CONTROLLED CROSSLINKING OF LATEX POLYMERS WITH POLYFUNCTIONAL AMINES

Abstract: The latex polymer compositions of the present invention exhibit latent crosslinking properties. Latent crosslinking in the polymers takes advantage of the fast interaction between the anionic latex charge and the cationic charge associated with polyfunctional amine crosslinkers. Once the latex is coated onto a substrate, the volatile base evaporates and the groups react to form a crosslinked coating with improved wash-off properties.
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CONTROLLED CROSSLINKING OF LATEX POLYMERS
WITH POLYFUNCTIONAL AMINES

PRIORITY
This application is a PCT international conversion of and claims priority to US nonprovisional application 14/856,917 filed September 17, 2016 and entitled "Controlled Crosslinking of Latex Polymers With Polyfunctional Amines". The above referenced application is hereby incorporated in entirety by reference for all purposes.

BACKGROUND
This disclosure covers the field of emulsion chemistry. In particular, it relates to distinct solution based polymerized latex compositions that are initially shelf stable emulsions prior to being used as coatings and/or paints. More specifically these latex compositions are kept shelf stable in the presence of a specific amount of ammonium hydroxide to maintain high pH in order to avoid premature interaction (pre-gelling) between latex particles leading to settling, and both inter and/or intraparticle crosslinking of the latex binders. These solutions are ammonia (NH3) rich (using ammonium hydroxide) and thus highly basic; therefore, when the NH3 evaporates quickly, the pH of the solutions are reduced as they are applied to surfaces. This process serves as a trigger for controlled crosslinking of the latex (binder) as it interacts with the polyfunctional amines of the present disclosure during application and drying. The pursuit of fast drying aqueous traffic paints requires there be strong and effective interactions between the latex binder and water-soluble polyfunctional amine crosslinkers, to ensure fast hardening at proper high build (in a single coat thick application) translating into corresponding water resistance.

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 reduces potentially harmful exposure to volatile organic compounds (VOC's) commonly found in solvent-based compositions. Migration from organic solvent-based to aqueous compositions allows for health and safety benefits, however, the aqueous coating compositions must meet or exceed the performance standards expected from solvent-based compositions. The need to meet or exceed the organic solvent based performance
standards places a premium on the characteristics and properties of waterborne polymer compositions used in aqueous coating compositions.

The latex industry and specifically the latex-based traffic paint products have historically held a long established goal of developing effective "one-pack" (proper high build - in a single coat thick application) - or single step crosslinking systems. The ideal system allows for film formation prior to substantial crosslinking as the latex is applied to surfaces. The nature of this coating technology requires that it is stable when being stored and fast drying only when being applied. The structural make-up of these aqueous systems must be unreactive in the wet state, but very capable of ionic bonding (in ambient conditions) in the dry state; referred to hereinafter as latent crosslinking. The result of latent crosslinking would be a good film-forming latex with excellent hardness that is very resistant to water wash-off.

Much published art regarding various "one-pack" chemistries exists, including those based on epoxies (specifically glycidyl methacrylate), silanes, isocyanates, and carbonyls (including acetoacetoxy ethyl methacrylate, and acetoacetoxy ethyl methacrylate - AAMA). Most of these publications and/or granted patents have demonstrated the presence of crosslinking by showing improved solvent resistance.

In order to increase the potlife (or shelf stability) of compositions containing acetoacetate and amine groups it has been known to block the amine groups of the polyamine with a ketone or aldehyde to form corresponding ketimine or aldime compounds prior to mixing with an acetoacetate-functional polymer. Examples of such non-aqueous compositions are disclosed in U.S. Pat. No. 4,772,680. Even though improved stability may be achieved by specific aromatic aldimines, volatile by-products are still formed and the compositions have no application in waterborne coatings and are restricted to coatings using organic solvents as the carrier.

WO 95/09209 describes a crosslinkable coating composition comprising an aqueous film forming dispersion of addition polymer comprising acetoacetate functional groups and an essentially non-volatile polyamine having at least two primary amine groups and wherein the mole ratio of acetoacetate to primary amine groups is between 1:4 to 40:1.

EP 555,774 and WO 96/1 6998 describe the use of carboxylated acetoacetoxy ethyl methacrylate latexes mixed with multifunctional amines (such as diethylene triamine) for a
shelf-stable, one-component system. In EP 555,774, the system is stabilized by using vinyl acid polymerized with AAEM and the latex is “neutralized” with a polyamine. The patent teaches that the carboxyl groups should be 70 to 96 mol percent relative to the acetoacetoxo groups. WO 96/16998 similarly describes a polymerization process with the vinyl acid and AAEM being polymerized in the first stage.

EP 744,450 describes aqueous coating compositions containing acetoacetate functional polymers with a weight-averaged molecular weight of 100,000 or greater and which contain acetoacetate functional groups and acidic functional groups, and multifunctional amine.

EP 778,317 describes an aqueous self-crosslinkable polymeric dispersion comprising a polymeric component (a relatively hydrophobic polymer having a Hansen number > 1.5, at least 5% of a carbonyl functional group capable of reacting with a nitrogen moiety, and at least 1% of a non-acidic functional group having hydrogen-bondable moieties); and a crosslinking agent comprising a nitrogen-containing compound having at least two nitrogen functional groups capable of reacting with a carbonyl functional moiety. Again it is reported that no gelation has taken place after ten days at 60°C.

U.S. Pat. No. 5,498,659 discloses a single-package aqueous polymeric formulation consisting essentially of an evaporable aqueous carrier, at least one polymeric ingredient having acid-functional pendant moieties able to form stable enamine structures, a non-polymeric polyfunctional amine having at least two amine functional moieties, and an effective amount of base for inhibiting gelation. It is stated in the patent that at least some of the crosslinking of the composition may take place in the liquid phase, possibly within one to four hours of adding the non-polymeric polyfunctional amine. It is postulated that addition of base to the reactor contents competes with the amine-functional moieties vis-a-vis the acetoacetoxo-type functional moieties, thereby reducing the degree of crosslinking and/or enhancing the colloidal stability of the polymer dispersion which forms when the crosslinking reaction takes place.

Geurink, et al., in their publication "Analytical Aspects and Film Properties of Two-Pack Acetoacetate Functional Latexes", Progress in Organic Coatings 27 (1996) 73-78, report that crosslinking of acetoacetate functional latexes with polyamine compounds is very fast, and that this crosslinking is hardly hindered by existing enamines. It is further stated that there are very strong indications that crosslinking takes place rapidly in the wet state, in or at the
surface of the particles just after mixing of the components. They conclude that as a result of
crosslinking in the particles, the film forming process is hampered.

In the publications described above, the usable pot life of the latex formulations is
demonstrated by lack of sedimentation. It is quite possible, however, that crosslinking is
taking place within each particle, without causing the latex to coagulate or gel (e.g. loss of
colloidal stability). This type of intra-particle crosslinking (before drying) limits the ability of
the latex to form a film upon drying. This in turn reduces the film integrity and performance
of the polymer. Therefore, a need still exists for truly latent crosslinking systems—those in
which intraparticle crosslinking is inhibited until after film formation. In particular, a need
exists for one-pack, latent crosslinking systems which are useful in a wide range of latex
applications that are simple and cost efficient. These would include decorative and protective
coatings, adhesives, non-woven binders, textiles, paper coatings, traffic markings, inks, etc.
In each case, the advantage would be a soft, ductile polymer that converts to a harder, more
resistant latex film after drying.

In general, the following acronyms are used throughout the body this specification and
provide information regarding chemical compounds and structures as follows;

TGIC = Triglycidyl isocyanurate
NPDGE = Neopentyl diglycidyl ether
AGE = Allyl glycidyl ether
BDGE = Butanediol diglycidyl ether
PEGDGE = Poly(ethylene glycol) diglycidyl ether
DAMPA = N,N-dimethyl amino propyl amine.
DEAP A = N,N-diethyl amino propyl amine.
DEA = diethyl amine
DAB = 1,4-diaminobutane
MAA = methacrylic acid
tBHP = t-butyl hydroperoxide
BA = butyl acrylate
MMA = methyl methacrylate
MAA = methacrylic acid
SDS = sodium dodecyl sulfate
APS = ammonium persulfate

**BRIEF DESCRIPTION OF THE DRAWINGS:**

FIG. 1 is a flowchart providing various options for preparing polyfunctional amines of the present disclosure.

FIG. 2 provides a photographic presentation of the water wash-off results of the latex paint formulations with and without crosslinker, as tested at 30 minutes dry time.

FIGS. 3a and 3b provides FTIR spectra of a latex formulation with a polyfunctional amine crosslinker of the present disclosure in comparison with other latex formulations absent these same amine crosslinkers.

**SUMMARY**

A first aspect of the present disclosure includes polyfunctional amine crosslinkers comprising recurring units derived from the reaction of one tri-glycidyl moiety and a single di-, or tri-functional amino monomers, or combination of mono/bi, mono/tri, mono/tetra, bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra, and tetra/tetra functional amino monomers resulting in a polyfunctional amine of formula (I-x):

\[
(I-x) \quad \begin{array}{c}
\text{R1} \\
\text{J} \\
\text{R2} \\
\text{n}
\end{array}
\]

Where the substituent J is the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety;

and wherein R1 is selected from the group consisting of: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, N,N,N-
trimethyl-1,2-ethane diamine, N,N,N-triethyl-1,2-ethane diamine, N-methyl-1-N,N-di-ethyl- 1,2-ethane diamine, N-ethyl-N,N-dimethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,3-propane diamine, N-ethyl-N,N-dimethyl-1,3-propane diamine, methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylaminio ethylene amine, amino ethyl-piperazine, N-methyl-1-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamino benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine, 2,2'-oxybis ethanamine, alanine, and lysine;

and wherein R2 is selected from group consisting of methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamino benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine, 2,2'-oxybis ethanamine, alanine, and lysine;

and where R1 is equal to or different than R2;

and where n is a number from 10 to 100.

More specifically, the polyfunctional amines are selected from one of the general structures of formulae (I-x) and/or (I-x-a) to (I-x-f):

(I-x)
wherein substituents J, J1, and J2 are the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety;

and wherein J is equal to or different than J1 and J2;

and wherein J1 is equal to or different than J2;

and wherein R1 is selected from the group consisting of: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, N,N,N-trimethyl-1,2-ethane diamine, N,N,N, triethyl-1,2-ethane diamine, N-methyl-N,N-di ethyl-1,2-ethane diamine, N-ethyl-N,N-dimethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,3-propane diamine, N-ethyl-N,N-dimethyl-1,3-propane diamine, methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1 ,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamino benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine, 2,2'-oxybis ethanamine, alanine, and lysine;

and R2 and R3 are selected from group consisting of methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl
propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-
dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-
diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-
diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-
diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine,2,2’-
oxybis ethanamine, alanine, lysine;

and wherein R1 is equal to or different than R2 and R3;

and wherein R2 is equal to or different than R3;

and where n is an number 10 to 100;

and where m is an number equal to or different than n.

