.36 g) in water (74.21 g) and a solution of sodium bisulfite (15.38 g) in water (161.56 g) were fed separately to the flask at 1.44 g/min and 2.95 g/min, respectively, to reduce the residual monomer. After completion of all feeds, the flask was cooled to room temperature. When the flask was cooled to 50 °C, NH_3 (52.46 g, 28% aq.) was added to the flask at 10.49 g/min over 5 min. The reactor was cooled to 40 °C, whereupon a solution of KATHON™ LX bactericide (24.74 g, 1.5%) in water (60 g) was added at a rate of 16.95 g/min over 5 min. After the reactor was cooled to room temperature, the contents were filtered to remove gel. The filtered dispersion was found to have a solids content of 46.1% and a pH of 6.

Table 1 illustrates the relationship between solids content and the end of the monomer emulsion feed viscosity (EOF) at the polymerization reaction temperature. C1 refers to Comparative Example 1, and 1 and 2 refer to Examples 1 and 2, respectively. PS refers to particle size of the latex particles; EOF refers to end of feed viscosity in centipoise (cP) and was measured using a Brookfield DV-II Pro Viscometer.

Table 1 – Effect of Sodium Hypophosphite CTA on PVA Latex Copolymer Viscosity

Ex.#	Solids (%)	PS (nm)	NaH_2PO_3 (%)	EOF (cP)	Composition
C1	44	117	0	2500	85 VA/11.88 BA/2 PEM/1.12 AMPS
1	44.3	122	0.1%	768	85 VA/10.88 BA/2 PEM/ 1 UMA/1.12 AMPS
2	46.1	124	0.1%	2240	86 VA/10.88 BA/2 PEM/1.12 AMPS

Table 1 shows that a small addition of sodium hypophosphite causes a marked reduction in EOF at the same solids content and approximately the same particle size, and even a 10% reduction in EOF with a significantly improved solids content (46.1 versus 44 % solids).

The PVA latex containing structural units of VA, BA, and AMPS – but without PEM – was also evaluated with and without sodium hypophosphite (NaH_2PO_3) as shown in Table 2. Comparative Example 2 can be prepared by conventional methods such as described for Comparative Example 1.

Table 2 – Effect of Sodium Hypophosphite CTA on PVA Latex Copolymer Viscosity

Ex. #	Solids (%)	PS (nm)	NaH_2PO_3 (%)	EOF (cP)	Composition
C2	56.2	223	0	22800	65.4 VA/34 BA/0.6 AMPS
3	56.4	218	0.1	9400	65.4 VA/34 BA/0.6 AMPS

Table 2 illustrates that the viscosity drop at constant solids content is observed for PVA latex copolymers that do not contain phosphorus acid functionalization.

Comparative Example 3 – Preparation of a VA Copolymer without a CTA

Monomer emulsion was prepared by first mixing DI water (368.8 g), PEM (60% active, 8.53 g), NaOH (50%, 5.29 g), TERGITOL™ 15-S-9 surfactant (A Trademark of The Dow Chemical Company or Its Affiliates, 17.1 g), Disponil FES-77 surfactant (27.38 g),), TERGITOL™ 15-S-40 surfactant (49.93 g), and dodecylbenzene sulfonate (22.5% aq., 32.55 g) followed by BA (570.15g), VA (1116.78 g) and Na-AMPS (19.1 g).

