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(54) **COMPOSITIONS POLYMERES AQUEUSES, STABLES ET A  
FAIBLE POUVOIR MOUSSANT CONTENANT DES  
POLY(ALKYLENEIMINES)**

(54) **STABLE LOW FOAM WATERBORNE POLYMER  
COMPOSITIONS CONTAINING POLY(ALKYLENEIMINES)**

(57) Cette invention se rapporte à des compositions polymères aqueuses, à faible pouvoir moussant, stabilisées par l'addition de tensioactifs vis à vis de la gélification pouvant résulter de l'addition d'une poly(alkylèneimine). De préférence, les tensioactifs utilisés sont non ioniques et possèdent un rapport hydrophile-lipophile (HLB) supérieur ou égal à 17,5 environ. Il s'est avéré que la polymérisation en présence de tensioactifs à base de phosphates permet de produire des polymères à faible pouvoir moussant. Ces compositions polymères, stables, à faible pouvoir moussant sont utilisées dans de nombreuses formulations de revêtement telles que, par exemple, les peintures, les encres, les matériaux d'étanchéité, les enductions d'envers d'articles textiles, les adhésifs et analogues. L'invention se rapporte également à des procédés de fabrication de tels polymères stables, à faible pouvoir moussant.

(57) This invention provides low foam waterborne polymer compositions stabilized against gelling due to the addition of a poly(alkyleneimine) by addition of surfactants. Preferably, the surfactants are nonionic surfactants having a hydrophilic-lipophilic balance (HLB) of at least about 17.5. Polymerization in the presence of phosphate surfactants has been found to yield low foam polymers. These stable low foam polymer compositions are useful in a variety of coating formulations such as, for example, paints, inks, sealants, textile backcoatings, adhesives and the like. Methods of making stable low foam polymer are also disclosed.



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<b>(21) International Application Number:</b> PCT/US98/18859 <b>(22) International Filing Date:</b> 4 September 1998 (04.09.98)  <b>(30) Priority Data:</b> 60/059,217           18 September 1997 (18.09.97)   US 09/022,801           13 February 1998 (13.02.98)     US  <b>(71) Applicant:</b> EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US).  <b>(72) Inventors:</b> RAYNOLDS, Peter, Webb; 878 Canton Road, Kingsport, TN 37663 (US). SCOTT, Duane, Allan; 149 Liberty Church Road, Kingsport, TN 37663 (US).  <b>(74) Agent:</b> ALLEN, Rose, M.; P.O. Box 511, Kingsport, TN 37662-5075 (US).		<b>(81) Designated States:</b> AU, BR, CA, CN, ID, JP, KR, MX, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> STABLE LOW FOAM WATERBORNE POLYMER COMPOSITIONS CONTAINING POLY(ALKYLENEIMINES)  <b>(57) Abstract</b> <p>This invention provides low foam waterborne polymer compositions stabilized against gelling due to the addition of a poly(alkyleneimine) by addition of surfactants. Preferably, the surfactants are nonionic surfactants having a hydrophilic-lipophilic balance (HLB) of at least about 17.5. Polymerization in the presence of phosphate surfactants has been found to yield low foam polymers. These stable low foam polymer compositions are useful in a variety of coating formulations such as, for example, paints, inks, sealants, textile backcoatings, adhesives and the like. Methods of making stable low foam polymer are also disclosed.</p>		

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**STABLE LOW FOAM WATERBORNE POLYMER COMPOSITIONS  
CONTAINING POLY(ALKYLENEIMINES)**

**5    FIELD OF THE INVENTION**

This invention belongs to the field of emulsion chemistry. In particular, it relates to stable low foam waterborne polymer compositions useful in a variety of coating formulations.

**10   BACKGROUND OF THE INVENTION**

In an increasing number of industries, aqueous coating compositions continue to replace traditional organic solvent-based coating compositions. Paints, inks, sealants, and adhesives, for example, previously formulated with organic solvents are now formulated as aqueous compositions. This  
15   reduces potentially harmful exposure to volatile organic compounds (VOC's) commonly found in solvent-based compositions. While the move from organic solvent-based to aqueous compositions brings health and safety benefits, the aqueous coating compositions must meet or exceed the performance standards expected from solvent-based compositions. The  
20   need to meet or exceed such performance standards places a premium on the characteristics and properties of waterborne polymer compositions used in aqueous coating compositions.

Waterborne polymer having various functional groups have been used to impart and achieve desired properties to a particular coating  
25   composition. For example, a coating composition should exhibit good film formation, print and block resistance, as well as adhesion and tensile properties. Polymers having acetoacetoxy- and enamine-functional groups represent one example of waterborne polymers which have such properties, may carry different functional groups, and are useful in aqueous  
30   coating compositions.



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U.S. Patent 5,296,530 discloses a quick-curing coating prepared from a polymer having acetoacetyl groups, in which substantially all of the acetoacetyl groups have been converted to enamine functional groups. This conversion occurs, for example, by treatment with ammonia or a  
5 primary amine. Coatings so prepared cure more quickly under sunlight or ultraviolet light than coatings which contain the acetoacetyl functional polymer but which have not been converted to an enamine form.

U.S. Patents 5,484,975 and 5,525,662 describe the preparation of polymers containing functional acetoacetate groups and then, following the  
10 polymerization, reacting the acetoacetate group with a functional amine to form an enamine. The resulting polymers are reported to have a variety of uses including coatings, sealants, adhesives, and saturant applications.

U.S. Patent 5,498,659 discloses polymeric formulations comprising an aqueous carrier, at least one polymeric ingredient, a non-polymeric  
15 polyfunctional amine, and a base. The polymeric ingredient has both acid-functional and acetoacetoxy-type functional moieties. The aqueous polymeric formulations produce crosslinked polymeric surface coatings on a substrate.