Any polyfunctional amine shown above can be used in latex paint formulas as crosslinkers. In addition, the polyfunctional amine crosslinker of any type formula (I-x) bearing -NH or -NH₂ groups with repeating units, n, can be further treated with glycidyl alkenyl compounds, favorably allyl glycidyl ether, and the polyfunctional amine of any formulae (I-x) and/or (I-x-
a) to (I-x-f) must carry a -NH or -NH₂ group, for further reaction with a glycidyl alkenyl compound for the introduction of an alkene group as shown below;

\[
\text{I-x-ene}
\]

\[
\begin{array}{c}
\text{CH} \quad \text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{R}^4 \\
\text{R}^1 \\
\text{R}^1' \\
\text{R}^2 \\
\text{R}^2 \\
\text{R}^2 \\
\end{array}
\]

and wherein the reaction between the polyfunctional amine selected from Formulae (I-x)
and/or (I-x-a) to (I-x-f) and allyl glycidyl ether occurs via the amino-glycidyl linkage;
and wherein the addition of the allyl reactive group to the structure of formula (I-x) occurs only once per molecule.

The polyfunctional amine crosslinkers (II-x) result from the reaction of the intermediate structure of formula (I-x-ene) with preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof. This reaction allows for polymerization and formation of the copolymers of generic formula II-x as shown:

(II-x)

wherein J is the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety;

and wherein R1, and R2 are selected from the group consisting of: methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-buty1 amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine, 2,2'-oxybis ethanamine, alanine, and lysine;
and wherein R1 is equal to or different than R2;

and wherein Rl' is the deprotonated R1 with proton loss at the NH or NH₂ site;

and wherein R4 is the connecting group between polyamine body and the alkene functionality. If AGE is employed in this preparation, the connecting group is -CH₂CH(OH)CH₂0-. Variations in R4 may be created from each different connecting glycidyl alkenyl group. Potentially, the connecting glycidyl alkenyl groups can be selected from one of the following: allyl glycidyl ether, vinyl glycidyl ether, vinyl cyclohexene oxide, glycidyl methacrylate, glycidyl acrylate, glycidyl acrylamide, and glycidyl methacrylamide.

and wherein n-1 is an number from four to nineteen;

and wherein m is an number from 1 to 100;

and wherein o is an number from 1 to 100;

and wherein p is an number from 1 to 100;

and wherein repeating substituent R5 results from polymerization of a water soluble monomer having a carbon - carbon double bond, -C=CH₂, preferably an acrylic acid or acrylic acid derivative;

and wherein repeating substituent R6 results from polymerization of a water soluble monomer having a carbon- carbon double bond, -C=CH₂, preferably an acrylamide or a derivative of acrylamide;

and where the resulting structure's atomic mass is greater than or equal to 50,000 Daltons.

As illustrated in the flowchart [100] of Figure 1, the polyfunctional amine latex crosslinker compositions are selected from at least one compound from the group consisting of Formulae (I-x) and/or (I-x-a to-I-x-f) [102], composed of a bi- or tri-glycidyl moiety [104] and amine(s) [106]. I-x for the purposes of this disclosure is shown (but is not limited a limiting example) forming structural compounds (I-x-1), (I-x-2"), and (I-x-3). These three structures are developed from a one-step synthesis creating the (I-x) products (structural compounds) [108] and do not include any -C=CH₂ bonds. If selected for use as a final product, the one-step (I-x) products can be used with no further treatment. Polyfunctional amine (I-x) products [108] containing an -NH or -NH₂ moiety [110] can be further treated to form final two-step process products [124] or be used without further treatment as a final -NH or -NH₂.
containing one-step products [116]. Polyfunctional amine (I-x) products [108] without an -NH or -NH2 moiety [110] can only be used as a final one-step product [118].

When the (I-x) structural compound [108], is reacted with AGE (or any of the provided glycidyl alkenyl compounds) [112] the result is the formation of the I-x-ene intermediate structure [114] (represented as I-x-ene), but can be prepared from any of the I-x and/or I-x-a to I-x-f structures [102] shown, that include either the -NH or -NH2 moieties [110]. The I-x-ene intermediate structure [114] is prepared so that one can add preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof [120] to increase molecular weight.

Alternatively a two-step process which forms the crosslinker structural compounds II-x-1 and II-x-3 requires the formation of the one step products (I-x-1 or I-x-3) that include -NH or -NH2 moieties (side groups) [110] and the addition of AGE (or other glycidyl alkenyl compounds) [112] resulting in the intermediate I-x-ene product [114]. This I-x-ene product [114] is followed by the addition of preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof [120] to provide the (II-x) products [122] which are examples of final two-step process products [124]. The structural features of each of these compounds are provided below:

(I-x-1)
(1-x-2^m)

(1-x-3)

\[ \text{Diagram 1} \]

\[ \text{Diagram 2} \]
In a further embodiment, the polyfunctional amine latex crosslinker compositions can also be an intermediate formed prior to the polymerization prepared with the addition of allyl glycidyl ether (AGE) comprising formula (I-x-1):

(I-x-1-ene)

The polyfunctional amine latex crosslinker intermediate composition above when reacted with preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof results in polymers of structures (II-x-1) and (II-x-3).
The structures (II-x-1) and (II-x-3) can also result in producing polymeric structures with molecular weights higher than those of the oligomers of the same compositional structures of (II-x-1) and (II-x-3).

The polyfunctional amines of the present disclosure are a result of a condensation reaction of a glycidyl group and an amine group and wherein resulting polyfunctional amines comprise at least three separate amino groups.

These polyfunctional amines thereby provide an ability to tailor the final molecular weight of these same polyfunctional amines.

Complete paint formulations utilizing both a latex and the polyfunctional amines described and provided above is also a subject of the present disclosure. The paint additionally includes
at least one dispersant, defoamer, surfactant, biocide, ammonia, rheology agent, pigment, solvent, coalescent, and water. The paint can be used as traffic paint for a pavement surface. Additionally, when the paint formulation is applied to pavement surfaces crosslinking of the paint occurs and early water resistance at 15-45 minutes can occur.

**DETAILED DESCRIPTION**

The present invention provides polyfunctional amine crosslinkers for use in latex polymer compositions and the latex polymer compositions containing them. The latex polymer compositions of the present invention typically include, but are not limited to, latexes, dispersions, microemulsions, or suspensions. The latex polymer compositions of the present invention 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. A film or coating formed with polymers of the present invention may be cured at room temperature (ambient cure) or at elevated temperatures (thermal cure).

The latex polymer binders used to prepare the waterborne polymer composition of the present disclosure are generally prepared as particles. The particles may be structured or unstructured. Structured particles include, but are not limited to, core/shell particles and gradient particles. The average polymer particle size may range from about 100 to about 300 nm.

The polymer particles have a spherical shape. In one embodiment, the spherical polymeric particle may have a core portion and a shell portion. The core/shell polymer particles may also be prepared in a multi-lobe 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.

The present disclosure includes compositions and methods for the preparation of water soluble polymeric and oligomeric polyfunctional amines for use as crosslinking agents in solutions of fast drying latex emulsions. The oligomeric/polymeric polyfunctional amine synthesized in a single step reaction by reacting bi- or tri-functional glycidyl and/or glycidyl isocyanurate groups with water soluble bi-, tri- and tetra-amines as the starting materials (reactants) serve as crosslinkers for latex paints. Oligomeric/polymeric polyfunctional amines
with lower molecular weight can be prepared from the same chemistry and the resulted product can be combined with glycidyl alkenyl compounds, allyl glycidyl ethers (AGE) is most favorable, in a two-step reaction process to form additional oligomers which are capable of molecular weight building via free radical initiated polymerization. The definition of whether the chemical structure is an oligomer or polymer depends on the final weight average molecular weight (as determined primarily by the number and molecular weight) of the repeating structural monomeric chains.

The fast drying and proper curing due to crosslinking of the latex emulsion is triggered by rapid evaporation of NH₃ in the paint formulation concurrent with a rise in the pH of the emulsion during and after being applied to the intended surface. The interaction of the latex binder together with the crosslinking polyfunctional amine (primarily) oligomers results in fast dry traffic latex polymers (as paint or coatings) which harden quickly. These polymeric/oligomeric amines provide for excellent water (especially rain water) resistant films due in part due to their rapid cure times. The waterborne fast dry paint serves as road and pavement marking paint which can be used to mark lines or symbols on roads, parking lots, and walkways etc.

In the present disclosure, the polyfunctional oligomeric amines possess structural chain extending groups that allow for tailoring the molecular weight of the crosslinker. More specifically, the polyfunctional oligomeric/polymeric amine examples of this disclosure are comprised of di or tri glycidyl monomers, or combination of di/di, di/tri, or tri/tri glycidyl monomers and either of bi, tri or tetra amino monomers, and combination of bi/bi, bi/tri, bi/tetra, mono/bi, mono/tri, mono/tetra, bi/tetra, tri/tetra functional amino monomers.

The synthesis of the final crosslinker can be completed as a one-step or two-step process. The one-step process provides novel crosslinkers resulting from glycidyl monomer/glycidyl monomers and amino monomer/amino monomers. The two-step process provides the crosslinkers of the one-step process that have been further reacted with AGE and polymerized or copolymerized with preferably MAA and ACR, or two other -C=C-functional groups and/or derivatives thereof, forming complex structures with pendant polyfunctional polymeric/oligomeric amine groups

**Selection of Monomers**
Triglycidyl isocyanurate is the only trifunctional glycidyl monomer used in this disclosure. Diglycidyl monomers include: poly(propylene glycol) diglycidyl ether, poly(ethylene glycol) diglycidyl ether, resorcinol glycidyl ether, neopentyl diglycidyl ether, and butanediol diglycidyl ether. The glycidyl monomer(s) employed in the disclosure can be single or in combination.

Amine monomers employed in this work can be bi-, tri- or terra- monomers or combinations of mono/bi, mono/tri, mono/tetra, bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra functional monomers. In amine monomers, the number of functionalities is defined by the number of N-H bonds.

A full list of mono-functional amine monomers include: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, N,N,N-trimethyl-1,2-ethane diamine, N,N,N,triethyl-1,2-ethane diamine, N-methyl-N,N-di ethyl-1,2-ethane diamine, N-ethyl-N,N-dimethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,3-propane diamine, and N-ethyl-N,N-dimethyl-1,3-propane diamine,

A full list of bi-functional amine monomers includes: methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, and N,N-diethylamino ethylene amine.

A full list of tri-functional amine monomers includes: amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1 ,2-ethane diamine, N-methyl-1 ,3-propane diamine, and N-ethyl-1,3-propane diamine.

A full list of tetra-functional amine monomers includes: 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine,2,2'-oxybis ethanamine, alanine, and lysine.

Creation of an alkenyl functional oligomeric polyamine for 2-step free radical polymerization involves a reaction between the corresponding oligomeric polyfunctional amine and glycidyl alkenyl compounds. A full list of glycidyl alkenyl compounds includes: allyl glycidyl ether,
vinyl glycidyl ether, vinyl cyclohexene oxide, glycidyl methacrylate, glycidyl acrylate, glycidyl acrylamide, glycidyl methacrylamide.

**Reaction Type 1: One-Step Process**

A first aspect of the present disclosure concerns polyfunctional amine crosslinkers comprising recurring units derived from the reaction of one tri-glycidyl moiety and a single di-, or tri-functional amino monomers, or combination of mono/bi, mono/tri, mono/tetra, bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra functional amino monomers resulting in a polyfunctional amine of formula (I-x):

(I-x)

Where the substituent J is the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety;

and wherein R1 is selected from the group consisting of all possible mono-functional, bi-functional, tri-functional or tetra-functional amines, as provided above;

and wherein R2 is selected from the group of all possible bi-functional, tri-functional or tetra-functional amines;

and where R1 is equal to or different than R2;

and where n is a number 10 to 100.