A 5-L 4-necked round bottom flask equipped with a mechanical stirrer, nitrogen gas blanket, thermometer, condenser, heating mantel and temperature controller was charged with deionized water (900 g) and heated to 71 °C while purged with N_2. To this flask was added a solution of $FeSO_4$ heptahydrate (0.1% in water, 18g), nitrilotriacetic acid (0.1% in water, 15 g) and EA/MMA/MAA pre-form seed (52/47/1, 40 nm particle size, 103.83 g). Co-feed catalyst (*t*-BHP, 1.51 g) and NaPS (2.27 g) in water (49.5 g) and co-feed activator (IAA, 2.26 g) and NaOH (1.02 g, 50% aq.) in water (50 g) were fed to the flask at a rate of 0.34 g/min. Five minutes later, the monomer emulsion was fed to the flask at a rate of 9.6 g/min. Fifteen minutes later, the monomer emulsion feed rate was increased to 19.2 g/min and the reaction temperature was controlled at 71 °C. After the monomer emulsion addition was complete, the monomer emulsion vessel was rinsed with DI water (40 g), and the co-feed solutions feed rates were decreased to 0.25 g/min. Feed was continued for an additional 45 min until completion. A solution of *t*-BHP (0.48 g) and H_2O_2 (8.25 g) in water (42 g) and a solution of IAA (5.12 g) and NaOH (2.3 g, 50% aq.) in water (42 g) were fed separately to the flask at 0.85 g/min to reduce the residual monomer. After completion of addition of all feeds, the flask was cooled to room temperature. When the flask temperature reached 50 °C, a solution of NH_3 (2.9 g, 28% aq.) in

water (8 g) was added to the flask dropwise. The flask was cooled to 45 °C, whereupon a solution of ROCIMA™ BT 2S bactericide (A Trademark of The Dow Chemical Company or Its Affiliates, 1.87 g, 19.3% aq.) in water (10 g) and a solution of KORDEK™ LX5000 bactericide (A Trademark of The Dow Chemical Company or Its Affiliates, 50%, in 10 g water) was added dropwise. After the flask was cooled to room temperature, the contents were filtered to remove gel. The filtered dispersion was found to have a solids content of 51.42% and a pH of 6.

Examples 4-8 and Comparative Examples 4-6 were carried out substantially as described for Comparative Example 3 except for the inclusion of CTAs of the monomer emulsion in the amounts described in Table 3. Comparative Examples 4-6 show examples of CTAs not within the scope of the present invention.

Table 3 – The Effect of Various Types of CTAs on PVA Copolymer Latex Viscosity

Ex. #	Solids (%)	PS (nm)	CTA/Concentration	EOF (cP)	composition
4	51.8	163.4	mercaptoethansulfonate 0.13%, 13 mmol	1200	65.5 VA/33.44 BA/ 0.56 AMPS/0.5 PEM
5	51.4	163.9	mercaptopropionic acid 0.1%, 17 mmol	2480	65.5 VA/33.44 BA/ 0.56 AMPS/0.5 PEM
6	51.3	164.5	Sodium Hypophosphite 0.08%, 13 mmol	3020	65.5VA/33.44 BA/ 0.56 AMPS/0.5 PEM
7	50.8	169.1	mercaptoethanol 0.07%, 13 mmol	2440	65.5 VA/33.44 BA/ 0.56 AMPS/0.5 PEM
C3	51.4	168.1	0	4200	65.5 VA/33.44 BA/ 0.56 AMPS/0.5 PEM
C4	51.6	164	*n*-Dodecyl mercaptan 0.15% 12 mmol	3880	65.5 VA/33.44 BA/ 0.56 AMPS/ 0.5 PEM
C5	51.0	166.9	Chloroacetic acid, sodium salt 0.1% 15.4 mmol	5100	65.5VA/33.44 BA/ 0.56AMPS/0.5 PEM
C6	51.0	166.7	Bromoacetic acid 0.1%, 13 mmol	5920	65.5VA/33.44 BA/ 0.56 AMPS/0.5 PEM

The data show that PVA latex copolymers prepared using CTAs within the scope of the present invention exhibit end of feed (EOF) viscosities that are lower and, in some cases, significantly lower, than comparable copolymers that contain either no CTA (Comparative Example 3) or *n*-dodecyl mercaptan (Comparative Example 4) or chloroacetic acid, sodium salt (Comparative Example 5) or bromoacetic acid.