Japanese Patent 61-21171 describes a fast-curing adhesive of two  
20 separate liquids. The first liquid is an aqueous solution and/or aqueous emulsion of a polymer compound containing an acetoacetyl group. The second liquid consists of polyethylenimine.

Even with current waterborne polymer formulations, a need remains for improved aqueous coating compositions and waterborne polymers for  
25 use in those compositions. In particular, a need exists for waterborne polymer compositions which may formulate as a single, stable composition but which undergo crosslinking upon film formation imparting one or more desired properties to the resulting coating. The present invention meets such needs.

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**SUMMARY OF THE INVENTION**

This invention provides stable low foam waterborne polymer compositions which are stabilized against gelling, upon addition of a poly(alkylenimine), preferably by post addition of a surfactant. Preferred  
5 surfactants for post addition are nonionic surfactants having a hydrophilic-lipophilic balance (HLB) of at least about 17.5. Polymerization in the presence of phosphate surfactants has been found to yield low foam polymers. These stable low foam polymer compositions are useful in a variety of coating formulations such as, for example, paints, inks, sealants,  
10 and adhesives. When used in coating formulations, the stable low foam polymer compositions of the invention provide adhesion and crosslinking in the final film or coating. The film or coating may be cured at ambient temperatures or may be thermally cured. Methods of preparing stable low foam polymer compositions are also disclosed.

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**DETAILED DESCRIPTION OF THE INVENTION**

The present invention provides stable low foam polymer compositions, that is compositions containing a polymer and water. Waterborne polymer compositions include, but are not limited to, latexes,  
20 dispersions, microemulsions, or suspensions. Waterborne polymer compositions of the present invention are stable and may be stored at room temperature or moderately above room temperature (e.g., about 50 to 60°C) and provide adhesion and crosslinking upon film formation when applied to a substrate. Yet, a film or coating formed with polymers of the  
25 invention may be cured at room temperature (ambient cure) or at elevated temperatures (thermal cure).

The polymers used to prepare the waterborne polymer composition of the present invention are generally prepared as particles. The particles may be structured or unstructured. Structured particles include, but are not



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limited to, core/shell particles and gradient particles. The average polymer particle size may range from about 25 to about 600 nm.

The polymer particles generally have a spherical shape. In one embodiment, the generally spherical polymeric particle may have a core  
5 portion and a shell portion. The core/shell polymer particles may also be prepared in a multilobe form, a peanut shell, an acorn form, or a raspberry form. It is further preferred in such particles that the core portion comprises about 20 to about 80 of the total weight of said particle and the shell portion comprises about 80 to about 20 of the total weight volume of the particle.

10 Although the following description will be directed to a discussion of specific types of polymers, it may be seen from the examples that other waterborne latex polymers that are susceptible to gelling upon addition of a poly(alkylenimine) are within the scope of the present invention.

Enamine-functional polymers represent a preferred embodiment of  
15 polymers used to form the stable low foam polymer compositions of the present invention. Enamine-functional polymers may be prepared by reacting a polymer having acetoacetoxy groups with ammonia or a primary or secondary amine. The primary or secondary amine may be a monoamine compound or a polyamine compound. Preferred amines  
20 include, for example, triaminononane,  $\text{H}_2\text{N}(\text{CH}_2)_3\text{CH}(\text{CH}_2\text{NH}_2)(\text{CH}_2)_4\text{NH}_2$  (CAS Registry No. 1572-55-0), available from Monsanto; 2-amino-2-methyl-1-propanol available as AMP-95 product from Angus Chemical Company, Buffalo Grove, IL; or, as described below, polyethylenimine, (PEI). In water-based latexes, the enamine functionality serves to further  
25 stabilize the acetoacetoxy-groups and protect them from hydrolysis.

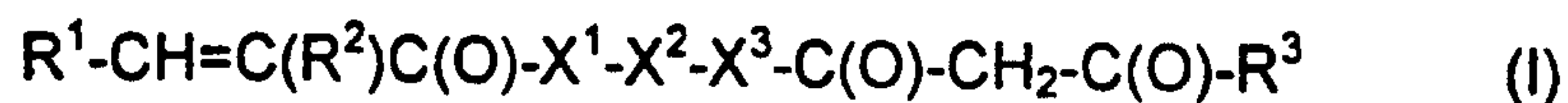
Enamine-functional polymers have been described in Moszner et al., Polymer Bulletin 32, 419-426 (1994); European patent Application No. 0 492 847 A2; U.S. Patent No. 5,296,530; and U.S. Patent No. 5,484,849. These documents are incorporated herein by reference.

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Acetoacetoxy-type functional polymers useable in the present invention may be prepared by free radical emulsion polymerization of vinyl monomers having an acetoacetoxy functionality such as those of Formula (I) below with other vinyl monomers. This combination of monomers provides water-based dispersion of polymer particles where the polymer has pendant acetoacetoxy groups. As used here, a "vinyl" monomer is an ethylenically unsaturated monomer. A pendant acetoacetoxy group is not strictly limited to those at the termini of the polymer. Pendant acetoacetoxy groups also include groups attached to the polymer's backbone and available for further reaction.

Acetoacetoxy-type functional polymers preferably contain about 0.5 to about 30 weight percent of vinyl monomers having acetoacetoxy-type functionality such as those of Formula I, and about 99.5 to about 70 weight percent of other vinyl monomers, preferably alkyl (meth)acrylates having 1 to 18 carbons. The weight percentage is based on the total amount of monomers in the composition. More preferably, the stabilized polymer has about 1 to about 15 weight percent acetoacetoxy monomers, and about 99 to about 85 weight percent of other vinyl monomers.