Further possible structures for providing polyfunctional amines using a one-step synthetic process are provided in general formulae (I-x) and/or (I-x-a) to (I-x-f):

(I-x)
Where the substituents J, Jl, and J2 are the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety, and wherein J is equal to or different than J1 and J2; and wherein J1 is equal to or different than J2; and wherein R1 is selected from the group consisting of all possible mono-functional, bi-functional, tri-functional or tetra-functional amines; and wherein R2 and R3 are selected from group consisting of all possible bi-functional, tri-functional or tetra-functional amines and wherein R1 is equal to or different than R2 and R3; and wherein R2 is equal to or different than R3; and where n is an number 10 to 100; and where m is an number equal to or different than n. For the one step synthesis of polyfunctional amines, it is possible to provide a combination of amines. The combination can be mono/bi, mono/tri, mono/tetra or bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra for tri-glycidyl monomer, and can be bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra for bi-glycidyl monomer. Combinations of mono/mono will not provide the required moieties for the present disclosure. To make the reactions in the current disclosure work, proper ratios between glycidyl monomers to amine monomers, ratios among all amines when combinations of amines are
involved and ratios among all glycidyl monomers when combinations of glycidyl monomers are used need to be controlled. The following relations have to be true for construction of desired polyamine in this disclosure:

1. Reaction between triglycidyl monomer and single bi, tri and tetra amines, or combinations of bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra amines:
   \[ \frac{M_a}{M_g} = 2n + 1 \]

2. Reaction between triglycidyl monomer and combination of mono/bi amines:
   \[ \frac{M_a}{M_g} = 2n + 1, \text{ and } \frac{M_{bi}}{M_g} \geq 1 - \frac{1}{n} \]

3. Reaction between triglycidyl monomer and combination of mono/tri amines
   \[ \frac{M_a}{M_g} = 2n + 1, \text{ and } 2 \frac{M_{tria}}{M_g} \geq 1 - \frac{1}{n} \]

4. Reaction between triglycidyl monomer and combination of mono/tetra amines
   \[ \frac{M_a}{M_g} = 2n + 1, \text{ and } 3 \frac{M_{tetra}}{M_g} \geq 1 - \frac{1}{n} \]

5. Reaction between biglycidyl monomer/combination of biglycidyl monomers and single bi, tri, tetra amines, or combinations of bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra amines:
   \[ \frac{M_a}{M_g} = n + 1 \]

6. Reaction between biglycidyl monomer/combination of biglycidyl monomers and combination of mono/tri amines:
   \[ \frac{M_a}{M_g} = n + 1, \text{ and } 2 \frac{M_{tri}}{M_g} \geq 1 - \frac{1}{n} \]

7. Reaction between biglycidyl monomer/combination of biglycidyl monomers and combination of mono/tetra amines:
   \[ \frac{M_a}{M_g} = n + 1, \text{ and } 3 \frac{M_{tetra}}{M_g} \geq 1 - \frac{1}{n} \]

Where:
- \( M_a \): molar amount of total amine used in reaction.
- \( M_g \): molar amount of total glycidyl monomer used in reaction.
- \( M_{bi} \): molar amount of total biamine used in reaction.
- \( M_{tria} \): molar amount of total triamine used in reaction.
- \( M_{tetra} \): molar amount of total tetraamine used in reaction.
- \( n \): designed polymerization degree of polyfunctional amine.

**Reaction Type II: Two-Step Process**
Oligomeric one step polyfunctional amines prepared from the reaction between tri-glycidyl monomer and a bi, a, tri-, and tetra functional amine, or combinations of bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra amines, or between bi glycidyl monomer and a tri or tetra amine, or combinations of bi/tri, bi/tetra, tri/tri, tri/tetra or tetra/tetra amines carry -NH or -NH$_2$ groups. A further aspect of the present disclosure include treatment of the obtained oligomeric with glycidyl alkenyl compounds to prepare alkenyl functional oligomeric polyamine (I-x-ene), and copolymerization of I-x-ene with other water soluble alkenyl monomers lead to two-step polyfunctional amine with increased molecular weight, generalized by formula (II-x).
Where the substituent \( J \), is the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety;

And wherein \( R_1 \) and \( R_2 \) are selected from the group consisting of a full list of bi, tri or tetra functional amines, or combination of bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra amines for triglycidyl monomer, and are selected from the group consisting of a full list of tri or tetra functional amines, or combination of bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra amines for diglycidyl monomers;

and wherein proton loss of \( R_1 \) in its \(-\text{NH} \) or \(-\text{NH}_2\) site results in \( R'_1 \);

and wherein \( R_4 \) is the connecting group between polyamine body and the alkene functionality. If AGE is employed in this preparation, the connecting group is \(-\text{CH}_2\text{CH(OH)CH}_2\text{O}-\). Variations in \( R_4 \) may be created from each different connecting glycidyl alkenyl compound. Potentially, the connecting glycidyl alkenyl compound can be selected from one of the following: allyl glycidyl ether, vinyl glycidyl ether, vinyl cyclohexene oxide, glycidyl methacrylate, glycidyl acrylate, glycidyl acrylamide, and glycidyl methacrylamide.

and wherein \( n-1 \) is an number from four to nineteen;

and wherein \( m \) is an number from 1 to 100;

and wherein \( o \) is an number from 1 to 100;

and wherein \( p \) is an number from 1 to 100;

and wherein repeating substituent \( R_5 \) results from polymerization of a water soluble monomer having a carbon - carbon double bond, \(-\text{C}=-\text{C}\), preferably an acrylic acid or acrylic acid derivative;

and wherein repeating substituent \( R_6 \) results from polymerization of a water soluble monomer having a carbon- carbon double bond, \(-\text{C}=-\text{C}\), preferably an acrylamide or a derivative of acrylamide;

and where said resulting structure's atomic mass is greater than or equal to 50,000 Daltons.

An extension list for water soluble alkenyl co-monomer includes: acrylamide, methacrylamide vinyl acetate, acrylic acid, methacrylic acid, ethacrylic acid, maleic acid,
The anionically stabilized latex binders used to provide the crosslinkable polymer latexes of the present disclosure are primarily formed by the reaction of three separate acrylic (styrene free) monomers - butyl acrylate (BA), methyl methacrylate (MMA) and methacrylic acid (MAA). Preparation of the latex binders were performed as discussed in the appropriate section on preparation of crosslinkable polymer latexes below.

The full, final, shelf-stable aqueous polymer latex coating composition (polymer) comprises anionically stabilized latex binders derived from the seed of Table 4 (shown below in the Method of Making Crosslinkable Latex Polymers Section below), exhibiting a glass transition temperature (Tg) of 20 to 40°C; more preferably, 25 to 30°C, and most preferably 25 to 27°C. The ammonium hydroxide is added in an amount that effectively raises the pH of the aqueous composition immediately after the latex is prepared. As the pH of the final latex composition reaches a range of 9.5 to 10.5, the addition of the polyfunctional oligomeric/polymeric amine crosslinker occurs, therefore preventing the trigger of the cross-linking activity with the final latex paint formulation during storage.

Additional formulae for fast dry latexes have been previously presented in US patent application No. 2014/0079888 which is hereby fully incorporated by reference.

To summarize, the final latex polymer emulsion composition of the present disclosure comprises:

(a) either the use of the constituents listed in Table 1 for seeding the latex and preparing the latex binder or the use of another anionically stabilized latex - the formula of which is an extension of those found in US patent application no. 2014/0079888

(b) a water soluble polyamine solution where the polyamine concentration varies between 10% -15%, which is made from the polymerization reaction between glycidyl monomers and amine functional monomers (with or without further treatment of glycidyl alkenyl compounds).

(c) ammonium hydroxide

(d) TiO2 as pigment and CaCO3 as filler
(e) auxiliary additives as needed - including co-solvents, plasticizers, deformers and thickeners.

The present disclosure describes a high build, fast drying, and fast hardening aqueous coating composition comprising: (a) an anionically stabilized polymer latex binder comprising: (i) 35 to 65% by weight, based on the latex binder weight.; (ii) 25 to 55% by weight, based on the latex binder weight.; and (iii) 0.5 to 15% by weight, based on the latex binder weight, or; (iv) 0.1% to 4% by weight, based on the latex binder weight, of at least one anionic surfactant; and the use of (v) 0.5 and 1.5% polyfunctional amine crosslinker, wherein the latex binder has a glass transition temperature less than 45 degrees Centigrade, when the latex binder has been applied to the appropriate surface and has an average particle diameter size of between 100 nanometers and 300 nanometers.

Formation of the water soluble polyfunctional amines is accomplished by the nucleophilic substitution ring opening reaction between glycidyl monomers and amino monomers.

The composition of the bi- and/or tri-glycidyl monomers can include each of the following reactants and subsequent moieties; triglycidyl isocyanurate (TGIC), poly(propylene glycol) diglycidyl ether, poly(ethylene glycol) diglycidyl ether, resorcinol glycidyl ether, neopentyl diglycidyl ether, butanediol diglycidyl ether. In the present disclosure, the use of TGIC is the primary choice and all compositions of the polyfunctional oligomeric and polymeric amines disclosed herein are based upon reactions with this glycidyl group, but this is not a limitation of the present disclosure. Both the molecular weight and the molecular structure of the polyfunctional oligomeric amines are controlled by the stoichiometric ratio of the total amount of glycidyl groups to that of the amino functional groups. This is also the ratio of each amine among amine combinations, and the ratio of each glycidyl monomer among combinations of glycidyl monomers. In this disclosure, mono-functional, bi-functional, tri-functional and tetra-functional amines or combinations of these may be used for the preparations shown. A complete listing of possible amines has been presented above.

To achieve the appropriate molecular weight for the polyfunctional oligomeric amines to be used for the present disclosure, a proper stoichiometric ratio between amine functional monomers and epoxy functional monomers needs to be controlled. For example, for structural formula (I-x-1), the ratio of glycidyl compounds to di-amine compounds is n: (2n+1). For the structural formula (I-x-2"), the ratio of glycidyl to mono to di-amine compounds is n: (n+1): n. For the structural formula (I-x-3), the ratio of glycidyl to diamine
compounds is \( n \times (2n+1) \). However, kinetic factors also play a role in the reactions between trifunctional glycidyl monomers and terra functional amines when attempting to ensure full water solubility of these compounds.

The molecular weights were determined using the following GPC Methodology for Amine testing in aqueous solutions. An HPLC unit Waters 2695 with selective gel permeation columns designated as; Guard and one 30 cm PL Aquagel-OH Mixed-M 8\( \mu \)m columns. The detectors used included a Waters 410 Differential Refractometer (RI) with a Viscotek Dual Detector 270 - (RALS, DP, IP, LALS). The running solvent used was deionized water with 0.2\% ethylenediameine (EDA).

The polyfunctional amine crosslinker samples were diluted in DI water and filtered through 0.22 um PTFE filters into 1.5mL vials and run through the GPC system at a flow rate of 1.0mL/min. Each vial had a run time of 30 minutes to allow samples to be entirely flushed out before the next run. To find the Molecular weights, a set of Polyethylene Glycol (Oxide) samples were run as a calibration curve ranging from 232 to over one million Daltons. Omnisec software was used to create a method to fit the molecular weight distributions of the amine samples to the calibration curve of the standardized PEG samples.

