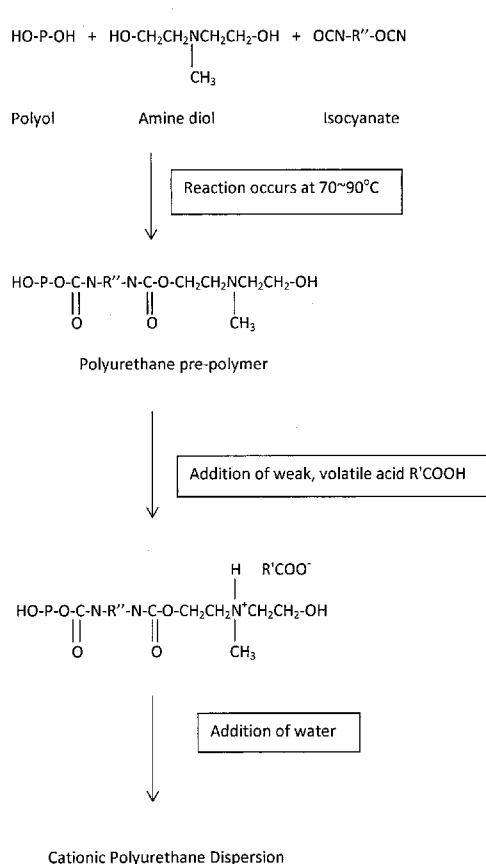




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(54) Title: AQUEOUS CATIONIC POLYURETHANE DISPERSIONS AND THEIR USES



(57) Abstract: There is described a cationic polyurethane dispersion comprising a reaction product of: a di-functional polyol, an isocyanate monomer or a polyisocyanate pre-polymer, and a tertiary amine containing diol in the presence of a solvent and a weak, volatile acid; and their use in blocking tannin migration from surfaces containing tannin.

Figure 1

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## Aqueous Cationic Polyurethane Dispersions and Their Uses

### Field of the Invention

5 The present invention is directed to aqueous cationic polyurethane dispersions, their use in forming tannin blocking coating compositions, processes for making them and uses thereof. In particular, the present invention is directed to aqueous cationic polyurethane dispersions that are capable of drying to a non-ionic state to effectively block the migration of tannin from a substrate.

### 10 Background

In recent years, environmental and safety concerns have placed great pressure on industry to develop water borne coatings to replace their solvent borne counterparts for all applications including for wood surfaces and substrates. However, among many performance related problems, 15 water borne wood coatings have one major disadvantage over solvent borne wood coatings – some components in the water borne wood coatings, such as water, surfactants, wetting agents and certain solvents, can extract some chromophoric substances, such as tannin, from the wood substrates into the wood coating, thus staining the coating. The tannin migration from the wood to the coating often continues even after dry film formation, whenever the dry film makes contact with 20 water, water vapor or moisture.

Many attempts have been made to block the migration of the tannin and other extractable organic stains from the wood into the water borne wood coating. One approach involves use of reactive pigments, which is generally effective, to some extent, in retarding the tannin migration. However, 25 reactive pigments often cause instability of the water borne wood coatings, increasing viscosity and even gelling. In addition, reactive pigments are generally not suitable for clear coat water borne wood coatings.

Another approach is to apply a primer or sealer onto the wood surface, prior to applying the water 30 borne topcoat. Attempted sealers for blocking tannin migration include solvent borne long oil alkyds, anionic latex based sealers, cationic latex based sealers, silane modified latex coating, anionic polyurethane dispersion based sealers, and cationic polyurethane based sealers. All these sealers have some shortcomings, making them ineffective in continued blocking of the tannin migration from the wood into the water borne topcoat.

35

The unsatisfactory tannin blocking performance of the above current art sealers is mainly due to the fact that tannin migration from the wood substrates depends on an array of substrate related factors (such as type of wood and wood water content), weather and climate related factors (such as humidity and water vapor), usage related factors (such as frequency of washing and cleaning) as 40 well as sealer coat related factors (such as low or high pH, solvents or components, film matrix

porosity or tightness, hydrophilic surfactants or wetting agents, water sensitive ionic charges of the polymer etc). The current art is vulnerable to one or more of the above-mentioned factors.

5 The solvent borne long oil alkyds based sealers are generally not suitable for water borne wood coating largely because of their ineffectiveness in tannin blocking due to the low molecular weight oil moiety of the alkyds capable of extracting tannin, high solvent content, an environmental concern, long curing time for tight film formation needed for effective tannin blocking, and the presence of driers which are capable of chelating with tannin to cause continuous tannin extraction from the wood surface.

10

Latex based sealers, both anionic and cationic, are generally not effective for tannin blocking. Anionic latex based sealers are generally not effective largely because of their high porosity in the dry film, high pH favourable for extracting the weak acid tannin, the presence of surfactants which are favourable for absorbing and retaining water or water moisture in the coating for continued  
15 extraction of tannin from the underneath wood substrate. Cationic latex based sealers are also not effective because, besides the higher porosity on the dry film porosity and surfactant contents, they have a permanent cationic charge on the dry film, making the dry film sensitive to water and thus downgrading the tannin blocking effectiveness.