Aspects of this emulsion polymerization and preferred embodiments are discussed below beginning with vinyl monomers as in Formula (I) which have an acetoacetoxy-type functionality.



For an acetoacetoxy-type monomer of Formula (1),  $R^1$  is a hydrogen or halogen.  $R^2$  is a hydrogen, halogen,  $C_1$ - $C_6$  alkylthio group, or  $C_1$ - $C_6$  alkyl group.  $R^3$  is a  $C_1$ - $C_6$  alkyl group.  $X^1$  and  $X^3$  are independently O, S, or a group of the formula  $-N(R')$ , where  $R'$  is a  $C_1$ - $C_6$  alkyl group.  $X^2$  is a  $C_2$ - $C_{12}$  alkylene group or  $C_3$ - $C_{12}$  cycloalkylene group. The alkyl and alkylene groups described here and throughout the specification may be straight or



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branched groups. Preferred monomers of Formula (I) are acetoacetoxy-ethyl methacrylate, acetoacetoxyethyl acrylate, acetoacetoxy (methyl)ethyl acrylate, acetoacetoxypropyl acrylate, allyl acetoacetate, acetoacetamido-ethyl (meth)acrylate, and acetoacetoxybutyl acrylate. Acetoacetoxyethyl methacrylate (AAEM) represents a particularly preferred monomer of Formula (I).

Suitable other vinyl monomers which may be reacted with the vinyl monomers having acetoacetoxy-type functionality include, but are not limited to, methyl acrylate; methyl methacrylate; ethyl acrylate; ethyl methacrylate; butyl acrylate; butyl methacrylate; isobutyl acrylate; isobutyl methacrylate; ethylhexyl acrylate; ethylhexyl methacrylate; octyl acrylate; octyl methacrylate; styrene; -methyl styrene; glycidyl methacrylate; carbodiimide methacrylate; C<sub>1</sub>-C<sub>18</sub> alkyl crotonates; di-n-butyl maleate; dioctylmaleate; allyl methacrylate; di-allyl maleate; di-allylmalonate; methoxybutenyl methacrylate; isobornyl methacrylate; hydroxybutenyl methacrylate; hydroxyethyl (meth)acrylate; hydroxypropyl (meth)acrylate; acrylonitrile, vinyl chloride; ethylene; methacrylamide; acrylamide; butyl acrylamide; ethyl acrylamide; vinyl (meth)acrylate; isopropenyl (meth)acrylate; cycloaliphatic epoxy (meth)acrylates; and ethylformamide. Such monomers are described in "The Brandon Worldwide Monomer Reference Guide and Sourcebook" Second Edition, 1992, Brandon Associates, Merrimack, New Hampshire; and in "Polymers and Monomers", the 1996-1997 Catalog from Polyscience, Inc., Warrington, Pennsylvania.

Vinyl esters of the general Formula (II) represent further examples of useful other vinyl monomers:



In Formula (II), R is independently hydrogen or an alkyl group of up to 12 carbon atoms. Particular monomers of Formula (II) include



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CH<sub>2</sub>=CH-O-C(O)-CH<sub>3</sub>, CH<sub>2</sub>=CH-O-C(O)-C(CH<sub>3</sub>)<sub>3</sub>,  
CH<sub>2</sub>=CH-O-C(O)-CH(C<sub>2</sub>H<sub>5</sub>)(C<sub>4</sub>H<sub>9</sub>), and CH<sub>2</sub>=CH-O-C(O)-CH<sub>2</sub>CH<sub>3</sub>. Vinyl  
ester monomers also include vinyl esters of vinyl alcohol such as the  
VEOVA series available from Shell Chemical Company as VEOVA 5,  
5 VEOVA 9, VEOVA 10, and VEOVA 11 products. See O.W. Smith, M.J.  
Collins, P.S. Martin, and D.R. Bassett, Prog. Org. Coatings 22, 19 (1993).

Optional monomers that may be incorporated into the polymer  
include styrene, butyl styrene, vinyl toluene,  $\alpha$ -methyl styrene,  
(meth)acrylamide, (meth)acrylonitrile, vinyl acetate, and vinyl esters of acids  
10 other than acetic acid, itaconic anhydride, maleic anhydride, vinyl formate,  
and salts of 2-sulfoethyl (meth)acrylate.

In one embodiment, the acetoacetoxy functional polymer may also  
incorporate nitrogen-containing, vinyl monomers known to promote wet  
adhesion. Exemplary wet adhesion monomers include, for example,  
15 t-butylaminoethyl methacrylate; dimethylaminoethyl methacrylate; diethyl-  
aminoethyl methacrylate; N,N-dimethylaminopropyl methacrylamide;  
2-t-butylaminoethyl methacrylate; N,N-dimethylaminoethyl acrylate;  
N-(2-methacrylamido-ethyl)ethylene urea; and N-(2-methacryloyloxy-  
ethyl)ethylene urea. N-(2-methacryloyloxyethyl)ethylene urea is available  
20 from RohmTech as 50% solution in water under the Rohamere 6852-O  
trade name and as a 25% solution in water under the Rohamere 6844 trade  
name. N-(2-methacrylamido-ethyl)ethylene urea is available from Rhone-  
Poulenc under the WAM trade name.

Small amounts of acid vinyl monomers may also be used to prepare  
25 acetoacetoxy emulsion polymers according to the invention. Such acid  
vinyl monomers include, for example, acrylic acid, methacrylic acid, crotonic  
acid, itaconic acid, maleic acid, fumaric acid, and 2-acrylamido-2-methyl-1-  
propanesulfonic acid (sodium, potassium, or ammonium salts).  
Incorporating acid vinyl monomers into the stabilized polymer may increase

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the viscosity of the resulting latex and may have a detrimental effect on the formation of an enamine-functional polymer according to the invention.