Polymerization between glycidyl monomers and amine monomers gives rise to polyfunctional amine structures. Above, it was noted that there are functional groups for building molecular weight associated with these polyfunctional amines. More specifically, the amino groups in the polyfunctional amine can themselves be categorized as two separate groups. The structural amine and/or amino groups, which can be secondary or tertiary, stem from the glycidyl ring opening reaction resulting from the monomeric amine in a nucleophilic substitution reaction. The functional amine groups allow for ionic interaction between the latex binder particles and the polyfunctional amine crosslinkers. Structural amino groups are sterically hindered and always exhibit decreased pKb compared to what they would normally exhibit in their simple monomeric state. These groups therefore possess very little capability to interact with anionically stabilized latex particles. Instead they only serve as molecular weight building blocks for the polyfunctional amines. On the contrary, the functional amines, which are either intended to be left unreacted or reacted but distribute peripherally with the polyfunctional amines, either possesses much stronger pKb values or are sterically approachable by the anionically stabilized latex particles. They are much more capable of providing crosslinker-latex reactivity when being triggered by the pH change.
The present disclosure involves the use of crosslinkers for final latex polymer compositions containing at least one polyfunctional amine primarily acting as an interaction component for ionic bonding. In some cases, the structural components may also act as interactive components if the structure of the polyfunctional amine is strictly linear. Examples of the resulting polyfunctional amines of the present disclosure are schematically represented below:

(I-x-1)

(I-x-2''')
A general method for achieving the reaction leading to the oligomeric polyfunctional amines as represented above is as follows:

A solution of the indicated amine is charged to a 2 liter reactor and an appropriate amount of rinsing water is used to ensure that no residual remains. This solution is heated to 20-30 °C and thoroughly agitated, where the first portion of TGIC is added to the amine solution. The TGIC, as a white powder, is dissolved gradually (approximate 10 minutes agitation) into the amine solution at a temperature range of between 10 and 100 °C and most preferably at or above 20 °C. The exothermic conditions of this reaction elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and the second portion of TGIC is added. The reaction is again agitated for approximately 10 minutes and the exothermic conditions of this reaction again elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and then TGIC of the third portion is added. It takes approximately 10 minutes for the TGIC powder to dissolve and the heat released from the reaction on the third addition elevates the reaction by 5-10 °C. If neopentyl glycol diglycidyl ether is used in the reaction, which occurs only in the preparation of I-x-3, it should be added to the reaction when the third portion of TGIC is dissolved in the reaction solution. The reaction then should be maintained at ambient temperature between 40-45 °C for another two hours. The reaction solution is thus discharged from the kettle and results in final concentrations of polyamine crosslinkers.

I-x-3

A general method for achieving the reaction leading to the oligomeric polyfunctional amines as represented above is as follows:

A solution of the indicated amine is charged to a 2 liter reactor and an appropriate amount of rinsing water is used to ensure that no residual remains. This solution is heated to 20-30 °C and thoroughly agitated, where the first portion of TGIC is added to the amine solution. The TGIC, as a white powder, is dissolved gradually (approximate 10 minutes agitation) into the amine solution at a temperature range of between 10 and 100 °C and most preferably at or above 20 °C. The exothermic conditions of this reaction elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and the second portion of TGIC is added. The reaction is again agitated for approximately 10 minutes and the exothermic conditions of this reaction again elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and then TGIC of the third portion is added. It takes approximately 10 minutes for the TGIC powder to dissolve and the heat released from the reaction on the third addition elevates the reaction by 5-10 °C. If neopentyl glycol diglycidyl ether is used in the reaction, which occurs only in the preparation of I-x-3, it should be added to the reaction when the third portion of TGIC is dissolved in the reaction solution. The reaction then should be maintained at ambient temperature between 40-45 °C for another two hours. The reaction solution is thus discharged from the kettle and results in final concentrations of polyamine crosslinkers.

I-x-3

A general method for achieving the reaction leading to the oligomeric polyfunctional amines as represented above is as follows:

A solution of the indicated amine is charged to a 2 liter reactor and an appropriate amount of rinsing water is used to ensure that no residual remains. This solution is heated to 20-30 °C and thoroughly agitated, where the first portion of TGIC is added to the amine solution. The TGIC, as a white powder, is dissolved gradually (approximate 10 minutes agitation) into the amine solution at a temperature range of between 10 and 100 °C and most preferably at or above 20 °C. The exothermic conditions of this reaction elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and the second portion of TGIC is added. The reaction is again agitated for approximately 10 minutes and the exothermic conditions of this reaction again elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and then TGIC of the third portion is added. It takes approximately 10 minutes for the TGIC powder to dissolve and the heat released from the reaction on the third addition elevates the reaction by 5-10 °C. If neopentyl glycol diglycidyl ether is used in the reaction, which occurs only in the preparation of I-x-3, it should be added to the reaction when the third portion of TGIC is dissolved in the reaction solution. The reaction then should be maintained at ambient temperature between 40-45 °C for another two hours. The reaction solution is thus discharged from the kettle and results in final concentrations of polyamine crosslinkers.

I-x-3

A general method for achieving the reaction leading to the oligomeric polyfunctional amines as represented above is as follows:

A solution of the indicated amine is charged to a 2 liter reactor and an appropriate amount of rinsing water is used to ensure that no residual remains. This solution is heated to 20-30 °C and thoroughly agitated, where the first portion of TGIC is added to the amine solution. The TGIC, as a white powder, is dissolved gradually (approximate 10 minutes agitation) into the amine solution at a temperature range of between 10 and 100 °C and most preferably at or above 20 °C. The exothermic conditions of this reaction elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and the second portion of TGIC is added. The reaction is again agitated for approximately 10 minutes and the exothermic conditions of this reaction again elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and then TGIC of the third portion is added. It takes approximately 10 minutes for the TGIC powder to dissolve and the heat released from the reaction on the third addition elevates the reaction by 5-10 °C. If neopentyl glycol diglycidyl ether is used in the reaction, which occurs only in the preparation of I-x-3, it should be added to the reaction when the third portion of TGIC is dissolved in the reaction solution. The reaction then should be maintained at ambient temperature between 40-45 °C for another two hours. The reaction solution is thus discharged from the kettle and results in final concentrations of polyamine crosslinkers.

I-x-3
preferably in the 10-80 weight % range and most preferably 20-25 weight % range, where previous reactions resulted in polyamine crosslinkers of 10% with no water removed.

Here, equation (1) describes how the w/o (weight percent) of the polyamine is determined:

$$\text{(1) weight \% polyamine} = \frac{\text{weight of reactants}}{\text{total weight (w/ water)}}$$

The primary solvent is water, and the epoxy/glycidyl compounds and amino compounds must be mixed with water. There are numerous methods to obtain the preferred concentration of the desired polyamine. Those preferred concentrations have been achieved by the removal of water from the final reaction solution. The highest concentrations possible for manufacturing purposes are approximately 50 - 60%, which avoids forming a solid. A polyamine system containing no water is undesirable for the purposes of creating the latex paint compositions described.

In at least one embodiment, the crosslinkers made from the glycidyl/amine condensation chemistry of the present disclosure should include at least three reactive amino group sites.

More specifically, for the synthesis of the structure of oligomer (I-x-1), the following reaction (Reaction 1) was performed;

$$\text{(A)+ (B) \rightarrow (I-x-1), where (A) is triglycidyl isocyanurate (TGIC)}$$

(B) is a bi-functional amine (such as piperazine), and

(I-x-1) is a polyfunctional amino group with repeating units, n, of structure (I-x-1).

As described in Table 1, a solution of 35.8 g piperazine and 343.2 g water were mixed in an 800 mL beaker. The solution was mixed with mechanically driven agitation of 200 rpm and the temperature was 31 °C. 18.0 g of TGIC was poured into this reactor as the first TGIC portion. After 18 minutes, all solid form TGIC was dissolved and temperature of the reaction increased to 35 °C. 16.0 g TGIC as the second batch was added. After 10 minutes, the solid form TGIC of the second portion was fully dissolved, and the solution was cooled to 25 °C. 16 g TGIC as the third batch was added. 20 minutes later, the third portion of TGIC was fully dissolved and the reaction temperature reached 32 °C. The reaction was allowed to cool down naturally. The reaction solution was thus discharged from the kettle to result in polyamine crosslinkers of 20 weight %, where previous reactions resulted in polyamine crosslinkers of 10 weight % with no water removed. The number average molecular weight (Mn) is
determined to be 45,728. The weight average molecular weight (Mw) of the (I-x-1) oligomer was determined to be 7300 using the GPC methodology described above. The one step synthetic route described herein generally provides oligomers or polymers with weight average molecular weight ranging from 500 to 50,000 Daltons.

Table 1: Summary of Method of Preparation of I-x-1 Polyamine Linker as Fast Dry Additive

<table>
<thead>
<tr>
<th>Chemical</th>
<th>MW</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglycidyl Isocyanurate</td>
<td>297.26</td>
<td>18</td>
</tr>
<tr>
<td>Triglycidyl Isocyanurate</td>
<td>297.26</td>
<td>16</td>
</tr>
<tr>
<td>Triglycidyl Isocyanurate</td>
<td>297.26</td>
<td>16</td>
</tr>
<tr>
<td>Piperazine</td>
<td>86.14</td>
<td>35.8</td>
</tr>
<tr>
<td>Water</td>
<td>18</td>
<td>343.2</td>
</tr>
</tbody>
</table>

REACTION 1:

![Diagram of Reaction 1]

I-x-1
The synthesis of the structure of oligomer (I-χ-2'”), as provided in Reaction 2, was performed using the following procedure:

\[(\text{A}) + (\text{C}) + (\text{D}) \rightarrow (\text{I-x-2'”})\]

where (A) is triglycidyl isocyanurate (TGIC)

(C) is a bi-functional amine (such as DEAPA),

(D) is a mono-functional amine (such as DEA), and

(I-x-2’’') is a polyfunctional amine group with repeating units, n, of structure (I-x-2).

As described in Table 2, a solution of 179.62 g DEAPA in 1518.49 g water was added to a 2 liter reactor. The aqueous solution was heated to 20-30 °C, and thoroughly agitation. 80.0 g of TGIC was poured into this reactor as the first TGIC portion. The resulting exothermic conditions of this reaction elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and the second portion of TGIC is added in the amount of 60 g TGIC. The reaction is again agitation for approximately 10 minutes and the exothermic conditions of this reaction elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and 60 g TGIC of the third portion is then added. It takes approximately 10 minutes for the TGIC powder dissolve and the heat released from the reaction would elevate the reaction by 5-10 °C. The reaction then should be maintained at ambient temperature between 40-45 °C for another two hours. The reaction solution is thus discharged from the kettle to result in polyamine linkers of 20%.

The weight average molecular weight (Mw) of the (I-x-2” ”) oligomer was determined to be 4800 using the GPC methodology described above.

**Table 2: Summary of Method of Preparation of I-x-2”” Polyamine Linker as Fast Dry Additive**
REACTION 2:

\[
\begin{align*}
&\text{(A)} + \text{[D]} \\
\rightarrow & \\
&\text{1-x-2}'''
\end{align*}
\]

The synthesis of the structure of oligomer (I-x-3), as shown in Reaction 3, was performed using the following procedure;

\[(\text{A}) + (\text{E}) \rightarrow (I-x-3), \text{ where (A) is triglycidyl isocyanurate (TGIC)}\]

\[(\text{E}) \text{ is a tetrafunctional amine (such as DAB)}, \text{ and}\]
(I-x-3) is a polyfunctional amino group with repeating units, n, of structure (I-x-3).