M_ws of selected oligomers were measured and shown in Table 4. The measured oligomer diffusion coefficients (ODC) are compared against the diffusion coefficients of polystyrene standards having an M_w ranging from 1300 to 200,000 Daltons. The M_w of the aqueous phase oligomers were obtained directly from the M_w versus diffusion coefficient log-log plot of the standards.

Table 4 - M_ws of Selected Oligomers

Ex. #	CTA, concentration	ODC	M_w
5	mercaptopropionic acid 0.1%, 17 mmol	1.2×10^{-10}	3160
6	Sodium Hypophosphite 0.08%, 13 mmol	1.0×10^{-10}	5010
C3	0	7.8×10^{-11}	6300
C4	*n*-Dodecyl mercaptan 0.15%, 12 mmol	6.4×10^{-11}	12500

The data show the oligomers arising from the CTAs of the present invention have a lower M_w than oligomers formed from polymerization reactions that include *n*-dodecyl mercaptan or no CTA.

Claims:

1. A composition comprising vinyl acetate polymer particles dispersed in an aqueous phase, wherein the aqueous phase comprises 1) a chain transfer agent; and 2) a vinyl acetate oligomer; wherein the chain transfer agent is sodium hypophosphite or X-R^1-SH, where R^1 is a C_1-C_4 alkyl group and X is sulfonate, hydroxyl, sulfate, phosphate, phosphonate, carboxylic acid or a salt thereof, or C_1-C_3-alkyl carboxylate; and wherein the vinyl acetate oligomer has a weight average molecular weight (M_w) in the range of from 1000 to 7000 Daltons.

2. The composition of Claim 1, wherein the vinyl acetate polymer is a copolymer that comprises structural units of vinyl acetate and at least one additional monomer selected from the group consisting of an acrylate, a methacrylate, a phosphorus acid monomer, an acrylamide, a sulfonate monomer, and a vinyl ester of a branched carboxylic acid monomer, wherein the concentration of the vinyl acetate oligomer is in the range of from 0.05 to 2.5 weight percent, based on the weight of the aqueous phase.

3. The composition of Claim 2, wherein the chain transfer agent is sodium hypophosphite, potassium hypophosphite, mercaptoethane sulfonate, mercaptopropionic acid or a salt thereof, or mercaptoethanol, and the concentration of the vinyl acetate oligomer is in the range of from 0.1 to 1 weight percent, based on the weight of the aqueous phase.

4. The composition of either of Claims 2 or 3, wherein the copolymer comprises from 50 to 95 weight percent structural units of vinyl acetate and from 5 to 50 percent structural units of butyl acrylate, ethyl acrylate, or ethylhexyl acrylate, or a combination thereof, based on the weight of the copolymer.

5. The composition of Claim 4, wherein the copolymer comprises from 5 to 90 weight percent structural units of vinyl acetate, from 10 to 40 weight percent structural units of butyl acrylate, from 0.2 to 3 weight percent structural units of phosphoethyl methacrylate, and from 0.1 to 3 weight percent structural units of 2-acrylamido-2-methylpropane sulfonic acid or a salt thereof, based on the weight of the copolymer.

6. The process of any of Claims 1 to 5, wherein the chain transfer agent is sodium hypophosphite or potassium hypophosphite, wherein the weight average molecular weight of the oligomer is from 2000 to 5500 Daltons.

7. The process of any of Claims 1 to 5, wherein the chain transfer agent is mercaptopropionic acid or a salt thereof, wherein the weight average molecular weight of the oligomer is from 2000 to 4000 Daltons.

8. The process of any of Claims 1 to 5, wherein the chain transfer agent is mercaptoethane sulfonate, wherein the weight average molecular weight of the oligomer is from 2000 to 5500 Daltons.

9. The process of any of Claims 1 to 5, wherein the chain transfer agent is mercaptoethanol, wherein the weight average molecular weight of the oligomer is from 2000 to 5500 Daltons.