Generally these monomers are used in small amounts. Preferably, the amount of acid vinyl monomers may range, for example, from 0 to 5 phr.

- 5 Larger amounts of acid vinyl monomers may be used to achieve a desired effect, such as increased viscosity.

The acetoacetoxy polymer may be prepared using emulsion polymerization techniques known in the art. The acetoacetoxy polymer may, as is known in the art, be prepared using free radical emulsion  
10 polymerization techniques which yield structured or unstructured particles. As mentioned above, structured particles include, for example, core/shell particles, raspberry particles, and gradient particles. Chain transfer agents, initiators, reducing agents, catalysts, and surfactants known in the art of emulsion polymerization, may be used to prepare the polymers.

- 15 Chain transfer agents may optionally be added, in an amount up to about 2 weight percent based on total monomer content, to control the molecular weight of the polymer. Use of chain transfer agents may be preferred when it is desired to obtain low molecular weight polymers. Exemplary chain transfer agents are butyl mercaptan, mercaptopropionic  
20 acid, 2-ethylhexyl mercaptopropionate, dodecylmercaptan, n-butyl mercaptopropionate, octyl mercaptan, isodecyl mercaptan, octadecyl mercaptan, mercaptoacetic acid, allyl mercaptopropionate, allyl mercaptoacetate, crotyl mercaptopropionate, crotyl mercaptoacetate, and the reactive chain transfer agents taught in U.S. Patent No. 5,247,040,  
25 incorporated here by reference. In particular, 2-ethylhexyl mercaptopropionate and dodecylmercaptan represents preferred chain transfer agents.



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Typical initiators include hydrogen peroxide, sodium, potassium or ammonium peroxydisulfate, dibenzoyl peroxide, lauryl peroxide, ditertiary butyl peroxide, 2,2'-azobisisobutyronitrile, t-butyl hydroperoxide, benzoyl peroxide, and the like.

5        Suitable reducing agents are those which increase the rate of polymerization and include for example, sodium bisulfite, sodium hydrosulfite, sodium formaldehyde sulfoxylate, ascorbic acid, isoascorbic acid, and mixtures thereof.

10       Polymerization catalysts are those compounds which increase the rate of polymerization and which, in combination with the above described reducing agents, may promote decomposition of the polymerization initiator under the reaction conditions. Suitable catalysts include transition metal compounds such as, for example, ferrous sulfate heptahydrate, ferrous chloride, cupric sulfate, cupric chloride, cobalt acetate, cobaltous sulfate, 15       and mixtures thereof. Peroxide-iron and peroxide-sulfite redox catalysts may also be used.

20       Crosslinking agents may optionally be added, in an amount up to about 2 weight percent, based on total monomer content, to control the molecular weight of the polymer. Use of crosslinking agents may be preferred when it is desired to obtain high molecular weight polymers. Useful crosslinkers include trimethylolpropane tri(meth)acrylate, 1,6-hexanediol di(meth)acrylate, allyl methacrylate and the like.

25       Any conventional polymerization surfactant may be used to form the polymer of the present invention. Useful surfactants include, but are not limited to, ionic and nonionic surfactants such as alkyl polyglycol ethers; alkyl phenol polyglycol ethers; alkali metal ammonium salts of alkyl, aryl or alkylaryl sulfonates, sulfates, phosphates, and the like, and reactive anionic or nonionic surfactants possessing styrene or allyl groups. Sulfonate containing surfactants such as sodium dodecyl benzene sulfonate, sodium 30       dodecyl sulfate, or the diesters of sodiosulfosuccinic acid such as sodium

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dioctylsulfo-succinate, and alpha olefin sulfonates are suitable. When persulfate catalysts are used, in-situ-generated oligomers with sulfate end groups may act as surfactants.

Although the above list of useful polymerization surfactants may  
5 include some of the same surfactants listed below for post-addition, incorporation of these particular surfactants into the polymerization process is a less preferred method of stabilizing the polymer against gelling upon addition of poly(alkylenimine) and pH adjustment of the polymer. Although they may be used in the emulsion polymerization process, they may  
10 contribute to processing problems such as increased particle size and increased amounts of coagulum in the polymer.

Organic phosphate esters and diesters represent a preferred class of surfactants for emulsion polymerization of the monomers used to prepare the stable low foam waterborne compositions of the present invention.  
15 These type surfactants have been found to provide polymers having low foam properties when compared to those prepared using conventional anionic surfactants bearing sulfonate or sulfate groups. Preferred are organic phosphate esters and organic phosphate diesters of aliphatic or aromatic alcohols and ethoxylated derivatives of those alcohols. Suitable  
20 phosphate surfactants include, but are not limited to, Triton QS-44 surfactant, available from Union Carbide Corporation; Naxonac 600 and 610 surfactants, available from Ruetgers-Nease Corporation; Maphos 30, 60A, 6600, and 8135 surfactants, available from PPG Industries; Rhodafac L6-36A, PE-9, PE-510, PL-620, RA-600, and RE-610 surfactants, available  
25 from Rhone Poulenc Company; and DeSophos 6 DNP, 5 BMP, 5 AP, and 9 NP surfactants, available from Witco Corporation.

The type and amount of surfactant used in the polymerization process depends on the specific composition, reaction conditions, and the desired final particle size, as is known in the art.



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Water-dispersible and water-soluble polymers may also be employed as surfactants/stabilizers in the water-based latexes of the invention. Examples of such polymeric stabilizers include water-dispersible polyesters as described in U.S. Patent Nos. 4,946,932 and 4,939,233; water-  
5 dispersible polyurethanes as described in U.S. Patent Nos. 4,927,876 and 5,137,961; alkali-soluble acrylic resins as described in U.S. Patent No. 4,839,413; and hydroxyethyl cellulose, as described in U.S. Patent 3,876,596 and British Patent 1,155,275.