As described in Table 3, a solution of 124.55 g DAB was added to a 1 liter reactor. An appropriate amount of water was used to rinse the addition funnel and the beaker to ensure full addition. The aqueous solution was heated to 20-30 °C, and thoroughly agitated. 80.0 g of TGIC was poured into this reactor as the first TGIC portion. Some TGIC remains attached to the addition funnel and the beaker charging it, therefore 107.7 g water was added to rinse the funnel and the beaker to ensure full addition. The resulting exothermic conditions of this reaction elevate the reaction temperature by 10 °C. The reaction is cooled to 25-35 °C, and the second portion of TGIC is added in the amount of 60 g TGIC. The reaction is again agitated for approximately 10 minutes and the exothermic conditions of this reaction elevate the reaction temperature by 10 ºC. The reaction is cooled to 25-35 ºC, and 60 g TGIC of the third portion is then added with 14.55 g neopentyl glycol diglycidyl ether (NPGDGE). It takes approximately 10 minutes for the TGIC powder dissolve and the heat released from the reaction would elevate the reaction by 5-10 ºC. The reaction then should be maintained at ambient temperature between 40-45 ºC for another two hours. The reaction solution is thus discharged from the kettle to result in polyamine linkers of 20%, where previous reactions resulted in polyamine linkers of 10% with no water removed.

**Table 3: Summary of Method of Preparation of I-x-3 Polyamine Linker as Fast Dry Additive**

<table>
<thead>
<tr>
<th>Chemical</th>
<th>MW</th>
<th>Weight (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triglyceridyl isocyanurate</td>
<td>297.26</td>
<td>80.00</td>
</tr>
<tr>
<td>Triglyceridyl isocyanurate</td>
<td>297.26</td>
<td>60.00</td>
</tr>
<tr>
<td>Triglyceridyl isocyanurate</td>
<td>297.26</td>
<td>60.00</td>
</tr>
<tr>
<td>Neopentyl glycol diglycidyl ether</td>
<td>216.27</td>
<td>14.55</td>
</tr>
<tr>
<td>diamino dibutane</td>
<td>88.15</td>
<td>124.55</td>
</tr>
<tr>
<td>Water</td>
<td>1356.00</td>
<td></td>
</tr>
</tbody>
</table>

The weight average molecular weight (Mw) of the (I-x-3) oligomer was determined to be 5300 using the GPC methodology described above.
REACTION 3:

The addition of the monofunctional allyl glycidyl ethers (AGEs) is in a molar amount that is always $1/n$ of that of the TGIC amount used in this preparation. Monofunctional allyl glycidyl ethers (AGEs) are also considered a member of the glycidyl reactive (functional) monomer groups that as the molecule introduces a site for orthogonal polymerization in the second step, as used for molecular weight expansion. Use of the AGEs allows for introducing an $\alpha,\beta$ unsaturated ethylene to the resulting oligomeric polyamine.
The reactants leading to the polyfunctional polymeric/oligomeric amine product shown above (I-x-1-ene), result in the introduction of an allylic double bond. Introduction of the allylic double bond serves as a monomeric moiety for the copolymerization with for example MAA and ACR, providing molecular weight building.

The synthesis of the structure of oligomer (I-x-1-ene), which includes the addition of allyl groups as shown in Reaction 4, was performed using the following procedure:

\[(A)+(B)+(F) \rightarrow (I-x-1-ene)\], where (A) is triglycidyl isocyanurate (TGIC)

(B) is a bi-functional amine (such as piperazine),

(F) is a allyl ether or allyl glycidyl ether containing molecule (such as AGE) and
to a 2 liter reactor, a solution of 24.35 g piperazine is charged together with an appropriate of water for rinsing. At room temperature, 40.03 g TGIC is added for which a separate appropriate amount of water was set aside for rinsing. The TGIC is a white powder at room temperature and is dissolved gradually into the piperazine solution. Within an hour, the combined solution was heated to 39 C. 1.57 g AGE was added in one portion. The reaction was allowed to remain at room temperature for another 20 minutes to cool to ambient conditions.

REACTION 4:

This product is then available for a subsequent reaction with preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof and an initiator (normally APS
ammonium persulfate) that is schematically depicted below, leading to free radical polymerization which provides a water soluble copolymer with a chain length of between 5,000 and 500,000 Dalton
Polymerization Process for Two-Step Polyfunctional Amine Crosslinkers:

\[
\text{II-x-1}
\]

\[
\text{I-x-1-ene}
\]

MAA and ACR

\[
\rightarrow
\]

Bruggolite FF6 and tBHP
This copolymer structure (II-x-1) shown above is representative of one of a group of polyfunctional polymeric amines which possess the necessary cationic charge and molecular weight so that when placed in solution with the latex binder allows for providing a final aqueous based crosslinked polymer latex coating that forms proper films is quick drying and exhibits increased wash-off.

To achieve polymerization of the oligomeric polyfunctional amine the following procedure was used; 0.53 g of Bruggolite FF6 (an initiator comprised of a sodium salt of an organic sulfinic acid derivative - CAS number 401900-10-5), together with 17.2 g acrylamide (H), and 7.1 g MAA (G) were dissolved in 30.2 g water. No chemical reaction occurs during this physical mixing process. This first solution was placed aside for later inclusion. Next, 0.37 g tBHP (70%) was added to 388.1 g of a second solution used to synthesize the polyfunctional oligomer of structure (II-x-1) shown above. Then, 40.7 g water was added to a separate 2 liter reactor and heated to 43.9 C. Into this separate reactor, the first solution and the second solution were added together over a period of 35 minutes. 7.6 g ammonium hydroxide (30%) was also added to the reactor during this addition. The final (production) solution was held at the 40-45 C for 15 minutes to convert all unreacted monomers. The reactants were then released from the reactor and stored without further purification. The weight average molecular weight (Mw) of the (II-x-1) oligomer was determined to be 32,400 using the same GPC methodology described above.

Based on the synthetic route described above, the following copolymer structures are also possible.

(II-x-3)
When the water soluble polyfunctional amines (shown above) are combined in solution with the latex binder, the pH of the solution (adjusted by adding ammonium hydroxide) should be at least 9.6 and preferably no greater than 10.5. This solution is a volatile basic solution in that the water and ammonium hydroxide will rapidly evaporate when the solution is applied to a substrate in the open atmosphere. After application, ammonia (as the volatile base) evaporates quickly from the paint film and the polyamine becomes protonated gradually. With water loss, the interaction between anionic latex particle and cationic polyamine is activated causing clustering of the latex particles which results in fast film formation.

The volatile base, specifically ammonium hydroxide, prevents a crosslinking of the polyfunctional co-polymeric amines with the latex binder to take place prior to substrate application. The ammonium hydroxide addition provides at least two functions - it stabilizes the polyfunctional amine copolymer crosslinkers and helps to neutralize the anionic (negative) surface charge of the latex binder. As the ammonia leaves due to volatility, it
triggers electrostatic interaction between the anionically charged latex binder and the cationic polyfunctional amines.

The polymer latex formulae of the present disclosure have been modified to meet the storage and fast drying film requirements described above where interaction between polyfunctional amine crosslinker and latex binder provides rapid crosslinking when applied to surfaces. The anionically stabilized fast dry latex formulae have been prepared from semi-continuous process, which allows better control of the particle size and zeta potential.

The latex polymer compositions of the present invention exhibit latent crosslinking properties. The rate of crosslinking is controlled by stabilizing the polyfunctional amines using the volatile (ammonium hydroxide) base.

Polyfunctional Amines

Polymers having repeating units of amine/amino and glycidyl groups are useful in the practice of the present invention. Examples of amine and amino groups include, but are not limited to: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, N,N,N-trimethyl-1,2-ethane diamine, N,N,N, triethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,2-ethane diamine, N,N-diethyl-1,3-propane diamine, N-ethyl-N, N-dimethy 1,1,3-propane diamine, methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-dicyclopentyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-dicyclopentyl ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N,N-dimethyl-1,2-ethane diamine, N-ethyl-1,3-propylene diamine, N-ethyl-1,3-propylene diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino butane, 1,3-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine,2,2'-oxybis ethanamine, alanine, and lysine.

Bi- and/or tri- glycidyl monomers can include each of the following reactants and subsequent moieties; triglycidyl isocyanurate (TGIC), poly(propylene glycol) diglycidyl ether, poly(ethylene glycol) diglycidyl ether, resorcinol glycidyl ether, neopentyl diglycidyl ether,
and butanediol diglycidyl ether. In the present disclosure, the use of TGIC is the primary choice for the glycidyl groups and all compositions of the polyfunctional amines disclosed herein are based upon reactions with this glycidyl group. Both the molecular weight and the molecular structure of the polyfunctional oligomeric amines are controlled by the stoichiometric ratio of total glycidyl reactive groups to amino functional groups, the ratio of each amine among amine combinations, and the ratio of each glycidyl monomer among combinations of glycidyl monomers.

The monofunctional amines include the following ones: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, N,N,N-trimethyl-1,2-ethane diamine, N,N,N,triethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,2-ethane diamine, N-ethyl-N,N-dimethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,3-propane diamine, N-ethyl-N,N-dimethyl-1,3-propane diamine, The difunctional functional amines include these ones: methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine. The trifunctional amines include the following ones: amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, N,N-diethyl-1,3-propane diamine. The tetra functional amine include these ones: 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine,2,2'-oxybis ethanamine, alanine, and lysine.

For the one-step synthesis of polyfunctional amines, a combination of amines can be used.

The combination can be mono/bi, mono/tetra, mono/tri, bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra, tetra/tetra for tri-functional glycidyl monomers, such as TGIC; the combination can be mono/tri, mono/tetra, bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra for bi-functional glycidyl monomers. As stated above, the combination of mono/mono does not provide the necessary crosslinker formulations for the present disclosure.

Method of Making Crosslinkable Latex Polymers
The latex polymer compositions of the present invention may vary in properties, depending on the end-use application. In general, the polymer component may have glass transition temperature (Tg) of 15 to 40°C and more preferably 20 to 30°C.

The weight average molecular weight of the latex polymer compositions may vary from about 5,000 to 5,000,000 Daltons; more preferably from 20,000 to 2,000,000 and most preferably from 40,000 to 100,000. Since the polymers of the present invention become highly crosslinked upon drying, there is no substantial disadvantage to starting with very low molecular weight polymers.

A waterborne polymer composition may be prepared using the latex polymer composition of the present invention along with other known additives and may use other emulsion polymerization methodologies.

The examples below illustrate the preparation of latex polymers and waterborne polymer compositions according to the invention.

First a latex seed must be prepared. Table 4 below provides the constituents of the example of one of the procedures used that follows: A 2 liter reactor was charged 210.9 g SDS solution (14% of the total solution), 4.6 g NaHCO₃, 503.3 g water, 158.0 g BA, 189.5 g MMA, 6.8 g MAA and 16.2 g APS. The solution was mechanically stirred and heated to 65°C. Radical polymerization occurred immediately to raise the temperature quickly. The exotherm was controlled using 410.1 g water which was added gradually over a period of four minutes. The seed solution was allowed to react for another 130 minutes to ensure the reaction proceeds to completion. The latex particle size obtained was determined to be 51 nm.

| Table 4: Constituents of Monomer Emulsion for Preparation of Latex Resin |
|-----------------------------|------------------|
| BA                         | 315.9            |
| MMA                        | 379              |
| MAA                        | 13.5             |
| NaHCO₃                     | 0.8              |
| SDS solution (14%)         | 81.92            |
| IGEPAL CA 407              | 10.2             |
| Water                      | 270              |

Latexes or other waterborne compositions contain small particle size seed polymers, those ranging from about 25 to about 700 nm, preferably from about 50 to about 500 nm and more preferably from about 75 to about 300 nm, represent one embodiment of the invention.
Next, it was necessary to prepare the latex. This procedure was performed as follows: a kettle
was charged with 23.19 g water, 32.5 acrylic seed (23% solids) and 0.8 g sodium bicarbonate.
Once charged, the kettle charge was heated to 80 C using a water bath. A solution of 2.1 g
APS in 30 g water and the monomer emulsion, as indicated in Table 4, above was feed into
the kettle over 195 minutes. To ensure no loss of reactants, 20 g of water was used to rinse
the solution. While maintaining the temperature, the latex polymerization and resulting latex
polymer binder was allowed to react for another 90 minutes to ensure reaction completion.
Ammonium hydroxide, 16.1 g. (30%) was added to the polymerized latex emulsion after it
was cooled to ambient conditions.

Once the latex polymerization yielding the latex binder was complete, it was possible to
complete the process by producing two separate latex paints, the constituents of which are
listed in Table 6. The procedure for a white latex paint, with and without crosslinkers, is
provided as follows. The following examples are intended to illustrate, not limit, the
invention:

Example 1

For the paint without the crosslinker (Example 1), to a quart can containing 460.0 g of latex
polymerized based on the procedure above for preparing the dry latex, 8.0 g of dispersant was
added along with 5.0 g defoamer, 3.0 g surfactant, and 0.2 g biocide while stirring with a high
sheer mixing blade at a moderate speed for 5 minutes. Next, a rheology agent was mixed with
1.5 g of water and added to the stirring mixture and stirred at high speed for another 5
minutes. To this, 0.8 g ammonia was added bringing the pH to 9.6. Then pigments were
added carefully while stirring at high speed for 15 minutes. After completion of the mixing
and accompanying grinding, 35.0 g of solvent was added slowly and at reduced stirring
speed. Then 22.0 g of the coalescent was added to the mixture, stirring continuously. Finally,
4.7 g of water was added and stirred into the mixture and the mixture was stirred for another
5 minutes until complete.

Comparative Example 1

For the paint with the crosslinker (Comparative Example 1), to a quart can containing 460.0 g
of latex polymerized based on the procedure above for preparing the dry latex, was added
30.0 g of untreated crosslinker solution and stirred for 5 minutes using a high sheer mixing
blade at moderate speed. Next 8.0 g dispersant was added along with 5.0 g defoamer, 3.0 g
surfactant, and 0.2 g biocide while stirring with a high sheer mixing blade at a moderate speed for 5 minutes. Next a rheology agent was mixed with 1.5 g of water and added to the stirring mixture and stirred at high speed for another 5 minutes. To this, 0.8 g ammonia was added bringing the pH to 9.6. Then pigments were added carefully while stirring at high speed for 15 minutes. After completion of the mixing and accompanying grinding, 35.0 g of solvent was added slowly and at a reduced stirring speed. Then 22.0 g of the coalescent was added to the mixture, stirring continuously. Finally, 4.7 g of water was added and stirred into the mixture and the mixture was stirred for another 5 minutes until complete.

Table 5 below summarizes the contents of the described procedure and resulting latex paint solutions:

<table>
<thead>
<tr>
<th>Components of Latex</th>
<th>Example 1</th>
<th>Comparative example 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Latex</td>
<td>460.0</td>
<td>460.0</td>
</tr>
<tr>
<td>Crosslinker</td>
<td>---</td>
<td>30.0</td>
</tr>
<tr>
<td>Dispersant</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Defoamer</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Surfactant</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Biocide</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Rheology agent</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>Water</td>
<td>30.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Pigment TiO2</td>
<td>150.0</td>
<td>150.0</td>
</tr>
<tr>
<td>Pigment Extenders</td>
<td>710.0</td>
<td>710.0</td>
</tr>
<tr>
<td>Solvent</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Coalescent</td>
<td>20.0</td>
<td>20.0</td>
</tr>
</tbody>
</table>

To determine the effectiveness of the polyfunctional amine crosslinkers, a water wash-off test was performed to compare 30 minutes dry time for both Example 1 and Comparative Example 1 according to the procedures detailed in ASTM D711-10. The results are found in Figure 2. The white latex paint patches on the left side are for the crosslinked version of the
latex paint (Comparative Example 1) [210] vs. that of Example 1 [220] without the crosslinker.

Example 2 and Comparative Example 2

For Example 2 and Comparative example 2, another white latex paint was prepared with and without the polyfunctional amine (oligomer (I-x-3) as shown in Reaction 3). For Comparative Example 2, the crosslinker (polyfunctional amine) was blended into the latex gently for over 2 minutes while the latex was being stirred before the remainder of the components, as shown in Table 6, were added. The common formulation method and techniques used for both providing both examples were as follows;

To a one quart can containing 444.0 g of the acrylic latex emulsion (with and without crosslinker) was added 8.0 g dispersant, 8.0 g defoamer, 2.5 g surfactant, and 0.2 g biocide while stirring with a high sheer mixing blade at moderate speed (normally not greater than 100 rpm) for 5 minutes. The thickener and rheology modifier were then mixed with 19.6 g of water and added to the stirring mixture and stirred at higher speeds (normally not greater than 1000 rpm) for another 5 minutes. Next, pigments, extender, and calcium carbonate were added carefully while stirring at the same higher speed for 15 minutes.

After grinding was completed, 30.0 g of methanol was added slowly and at reduced stirring speed Then 5.6 g of coalescent was added to the mixture while stirring continuously. Next 20.0 g of co-solvent was added and stirred into the mixture. The total content of the solution was then continuously stirred for another 5 minutes until completed and is found in Table 6

This is the procedure for paint film preparation and dry time test: a sample of paint is drawn to 15 mil wet film thickness onto to a clean black scrub test panel and allowed to dry horizontally in a conditioned room at 23°C ± 2°C and 75% relative humidity under a constant 2 mph air flow. Standard method of ASTM D711-10 has been used to judge the no tire pick up dry time.

Dry time of comparative example 2 is 7.15 minutes and this value for example 2 is 10.63 minutes.

Table 6 below summarizes the contents of the described procedure and resulting latex paint solutions;
Table 6: Constituents of Two Latex Paints with and without Crosslinkers; Example 2
and Comparative Example 2

<table>
<thead>
<tr>
<th>Components of Latex</th>
<th>Example 2</th>
<th>Comparative example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylic Latex Emulsion</td>
<td>444.0</td>
<td>444.0</td>
</tr>
<tr>
<td>Crosslinker</td>
<td>---</td>
<td>Rxn 3 11.1</td>
</tr>
<tr>
<td>Dispersant</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Defoamer</td>
<td>8.0</td>
<td>8.0</td>
</tr>
<tr>
<td>Nonionic Surfactant</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Biocide</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>Ammonia</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Rheology agent</td>
<td>2.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Water</td>
<td>19.6</td>
<td>19.6</td>
</tr>
<tr>
<td>Calcium Carbonate</td>
<td>615.0</td>
<td>615.0</td>
</tr>
<tr>
<td>Pigment Extenders</td>
<td>156.0</td>
<td>156.0</td>
</tr>
<tr>
<td>Solvent</td>
<td>30.0</td>
<td>30.0</td>
</tr>
<tr>
<td>Coalescent</td>
<td>5.6</td>
<td>5.6</td>
</tr>
<tr>
<td>TiO2 Pigment</td>
<td>70.0</td>
<td>70.0</td>
</tr>
<tr>
<td>Co-Solvent</td>
<td>20.0</td>
<td>20.0</td>
</tr>
<tr>
<td>Thickener</td>
<td>0.20</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Test Methods

Known commercially available latex paints were sampled and compared to the latex paint of the present disclosure. Figure 3a provides a complete visual comparison utilizing the full FTIR spectrum [300] from a standard FTIR analyser, the Thermo Nicolet 380 for four different latex paint compositions. Three of these compositions are commercially available and the fourth represents a paint utilizing the polyfunctional amines of the present disclosure. The same data is presented in the spectrum provided within the narrower range of 1550 cm⁻¹ to 1870 cm⁻¹ wavelength, as shown in Figure 3b (narrowed range and enlarged) which indicates the defining characteristics of the one of the compositions of the present disclosure distinguished by the characteristic peak [3 10] as identified and shown.

Resistance Minimum Film Forming Temperature

Resistance minimum film forming temperature (MFFT resist) is determined by casting a wet latex film with a 1-mil applicator cube on an MFFT bar set at a temperature range in which
the film will coalesce during drying, pulling the edge of a brass spatula blade through the film from cold to hot end on the MFFT bar after 30 minutes, and recording the temperature at which the film offers significant resistance to the spatula.

**Water-Wash Off**

The water wash-off procedure generally follows ASTM D7377-08 and is modified by using section 4.6.2 of ASTM D711-10 for controlled air flow. Paint viscosity is determined by measuring Krebs Units (KU) using a paddle type viscometer. Viscosities of 80 to 90 KU are considered suitable for testing.

**Drawdown samples are prepared via the procedure provided herein:**

A sample of paint is drawn to 15 mil wet film thickness onto to a clean black scrub test panel and allowed to dry horizontally for 15 to 60 minutes in a conditioned room at 23°C ± 2°C and 50 to 55% relative humidity under a constant 2 mph air flow. When the drying time is complete, the samples are placed under a stream of 25°C tap water flowing at a rate of 1.5 gal/min and allowed to remain there for 5 minutes, during which the time of film break through is recorded. After completion of the test, the samples are then removed from the flowing water and observed noting the percentage of wash off.

**Surfactants**

In the present disclosure, a combination of an anionic surfactant and a non-ionic surfactant is used. The anionic surfactant included are provided but not limited to: sodium dodecyl sulfate (SDS), ammonium dodecylsulfate (ADS), disodium salt of ethoxylated lauryl sulfosuccinate and sodium benzyl dodecyl sulfate. The nonionic surfactant includes but is not limited to IGEPAL CA-407®, Triton™ X-100 (Dow), Triton™ X-405 (Dow) and E-Sperse® 703 (Ethox).

The 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 adhesives. Examples of such coating formulations adapted for particular uses include, but are not 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 waterbome polymer composition of the invention, preferably a water-based latex. The polymers and waterbome 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. 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 latex polymer or waterbome 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 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 aspect, the present invention relates to a shaped or formed article which has been coated with coating formulations of the present invention.