10 The acetoacetoxy functionality in the polymer may be present as free acetoacetoxy groups or as derivatives of those groups such as, for example, an enamine group or acetoacetamide group. The acetoacetoxy-functional polymer may contain both free acetoacetoxy groups and acetoacetoxy derivatives.

As discussed above, enamine-functional polymers may be prepared  
15 by addition of a primary or secondary amine to the acetoacetoxy polymer. Preferred amines are poly(alkyleneimines). Poly(alkylenimines) for use in the invention may have a weight average molecular weight of about 800 to about 750,000. The poly(alkylenimine) is preferably a poly(ethylenimine) (PEI) and more preferably PEI having a weight average molecular weight of  
20 about 800 to about 25,000. The PEI may contain primary, secondary, and tertiary amine groups, for example, in a ratio of 1.5:1.4:1.0, respectively. Such PEI compounds are commercially available from BASF Corporation as LUPASOL™ G-35 poly(ethylenimine). Depending on the requirements of the end-use of the formulation, the content of polyethylenimine can vary  
25 from 0.5 to 25 weight percent based on the dry weight of the acetoacetoxy polymer. More preferably, the content of polyethylenimine can vary from 2 to 12 weight percent based on the dry weight of the acetoacetoxy polymer.

However, poly(alkyleneimines), particularly poly(ethylenimine), are known to flocculate latexes, and are actually sold for that purpose. The pH  
30 of the prepared latex is normally greater than 11, much too high for many

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commercial applications. After addition of a poly(alkylenimine), upon adjustment of the pH of the latex to a pH of less than about 10, the latex normally gels.

It has been unexpectedly found that the thus formed enamine  
5 polymers may be stabilized against gelling due to the addition of poly(alkylenimine), by post-addition of a surfactant. Preferably the surfactant is a nonionic surfactant having a hydrophilic-lipophilic (HLB) value of at least about 17.5. The surfactant may be added either prior to, with or after addition of the poly(alkylenimine), but before pH adjustment.  
10 The choice of surfactant for addition to the emulsion polymer does not depend on the chemical structure of the surfactant, but only on the surfactant having an HLB value of at least about 17.5. In contrast to polymers that flocculate upon addition of a poly(alkylenimine), the addition of a poly (alkyleneimine), particularly poly(ethylenimine), to polymers to  
15 which surfactants having an HLB of at least about 17.5 has been added, does not cause flocculation, but provides a stable, waterborne polymer composition.

Suitable nonionic surfactants meeting the HLB criteria include certain types of surfactants such as alkyl polyglycol ethers including the  
20 ethoxylation products of lauryl, oleyl, and stearyl alcohols; alkyl phenol polyglycol ethers including the ethoxylation products of octyl- or nonyl-phenol, diisopropyl phenol, and triisopropyl phenol; and EO-PO-EO block copolymers. Preferred nonionic surfactants are TERGITOL 15-S-40 and TERGITOL NP-40 surfactants available from Union Carbide, IGEPAL CO  
25 990 and IGEPAL DN-970 surfactants available from Rhone-Poulenc Inc. Pluronic F-77, Pluronic F-87, Pluronic F-127, Pluronic F-68 and Pluronic F-108 surfactants available from BASF Corporation.

The addition of poly(ethylenimine) may be accomplished by adding, with stirring, poly(ethylenimine) to an emulsion of the acetoacetoxy polymer  
30 to which has also been added, a nonionic surfactant having an HLB value



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of at least about 17.5. Sufficient surfactant should be added to stabilize the enamine polymer. Typically, the surfactant may be added in an amount of from about 0.5 phr to about 5 phr based on dry polymer weight. Optionally, the surfactant may be added, with stirring, after addition of the  
5 poly(ethyleneimine) but prior to adjustment of the pH of the polymer. Other surfactants and property modifying ingredients may also be added that do not impact on the stability of the waterborne composition.

The pH of the stable low foam enamine polymer of the invention may then be adjusted by the addition of an acid or buffer. For example, buffers  
10 such as sodium bicarbonate, ammonium bicarbonate, ammonium dihydrogenphosphate, an ammonium polyacrylate, or a mixture of such buffers may be used. The buffer, such as ammonium bicarbonate, may generally be added to the stable, waterborne enamine polymer to adjust and/or buffer the pH of the composition to less than about 10. Waterborne  
15 enamine polymer compositions having pH values in the range of about 7.0 to 9.8, preferably 8.4 to 9.2, may be achieved using ammonium buffers. Buffered compositions of the invention are particularly useful in coating formulations.

The stable enamine polymers of the present invention will vary in  
20 properties, depending on the end-use application. In general, the polymer composition may have a second cycle glass transition temperature ( $T_g$ ) of -50 to +100°C; more preferably, -35 to +50°C.

The weight average molecular weight of the stable enamine polymers may vary from about 20,000 to 5,000,000 daltons; more  
25 preferably from 100,000 to 2,000,000 and most preferably from 200,000 to 1,000,000. The molecular weight range may be controlled by reaction conditions, as is known in the art, or by the use of a chain transfer agent or crosslinkers, as discussed above.

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A waterborne polymer composition of the invention may also contain other additives known in those compositions and may use other emulsion polymerization methodology. U.S. Patent No. 5,371,148 provides a good description of possible additives and is incorporated here by reference.

5 In a waterborne composition of the invention, the stable acetoacetoxy-functional, or enamine-functional polymers, may be present from about 5 to about 60 weight percent based on dry resin and more preferably from about 25 to about 55 weight percent. The examples below illustrate the preparation of polymers and water-based compositions  
10 according to the invention.