A waterbome polymer composition according to the invention may further comprise water, along with a solvent, a pigment (organic or inorganic) and/or other additives and fillers 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 waterbome 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 limited to, leveling, rheology, and flow control agents such as siloxanes, 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. Pat. No. 5,349,026; flattering agents; pigment wetting and dispersing agents and surfactants; ultraviolet (UV) absorbers; 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 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 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 U.S. Pat. No. 5,539,073, styrene-butadiene polymers, vinyl-acetate-ethylene copolymers, and the like.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.
We claim;

1. Polyfunctional amines comprising recurring units derived from the reaction of one tri-glycidyl moiety and a single, di-, or tri-functional amino monomer(s), or combination of mono/bi, mono/tri, mono/tetra, bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra, and tetra/tetra functional amino monomers resulting in one or more polyfunctional amines of formula (I-x):

\[(I-x)\]

\[
\begin{array}{c}
R1 \\
\hline
\downarrow \quad j \quad \downarrow \\
R2 \\
\hline
\end{array}
\]

wherein \( J \) is a substituent that is the result of a ring-opening reaction during nucleophilic substitution of said bi- or tri-glycidyl moiety,

and wherein \( R1 \) is selected from the group consisting of: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, \( \text{N,N,N-} \) trimethyl-1,2-ethane diamine, \( \text{N,N,N-} \) triethyl-1,2-ethane diamine, \( \text{N-methyl-N,N-di-} \) ethyl-1,2-ethane diamine, \( \text{N-ethyl-N,N-dimethyl-} \) 1,2-ethane diamine, \( \text{N-methyl-N,N-diethyll-1,3-} \) propane diamine, \( \text{N-ethyl-N,N-} \) dimethyl-1,3-propane diamine, methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, \( \text{N,N-} \) dimethyl-ethyl diamine, \( \text{N,N-} \) diethyl-ethyl diamine, \( \text{N,N-} \) dimethyl propyl diamine, \( \text{N,N-} \) diethyl-propyl diamine, \( \text{N,N-} \) dimethyl amino propylene amine, \( \text{N,N-dimethyl ethylene amine, N,N-} \) diethyl amino propylene amine, \( \text{N,N-} \) diethylamino ethylene amine, amino ethyl-piperazine, \( \text{N-methyl-1,2-} \) ethane diamine, \( \text{N-ethyl-1,2-} \) ethane diamine, \( \text{N-methyl-1,3-} \) propane diamine, \( \text{N-ethyl-1,3-} \) propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine, \( 2,2'-\) oxybis ethanamine, alanine, and lysine;
and wherein R2 is selected from group consisting of methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-l,2-ethane diamine, N-ethyl-l,2-ethane diamine, N-methyl-l,3-propane diamine, N-ethyl-l,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-l,3,3-trimethylcyclohexanemethylamine,2,2'-oxybis ethanamine, alanine, and lysine;

and where R1 is equal to or different than R2;

and where n is a number from 10 to 100.

2. Polyfunctional amines of Claim 1, wherein said polyfunctional amine structure of formula (I-x) is selected from one of the general structures of formulae (I-x) and/or (I-x-a) to (I-x-f):

(I-x)

```
   R1
 /
 J ---- R2
```

(I-x-a)

```
   J ---- R
```

(I-x-f)
5

(I-x-b)

(I-x-c)

10

(I-x-d)

(I-x-e)

15

(I-x-f)
Wherein the substituents J, Jl, and J2 are the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety,

and wherein J is equal to or different than J1 and J2;

and wherein J1 is equal to or different than J2;

and wherein R1 is selected from the group consisting of: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, N,N,N-trimethyl-1,2-ethane diamine, N,N,N-triethyl-1,2-ethane diamine, N,N-diethyl-1,2-ethane diamine, N-ethyl-N,N-diethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,3-propane diamine, N-ethyl-N,N-diethyl-1,3-propane diamine, methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piparazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-diethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamino ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamino benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine, 2,2'-oxybis ethanamine, alanine, and lysine;

and R2 and R3 are selected from groups consisting of: methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-lycmethyl-2-propyl amine, piparazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-diethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamino benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine, 2,2'-oxybis ethanamine, alanine, and lysine;

and wherein R1 is equal to or different than R2 and R3:
and wherein R2 is equal to or different than R3.

and where n is a number 1 to 100;

and where m is a number equal to or different than n.

3. Polyfunctional amines of Claim 1, wherein the polyfunctional amine of type formula (I-x) is a crosslinking agent bearing -NH or -NH₂ groups with repeating units, n that are further treated with glycidyl alkenyl compounds wherein said compounds are preferably ally glycidyl ethers; and wherein the polyfunctional amine of any of formulae (I-x) and/or (I-x-a) to (I-x-f) must include a -NH or -NH₂ group for further reaction with a glycidyl alkenyl compound that introduces an alkene group thereby forming the intermediate structure of formula (I-x-ene);

\[
\text{I-x-ene}
\]

and wherein introduction of said glycidyl alkenyl compounds to said structure of formula (I-x) occurs only once per repeating unit, n, creating a repeating unit of n-1 when treated with additional polyfunctional amines.

4. Polyfunctional amine compositions of claim 3 wherein said intermediate structure of formula (I-x-ene) when reacted with preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof forms copolymers of formulae (II-x);
wherein substituents J, J1, and J2 are the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety,

and wherein J is equal to or different than J1 and J2;

and wherein J1 is equal to or different than J2;

and wherein R1 is selected from the group consisting of: methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-l,2-ethane diamine, N-ethyl-l,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-l,3,3-trimethylcyclohexanemethylamine,2,2'-oxybis ethanamine, alanine, and lysine;

and R2 and R3 are selected from groups consisting of methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine.
amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-l,3,3-trimethylcyclohexanemethylamine,2,2'-oxybis ethanamine, alanine, and lysine;

and wherein R<sub>1</sub> is equal to or different than R<sub>2</sub> and R<sub>3</sub>;

and wherein R<sub>2</sub> is equal to or different than R<sub>3</sub>;

and wherein R<sub>1</sub>’ is deprotonated R<sub>1</sub> except with a loss of a proton loss at the NH or -NH<sub>2</sub> site;

and wherein R<sub>4</sub> is the linking group between the polyamine body of (II-x) and the alkene functionality and wherein n-1 is a number from four to nineteen;

and wherein m is a number from 1 to 100;

and wherein o is a number from 1 to 100;

and wherein p is a number from 1 to 100;

and wherein repeating substituent R<sub>5</sub> results from polymerization of a water soluble monomer having a carbon-carbon double bond, -C=CH-, preferably an acrylic acid or acrylic acid derivative;

and wherein repeating substituent R<sub>6</sub> results from polymerization of a water soluble monomer having a carbon-carbon double bond, -C=C-, preferably an acrylamide or a derivative of acrylamide;

and where the resulting structure exhibits an atomic mass that is greater than or equal to 50,000 Daltons.

5. The polyfunctional amines of claim 4, wherein when AGE is present during synthesis, said linking group is -CH2CH(OH)CH2O, and wherein said linking group can also be a connecting glycidyl alkenyl compound that is selected from the group consisting of allyl glycidyl ether, vinyl glycidyl ether, vinyl cyclohexene oxide, glycidyl methacrylate, glycidyl acrylate, glycidyl acrylamide, and glycidyl methacrylamide.
6. Polyfunctional amines of claim 2, wherein said compositions are selected from at least one compound of the group consisting of (I-x-1), (I-χ-2'''), and (I-x-3);

(I-x-1)

(I-x-2'''')
7. Polyfunctional amine compositions of claim 3 wherein said composition is an intermediate (I-x-l-ene) formed prior to the polymerization prepared with the addition of allyl glycidyl ether (AGE) resulting as formula (I-x-1);
8. The polyfunctional amine intermediate composition of claim 7 wherein the reaction of said intermediate with preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof results in oligomeric structures (II-x-1) or (II-x-3) or modified structures thereof; (II-x-1)
9. The synthesis of intermediate polyfunctional amines of claim 7 wherein said intermediate amines are reacted with a combination consisting of mono/bi, mono/tri, mono/tetra or bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra for tri-glycidyl monomers, and bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra for bi-glycidyl monomers.

10. The synthesis of polyfunctional amines of claim 8 wherein ratios of glycidyl monomers to amine monomers are as follows; for

(i) the reaction between triglycidyl monomer and single bi, tri and tetra amines, or combinations of bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra amines is represented as:

\[ \frac{M_a}{M_g} = 2n + 1 \]

(ii) the reaction between triglycidyl monomer and a combination of mono/bi amines is:

represented as \( \frac{M_d}{M_g} = 2n + 1 \), and \( \frac{M_{ia}}{M_g} \geq 1 - \ln n \)
the reaction between triglycidyl monomer and a combination of mono/tri amines is represented as \( \frac{M_a}{M_g} = 2n + 1 \), and \( 2M_{\text{tria}}/M_g \geq 1 - l/n \)

the reaction between triglycidyl monomer and a combination of mono/tetra amines is represented as: \( \frac{M_a}{M_g} = 2n + 1 \), and \( 3M_{\text{tetra}}/M_g \geq 1 - l/n \)

the reaction between biglycidyl monomer/combination of biglycidyl monomers and single bi, tri, tetra amines, or combinations of bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra and tetra/tetra amines is represented as \( M_a/M_g = n + 1 \)

the reaction between biglycidyl monomer/combination of biglycidyl monomers and combination of mono/tri amines is represented as:

\[
\frac{M_a}{M_g} = n + 1, \quad \text{and} \quad 2M_{\text{tria}}/M_g \geq 1 - l/n \quad \text{and}
\]

\[
\frac{M_a}{M_g} = n + 1, \quad \text{and} \quad 3M_{\text{tetra}}/M_g \geq 1 - l/n,
\]

wherein \( M_a \) is the molar amount of total amine used in said reaction, \( M_g \) is the molar amount of total glycidyl monomer used in said reaction, \( M_{\text{tria}} \) is the molar amount of total biamine used in said reaction, \( M_{\text{tria}} \) is the molar amount of total triamine used in said reaction and \( M_{\text{tetra}} \) is the molar amount of total tetra-amine used in said reaction and wherein \( n \) is the designated degree of polymerization of said polyfunctional amine.

11. The polyfunctional amines of claim 1, wherein said polyfunctional amines are crosslinking agents.

12. Polyfunctional amines of claim 1 wherein said amines are selected from at least one compound from the group consisting of formulae (I-x) and/or (I-x-a-I-x-f) also comprising additional bi- or tri-glycidyl and amine moieties, wherein lb of said formulae forms structural compounds (I-x-1), (I-x-2’), and (I-x-3) and wherein said structural compounds are derived from a one-step synthesis product excluding any C=C bonds and wherein said amines also containing an \(-\text{NH}\) or \(-\text{NH}_2\) moiety that can either be further treated to form final two-step synthesis products or be used without further treatment to form final \(-\text{NH}\) or \(-\text{NH}_2\) containing one-step synthesis products.
One or more latex formulations comprising polyfunctional amine crosslinking agents with recurring units derived from the reaction of one tri-glycidyl moiety and a single di-, or tri- functional amino monomers, or combination of mono/bi, mono/tri, mono/tetra, bi/bi, bi/tri, bi/tetra, tri/tri, tri/tetra, and tetra/tetra functional amino monomers result in a polyfunctional amine of formula (I-x):

\[
(I-x)
\]

wherein the substituent \( J \) is the result of a ring-opening reaction during nucleophilic substitution of said bi- or tri-glycidyl moiety,

and wherein \( R_1 \) is selected from the group consisting of: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, \( N,N,N \)-trimethyl-1,2-ethane diamine, \( N,N,N \)-triethyl-1,2-ethane diamine, \( N \)-methyl-1-\( N,N \)-diethyl-1,2-ethane diamine, \( N \)-ethyl-\( N,N \)-dimethyl-1,2-ethane diamine, \( N \)-methyl-\( N,N \)-diethyl-1,3-propane diamine, \( N \)-ethyl-\( N,N \)-dimethyl-1,3-propane diamine, methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, \( N,N \)-dimethyl-ethyl diamine, \( N,N \)-diethyl-ethyl diamine, \( N,N \)-dimethyl propyl diamine, \( N,N \)-diethyl-propyl diamine, \( N,N \)-dimethyl amino propylene amine, \( N,N \)-dimethyl ethylene amine, \( N,N \)-diethyl amino propylene amine, \( N,N \)-diethylamino ethylene amine, amino ethyl-piperazine, \( N \)-methyl-1,2-ethane diamine, \( N \)-ethyl-1,2-ethane diamine, \( N \)-methyl-1,3-propane diamine, \( N \)-ethyl-1,3-propane diamine, 1,2-diamino ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine, 2,2'-oxybis ethanamine, alanine, and lysine;

and wherein \( R_2 \) is selected from group consisting of methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, \( N,N \)-dimethyl-ethyl diamine, \( N,N \)-diethyl-ethyl diamine, \( N,N \)-dimethyl...
propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-l,3,3-trimethylcyclohexanemethylamine, 2,2'-oxybis ethanamine, alanine, lysine;

and where R1 is equal to or different than R2;

and where n is an number 10 to 100.

14. One or more latex formulations comprising said polyfunctional amine crosslinking agents of Claim 13, wherein said polyfunctional amine structure of formula (I-x) is selected from one of the general structures of formulae (I-x) and/or (I-x-a) to (I-x-f):

(I-x)

\[
\begin{array}{c}
R1 \\
\mid \\
J \quad R2 \\
\mid \\
\mid \\
n
\end{array}
\]

(I-x-a)

\[
\begin{array}{c}
J \quad R \\
\mid \\
n
\end{array}
\]
wherein the substituents $J$, $J_1$, and $J_2$ are the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety,
and wherein J is equal to or different than J1 and J2;

and wherein J1 is equal to or different than J2;

and wherein R1 is selected from the group consisting of: dimethyl amine, diethyl amine, diethanol amine, dipropyl amine, pyrrolidine, piperidine, 1-methyl piperazine, N,N,N-trimethyl-1,2-ethane diamine, N,N,N-triethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,2-ethane diamine, N-ethyl-N,N-dimethyl-1,2-ethane diamine, N-methyl-N,N-diethyl-1,3-propane diamine, N-ethyl-N,N-dimethyl-1,3-propane diamine, methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamino benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine,2,2'-oxybis ethanamine, alanine, and lysine;

and R2 and R3 are selected from group consisting of methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine,2,2'-oxybis ethanamine, alanine, and lysine;

and wherein R1 is equal to or different than R2 and R3;

and wherein R2 is equal to or different than R3;

and where n is a number 1 to 100;
and where \( m \) is a number equal to or different than \( n \).

15. One or more polyfunctional amine latex compositions of Claim 13, wherein said compositions are crosslinking agents represented by formula (I-x) which when bearing -NH or -NH2 groups with repeating units, \( n \), are further treated with glycidyl alkenyl compounds, and wherein the polyfunctional amine of any of formulae (I-x) and/or (I-x-a) to (I-x-f) must carry a -NH or -NH2 group, for further reaction with a glycidyl alkenyl compound such that introduction of an alkene group forming the intermediate structure of formula (I-x-ene) can occur:

![Diagram of I-x-ene]

and wherein introduction of said glycidyl alkenyl compounds to said structure of formula (I-x) occurs only once per repeating unit, \( n \), creating a repeating unit of \( n-1 \) when treated with additional polyfunctional amines.

16. One or more latex formulations with polyfunctional amine crosslinking agents of claim 13, wherein said intermediate structure of formula (I-x-ene) when reacted with preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof forms oligomers or copolymers of formula (II-x);

\[(II-x)\]
wherein the substituent J, is the result of a ring-opening reaction during nucleophilic substitution of a bi- or tri-glycidyl moiety,

and wherein R1 is selected from the group consisting of: piperidine, piperazine, methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethyamine, 2,2'-oxybis ethanamine, alanine, and lysine;

and R2 and R3 are selected from the group consisting of methyl amine, ethyl amine, 1-propyl amine, ethanol amine, 2-propyl amine, 1-butyl amine, 2-butyl amine, 2-methyl-2-propyl amine, piperazine, N,N-dimethyl-ethyl diamine, N,N-diethyl-ethyl diamine, N,N-dimethyl propyl diamine, N,N-diethyl-propyl diamine, N,N-dimethyl amino propylene amine, N,N-dimethyl ethylene amine, N,N-diethyl amino propylene amine, N,N-diethylamino ethylene amine, amino ethyl-piperazine, N-methyl-1,2-ethane diamine, N-ethyl-1,2-ethane diamine, N-methyl-1,3-propane diamine, N-ethyl-1,3-propane diamine, 1,2-diamine ethane, 1,3-diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethyamine, 2,2'-oxybis ethanamine, alanine, and lysine;
diamino propane, 1,4-diamino butane, cadaverine, cystamine, 1,6-diamino hexane, 1,2-
diamine benzene, 1,3-diamino benzene, 1,4-diamino benzene, 1,4-diamino butanol, 4,4-
diamino-3-hydroxy butanoic acid, 5-amino-1,3,3-trimethylcyclohexanemethylamine,2,2’-
oxylbis ethanamine, alanine, and lysine;

and wherein R1 is equal to or different than R2 and R3;

and wherein R2 is equal to or different than R3;

and wherein R1' is the deprotonated R1 with proton loss at it NH or NH₂ site;

and wherein R4 is the linking group between polyamine body and the alkene functionality. If AGE is employed in this preparation, the linking group is -CH₂CH(OH)CH₂O-. Variations in R4 may be created from each different linking glycidyl alkenyl compound. Potentially, the linking glycidyl alkenyl compound can be selected from one of the following: allyl glycidyl ether, vinyl glycidyl ether, vinyl cyclohexene oxide, glycidyl methacrylate, glycidyl acrylate, glycidyl acrylamide, and glycidyl methacrylamide;

and wherein n-1 is a number between four and nineteen;

and wherein m is a number from 1 to 100;

and wherein o is a number from 1 to 100;

and wherein p is a number from 1 to 100;

and wherein repeating substituent R5 results from polymerization of a water soluble monomer having a carbon - carbon double bond, -C=CH-, preferably an acrylic acid or acrylic acid derivative;

and wherein repeating substituent R6 results from polymerization of a water soluble monomer having a carbon- carbon double bond, -C=C-, preferably an acrylamide or a derivative of acrylamide;

and wherein said resulting structure is greater than or equal to an atomic mass of 50,000 Daltons.
17. One or more latex formulations with polyfunctional amine latex crosslinking agents of claim 13, wherein said compositions are selected from at least one compound from the group consisting of (I-x-1), (I-x-2'''), and (I-x-3):

(I-x-1)

(I-x-2''')

(I-x-3)
18. One or more latex formulations comprising polyfunctional amine latex crosslinking agents of claim 17 wherein said composition is an intermediate (I-x-l-ene) formed prior to the polymerization prepared with the addition of allyl glycidyl ether (AGE) comprising formula (I-x-I);

19. One or more latex formulations of polyfunctional amine latex crosslinking agents with an intermediate composition of claim 18, wherein the reaction of said intermediate with
preferably MAA and ACR, or two other -C=C- functional groups and/or derivatives thereof can result in oligomeric structures (II-x-1) or (II-x-3) or modified structures thereof;

(II-x-1)
20. One or more latex formulations with the structures of claim 19, wherein said structures are polymeric structures of (II-x-1) and (II-x-3).

21. A paint formulation wherein both a latex and the polyfunctional amines of claim 1 is included.

22. The paint formulation of claim 21, wherein said paint additionally includes at least one of the group consisting of: dispersant, defoamer, surfactant, biocide, ammonia, rheology agent, pigment, solvent, coalescent, and water.
23. The paint formulation of claim 21, wherein said paint is used as traffic paint for a pavement surface.

24. The paint formulation of claim 23, wherein when said paint is applied to said pavement surface crosslinking of said paint occurs and said paint dries within 15 minutes so that no early water wash-off can occur.

25. The polyfunctional amines of claim 1, wherein said amines are a result of a condensation reaction of a glycidyl group and an amine group and wherein resulting polyfunctional amines comprise at least three separate amino groups.

26. The polyfunctional amines of claim 25, wherein said polyfunctional amines provide an ability to tailor the final molecular weight of said polyfunctional amine.
FIG. 1

102 Select from (I-x) generic structures (I-x) and/or (I-x-e) to (I-x-f)

104 Select Bi- or Tri- Glycidyl Mieisy

106 Select Amine(s)

108 Make (I-x) product

Eg: I-x

110 Does (I-x) product contain -NH or -NH2 moiety?

No

(Eg: I-x-2)

Yes

112 Add Glycidyl alkyl moiety to (I-x) product

114 Make (I-x-ene) intermediate

Eg: I-x-ene

Eg: I-x-1

Eg: I-x-3

118

(Eg: I-x-1)

116

118

(Eg: I-x-2)

(Eg: I-x-3)

(Eg: II-x-3)

120 Add MAA, ACR, or any C=C functionality or derivative thereof

122 Make (II-x) product

Eg: II-x

124 Make (II-x) product

(Eg: II-x) is used as final product

(Eg: II-x-1)
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC (2016.01) C08K 5/349200, C07D 251/30, C09D 133/12, C09D 121/02, C09D 500, C09D 7/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC (2016.01) C08K 5/349200, C07D 251/30, C09D 133/12, C09D 121/02, C09D 500, C09D 7/12

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See extra sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>U.S. 4265745 A. TELIN LTD. 05 May 1981 (1981/05/05) column 17, line 15; Tables 3-5; column 20, line 25; Table 12, Example 67; Tables 1-13; column 18, line 5; claim 1</td>
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<td>U.S. 5601907 A. AIR PROD &amp; CHEM. [US] 28 Oct 1997 (1997/10/28) Abstract; column 3, line 5; column 4, line 15; column 4, line 35; column 5, line 60; claim 12</td>
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* Special categories of cited documents
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Date of the actual completion of the international search 08 Dec 2016
Date of mailing of the international search report 11 Dec 2016

Name and mailing address of the ISA:
Israel Patent Office
Technology Park, Bldg.5, Malcha, Jerusalem, 9695101, Israel
Facsimile No. 972-2-5651616

Authorized officer NAHAMANI Moshe
Telephone No. 972-2-5651739

Form PCT/ISA/2/16 (second sheet) (January 2015)
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Fomi PCT/ISA/210 (patent family annex) (January 2015)
**B. FIELDS SEARCHED:**

* Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Databases consulted: PATENTSCOPE, USPTO, THOMSON INNOVATION, Epoonline, Esp@cenet, Google Patents, CAPLUS, Google Scholar, Web of Science

Search terms used: TGIC (Triglycidyl isocyanurate), NPDGE (Neopentyl diglycidyl ether), AGE (Allyl glycidyl ether), BDGE (Butanediol diglycidyl ether), DMAPA (N,N-dimethyl amino propyl amine), DEAPA (N,N-diethyl amino propyl amine), DEA (diethyl amine), DAB (1,4-diaminobutane), Polyfunctional amines, amino monomer(s), ring-opening, nucleophilic substitution, crosslinking agents, latex polymer, paint, fast drying/curing