Latexes or other water-based compositions containing small particle size polymers, those ranging from about 25 to about 100 nm and more preferably from about 45 to about 85 nm, represent one preferred embodiment of the invention.

15 The stable polymers and waterborne polymer compositions of the invention are useful in a variety of coating formulations such as architectural coatings, metal coatings, wood coatings, plastic coatings, textile coatings, cementitious coatings, paper coatings, inks, and adhesive. Examples of such coating formulations adapted for particular uses include, but are not  
20 limited to, corrosion inhibitors, concrete coatings, maintenance coatings, latex paints, industrial coatings, automotive coatings, textile backcoatings, surface printing inks and laminating inks. Accordingly, the present invention relates to such coating formulations containing a waterborne polymer composition of the invention, preferably a water-based latex. The polymers  
25 and waterborne polymer compositions of the invention may be incorporated in those coating formulations in the same manner as known polymer latexes and used with the conventional components and or additives of such compositions. The coating formulations may be clear or pigmented.



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With their crosslinking ability, adhesion properties, and resistance properties, the water-based latexes of the invention impart new and/or improved properties to the various coating formulations.

Upon formulation, a coating formulation containing a stable polymer  
5 or waterborne polymer composition of the invention may then be applied to a variety of surfaces, substrates, or articles, e.g., paper, plastic, steel, aluminum, wood, gypsum board, concrete, brick, masonry, or galvanized sheeting (either primed or unprimed). The type of surface, substrate, or article to be coated generally determines the type of coating formulation  
10 used. The coating formulation may be applied using means known in the art. For example, a coating formulation may be applied by spraying or by coating a substrate. In general, the coating may be dried by heating but preferably is allowed to air dry. Advantageously, a coating employing a polymer of the invention may be thermally or ambiently cured. As a further  
15 aspect, the present invention relates to a shaped or formed article which has been coated with a coating formulations of the present invention.

A waterborne polymer composition according to the invention may comprise the stabilized polymer of the invention and water, along with a solvent, a pigment (organic or inorganic) and/or other additives and fillers  
20 known in the art, and enumerated below. When a solvent is used, water-miscible solvents are preferred. A latex paint composition of the invention may comprise a waterborne polymer composition of the invention, a pigment and one or more additives or fillers used in latex paints.

Additives or fillers used in formulating coatings include, but are not  
25 limited to, leveling, rheology, and flow control agents such as silicones, fluorocarbons, urethanes, or cellulosics; extenders; curing agents such as multifunctional isocyanates, multifunctional carbonates, multifunctional epoxides, or multifunctional acrylates; reactive coalescing aids such as those described in U.S. Patent No. 5,349,026; flatting agents; pigment  
30 wetting and dispersing agents and surfactants; ultraviolet (UV) absorbers;

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UV light stabilizers; tinting pigments; extenders; defoaming and antifoaming agents; anti-settling, anti-sag and bodying agents; anti-skinning agents; anti-flooding and anti-floating agents; fungicides and mildewcides; corrosion inhibitors; thickening agents; plasticizers; reactive plasticizers; drying  
5 agents; catalysts; crosslinking agents; or coalescing agents. Specific examples of such additives can be found in Raw Materials Index, published by the National Paint & Coatings Association, 1500 Rhode Island Avenue, NW, Washington, D.C. 20005.

A polymer or waterborne polymer composition of the present  
10 invention can be utilized alone or in conjunction with other conventional waterborne polymers. Such polymers include, but are not limited to, water dispersible polymers such as consisting of polyesters, polyester-amides, cellulose esters, alkyds, polyurethanes, epoxy resins, polyamides, acrylics, vinyl polymers, polymers having pendant allyl groups such as described in  
15 U.S. Patent No. 5,539,073, styrene-butadiene polymers, vinylacetate-ethylene copolymers, and the like.

The following examples are intended to illustrate, not limit, the invention:

20 EXAMPLES

Example 1:

Latex Synthesis:

The reactor configuration was a 4 liter jacketed kettle held at 80°C with circulating water. Deionized water was used and the atmosphere  
25 above the reaction was inerted with nitrogen. The reactor was charged with 1000 g water, 3 g of sodium bicarbonate and 54.5 g (1.5 phm) of Rhodacal A246L surfactant (a C<sub>12,14</sub> alpha olefin sodium sulfonate surfactant available from Rhone-Poulenc as a 38.5% solution in water), and heated to 80°C. An emulsion was made with 700 g of water, 10.9 g (0.3 phm) of  
30 Rhodacal A246L surfactant, 672 g of styrene, 476 g of butyl acrylate,



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70 g of 2-hydroxyethyl methacrylate (HEMA), 140 g of acetoacetoxyethyl methacrylate (AAEM) and 84 g of sodium 2-acrylamido-2-methylpropane sulfonate (AMPS 2405 monomer, available from Lubrizol Corporation as a 50% solution in water). To the reactor was added 110 g of the above  
5 emulsion, followed by a solution of 2.7 g of sodium persulfate in 20 g of water. After 5 minutes, the remainder of the emulsion was fed to the reactor over a 2 hour period. At the same time a solution of 1.5 g of sodium persulfate in 50 g of water was added to the reactor over a 1 hour period. The reaction mixture was held at 80°C for 30 minutes after addition was  
10 complete, and the reactor was then cooled. As the reactor was cooled, a solution of 1.5 g of t-butylhydroperoxide in 30 g of water was added rapidly through the emulsion feed, and a solution of 1.5 g of sodium metabisulfite, 1.0 g of 50% sodium hydroxide solution and 80 g of water was added over 30 minutes. The pH of the latex was 6.90, particle size was 77 nm, and  
15 second cycle glass transition temperature (T<sub>g</sub>) of +38°C.

#### Addition of Polyethylenimine:

A mixture of 336 g of LUPASOL™ G-35 polyethylenimine (50% solids, a product of BASF), 60 g of Tergitol 15-S-40 surfactant (70% active,  
20 C<sub>11</sub> - C<sub>15</sub> secondary alcohol ethoxylate with an HLB of 18.0, a product of Union Carbide), and 84 g of water was added to the reactor over 30 minutes with a sub-surface feed. The pH of the latex was 11.2 and the particle size was 81 nm.

#### 25 pH Adjustment

After 15 minutes a solution of 5% ammonium carbonate and 15% ammonium bicarbonate in water was added (550 g) to achieve a pH of 9.84. The entire batch filtered rapidly through a 40 mm, 100 mesh stainless

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steel screen. The pH of the latex was 9.84, the particle size was 80 nm, and percent solids was 37.25%. This latex showed no significant thickening after 2 weeks at 60°C.

5    Example 2 - Comparative Example:

100 g of a latex similar to the one described in Example 1 was treated with the same proportion of PEI, but without post-addition of Tergitol 15-S-40, adjustment of the pH of the latex to 9.8 caused the mixture to gel within ten minutes.

10

Example 3:- Latex Polymer without Acetoacetoxy/Enamine Functionality

Latex Synthesis:

The reactor configuration was a 4 liter jacketed kettle held at 80°C with circulating water. Deionized water was used and the atmosphere above the reaction was inerted with nitrogen. The reactor was charged with 800 g water, 60 g of Maphos 60A surfactant (an aliphatic phosphate ester surfactant product of PPG Ind., 30% solution in water, neutralized to pH 8.6 with 50% sodium hydroxide) and 3.5 g of acrylic acid. The contents of the reactor were adjusted to pH 8 with a 50% sodium hydroxide solution. An emulsion was made from 700 g water, 23.3 g of 30% Maphos 60A surfactant, 714 g styrene, 602 g butyl acrylate, 70 g of 2-hydroxyethyl methacrylate and 14 g of methacrylic acid. To the reactor was added a solution of 2 g of sodium persulfate in 20 g of water. After five minutes, the monomer emulsion was feed to the reactor over a two hour period. After 30 minutes, a solution of 1.5 g of sodium persulfate in 50 g water was added over 1 hour. One hour after the emulsion feed was started, 4.2 g of 2-ethylhexylmercapto propionate, a chain transfer agent, was added to the monomer emulsion. The reactor was held at 80°C for 30 minutes after the addition was complete. As the reactor was cooled, a solution of 1.5 g of t-butylhydroperoxide in 30 g of water was added rapidly, and a solution of 1.5



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g of sodium metabisulfite, 4.0 g of 50% sodium hydroxide solution and 50 g of water was added over 30 minutes. The pH of the latex was 6.5, the latex was 45.6 % solids, particle size was 90 nm, and Tg +31°C.

5 Addition of Polyethylenimine:

To 100 g of the latex was added 5.87 g of a 23.3 % solution of Tergitol 15-S-40 surfactant (70% active, HLB of 18.0), followed by 11.3 g of LUPASOL™ G-35 polyethylenimine (50% solids, a product of BASF). The mixture filtered readily through a 100 mesh stainless steel screen. The mixture did not gel and did not increase markedly in viscosity after one week at 60°C.

pH:

The pH of the latex was not adjusted.

15

Example 4 - Comparative Example:

100 g of the latex of Example 7 was treated with the same proportion of PEI, but without post-addition of Tergitol 15-S-40 surfactant. The pH of the latex was not adjusted. The addition of PEI, without post addition of a nonionic surfactant having an HLB of greater than about 17.5, caused the mixture to gel immediately.

20

Example 5 - Low Foam Laminating Ink Latex

Latex Synthesis:

25 The reaction configuration was the same as in Example 1. The reactor was charged with 800 g water and 21 g of Maphos 60A (an aliphatic phosphate ester surfactant product of PPG, Ind., neutralized to pH 7.8 with 50% sodium hydroxide solution). An emulsion was made from 700 g of water, 4.2 g of Maphos 60A surfactant (neutralized to pH 7 with 50%

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sodium hydroxide), 658 g styrene, 490 g butyl acrylate, 70 g hydroxyethyl methacrylate, 140 g of aceto-acetoxyethyl methacrylate and 84 g sodium 2-acrylamido-2-methylpropane sulfonate (AMPS 2405 monomer, a 50% solution in water, available from Lubrizol). To the reactor was added 110 g of the emulsion, followed by a solution of 2.7 g of sodium persulfate in 20 g of water. After 5 minutes, the emulsion was fed to the reactor over a 2 hour period. At the same time a solution of 1.5 g of sodium persulfate in 50 g of water was added over a 1 hour period. The reaction mixture was held at 80°C for 30 minutes after addition was complete, and the reactor cooled. As the reactor was cooled, a solution of 1.5 g of t-butylhydroperoxide in 30 g of water was added rapidly through the emulsion feed, and a solution of 1.5 g of sodium metabisulfite, 1.0 g of 50% sodium hydroxide solution and 80 g of water was added over 30 minutes. The entire batch filtered readily through a 40 mm diameter 100 mesh screen and the amount retained on the mesh was 9 ppm, dry basis. The latex had a pH of 6.8, 45.3% solids, second cycle glass transition temperature of 25.1°C and particle diameter in 0.01 M NaCl was 85 nm.

Addition of Polyethylenimine and pH Adjustment:

The pH of a mixture of 700 g of the latex described above, 27.2 g of a 23.3% solution of Tergitol 15-S-40 surfactant, and 3.2 g of Pluronic L-121 surfactant (an EO-PO-EO block copolymer containing 10% ethylene oxide, available from Union Carbide Corporation) was adjusted to pH 9.6 with a 7% solution of ammonium hydroxide in water. To this mixture was added over 30 seconds 95 g of a 40% solution of LUPASOL™ G-35 polyethylenimine (a 50% solids product of BASF) in water. After one hour, the particle size was 88 nm, as determined in a 0.1% sodium carbonate and 0.5% Tergitol 15-S-7 surfactant solution. The pH was 11.2. The pH of the mixture was then adjusted to 9.8 with 86 g of a solution of 5% ammonium carbonate and 15% ammonium bicarbonate in water. The particle size



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was 87 nm. The mixture contained 2 parts per hundred Tergitol 15-S-40 surfactant and 12 parts PEI per 100 parts latex polymer on a dry weight basis. The particle size was monitored with time at three temperatures as a method of quantitating stability. The results are shown below in Table I.

5

Table I. Change in Particle Size with Time

Temperature	Start	1 day	3 days	7 days	14 days
22°	87	94	93	93	94
50°	--	91	92	91	97
60°	--	93	96	96	103

Example 6: - Foaming of the Latex:

10        200 ml of the latex of Example 5 containing PEI, with pH adjusted to 9.8, was stirred at high speed for one minute in a graduated Waring Blender container. The top of the foam was marked initially at the 380 ml level and fell to 340 ml over 30 minutes. In contrast, the PEI-containing latex of

15        Example 1 (also pH 9.8), which used a sodium sulfonate surfactant instead of a phosphate ester surfactant in the emulsion polymerization, had an initial foam level of 480 ml, and this fell to 400 ml over 30 minutes. The latex containing a phosphate ester surfactant in the polymer generated less foam than a latex containing a sodium sulfonate surfactant.

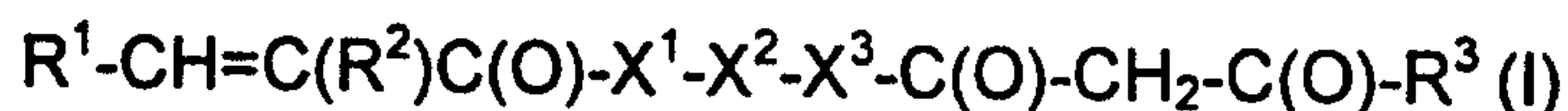
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**CLAIMS**

What is claimed is:

1. A stable low foam waterborne polymer composition comprising a polymer; a poly(alkylenimine); and a surfactant; wherein said polymer is polymerized in the presence of a phosphate containing surfactant.

2. The stable low foam polymer composition of claim 1 wherein said polymer comprises the reaction product of:  
about 0.5 to about 30 weight percent of vinyl monomers having acetoacetoxy-type functionality of Formula (I):



where  $R^1$  is a hydrogen or halogen;  $R^2$  is a hydrogen, halogen,  $C_1-C_6$  alkylthio group, or  $C_1-C_6$  alkyl group;  $R^3$  is a  $C_1-C_6$  alkyl group;  $X^1$  and  $X^3$  are independently O, S, or a group of the formula  $-N(R')$ , in which  $R'$  is a  $C_1-C_6$  alkyl group;  $X^2$  is a  $C_1-C_{12}$  alkylene group or  $C_3-C_{12}$  cycloalkylene group; and

about 99.5 to about 70 weight percent of other vinyl monomers.

3. The stable low foam polymer composition of claim 1 wherein said poly(alkylenimine) is present in an amount from about 0.5 to about 25 weight percent based on the dry weight of the polymer.

4. The stable low foam polymer composition of claim 1 wherein said poly(alkylenimine) is poly(ethyleneimine).



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5. The stable low foam polymer composition of claim 1 wherein said surfactant is a nonionic surfactant having a hydrophilic-lipophilic balance (HLB) of at least about 17.5.

5 6. The stable low foam waterborne polymer composition of claim 1 wherein said phosphate surfactant is selected from the group consisting of organic phosphate esters and organic phosphate diesters of aliphatic or aromatic alcohols, and ethoxylated derivatives of said alcohols.

10 7. A coating formulation, selected from an architectural coating, a metal coating, a wood coating, a plastic coating, a textile coating, a cementitious coating, a paper coating, an ink, and an adhesive, comprising the stable low foam polymer composition of claim 1 and at least one additive selected from a solvent, a pigment, a buffer, a leveling agent, a rheology agent, a curing agent, a flow control agent, an extender, a reactive  
15 coalescing aid, a flatting agent, a pigment wetting agent, a dispersing agent, a surfactant, an ultraviolet (UV) absorber, a UV light stabilizer, a defoaming agent, an antifoaming agent, an anti-settling agent, an anti-sag agent, a bodying agent, an anti-skinning agent, an anti-flooding agent, an  
20 anti-floating agent, a fungicide, a mildewcide, a corrosion inhibitor, a thickening agent, a plasticizer, a reactive plasticizer, a drying agent, a catalyst, a crosslinking agent, and a coalescing agent.

25 8. A method of making a stable low foam polymer composition comprising polymerizing a vinyl monomer having an acetoacetoxy functionality with other vinyl monomers in the presence of a phosphate containing surfactant to form a polymer; adding a poly(alkylenimine) and a surfactant; and adjusting the pH of the waterborne polymer composition.

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9. The method of claim 8 wherein said phosphate surfactant is selected from the group consisting of organic phosphate esters and organic phosphate diesters of aliphatic or aromatic alcohols, and ethoxylated derivatives of said alcohols.

5

10. The method of claim 8 wherein said surfactant is a nonionic surfactant having a hydrophilic-lipophilic balance (HLB) of at least about 17.5.