20 Although silane modified latex sealers are able to produce a tighter and less porous coating system than using the latex alone, the polymeric matrix is an ionic bonding between the anionic latex emulsion and the amine cationic counter ion of the silane. Such ionic bonding can be easily dissolved by water, thus weakening its effectiveness of blocking tannin migration.

25 Most current art of anionic and cationic polyurethane dispersion based sealers has several limitations with respect to tannin blocking. The current art of anionic polyurethane based sealers, like their latex emulsion counterparts, are high pH and contain NMP (N-methyl pyrrolidone, an efficient extracting solvent for tannin) and surfactant - all of which are higher risk factors favourable for tannin migration. The current art of cationic polyurethane dispersion based sealers, although low  
30 in pH, contain NMP and have a permanent positive ionic charge on the dry film, which can easily be dissolved by contact with water.

Some prior art has tried to address some of the above problems, only with limited or no success. For example, for the wood tannin blocking applications, US Patent No. 6,531,223 describes a one-  
35 coat system of latex polymers with microspheres and reactive pigments intended to block tannin extraction from wood surfaces. Due to the porosity of the coating, tannin extraction can still take place, especially in the presence of bases in the coating, for example amine pH adjuster - a common ingredient in most latex paint formulations. Furthermore, the use of microspheres in this prior art is not suitable for clear coat applications due to the reduction of clarity by the microsphere.

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US Patent No. 5,527,619 describes a method of improving tannin blocking which involves using an anionic latex modified with silane by blending the latex with organosilane. As aforementioned, although this approach can produce a tighter and less porous system than using the latex alone, the resultant polymeric matrix nonetheless is composed of an ionic bonding between the anionic latex emulsion and the amine cationic counter ion of the silane. Such ionic bonding can be easily dissolved by water, thus weakening the effectiveness of blocking tannin migration. Further, the silane component often causes instability of the silane modified latex sealer.

Published US Patent Application No. 2010/0047598 A1, describes a tannin blocking coating system using a blend of alkyd emulsion and a latex emulsion. This system was capable of only partially blocking tannin migration.

US Patent No. 7,157,120 describes a tannin blocking coating system composed of an anionic polyurethane dispersion and a cross linker of the polyurethane dispersion. This system is only able to reduce the migration of extractable from wood, not block it. The ineffectiveness of this system to block tannin migration is mainly due to the water sensitivity of the polyurethane dispersion and the presence of strong base in the coating. Furthermore, the cross-linker used are carbodiimides, isocyanates, aziridines and melamines; which are all generally considered toxic materials.

Among the current art, a polyurethane dispersion based system has the highest potential of achieving the aforementioned performance target mainly due to their capability of forming a tight film matrix, one of the most critical attributes require for good tannin blocking.

The majority of polyurethane dispersions presently in use are anionic in the wet stage, but convert to a non-ionic state upon dry film formation due to evaporation of the counter amine ion. Although the anionic class of polyurethane dispersions has been used in the aforementioned applications, a number of performance problems remain in the prior art. For example in coating applications, anionic polyurethane dispersions tend to: have corrosion problems due to their acidic terminal groups and water sensitivity; give lower film build and lower gloss due to them being readily soaked into substrates such as woods; extract tannin or other extractables from wood surfaces due to their strong base counter ions in the wet stage; be sensitive to water due to the acid terminal groups, and be sensitive to alkaline agents due to the acid terminal groups.

The other class of polyurethane dispersions presently in use are cationic in the wet stage as well as after dry film formation. Although the cationic charges on the surface of the film give certain performance advantages, such as better adhesion to some surfaces, particularly hydrophobic surfaces, there are a number of problems associated with their applications. In coating applications, for example, cationic polyurethane dispersions have water sensitivity due to the ionic charges causing paint film swelling upon contact with water, and have salting marks after hand touching due to extraction of the  $\text{HSO}_3$  or  $\text{CH}_3\text{SO}_3$  ions from human sweat.

Several processes of making cationic polyurethane dispersion have been known from the prior art. For example, US Patent No. 6,339,125 describes a process of making cationic dispersions using a bis(hydroxyalkyl) quaternary ammonium as the cationic moiety in the presence of methane sulfonic acid. Similarly, US Patent No. 6,518,351 describes a process of making a dispersion of cationic polyurethane acrylic copolymers containing fluorinated acrylic monomers; the cationic moiety of this hybrid polyurethane dispersion is from tertiary amines such as N-methyl diethanol amine in the presence of methane sulfonic acid. The fluorinated moiety may contribute to lack of adhesion between the primer coat and the topcoat.

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The aforementioned prior art processes have produced polyurethane dispersions which are cationic in both wet and dry stage, and accordingly they will have the aforementioned problems associated with the use of such a class of cationic polyurethane dispersion. Furthermore, the resultant polyurethane dispersions produced by much of this prior art contains N-methyl pyrrolidone (NMP), a toxic solvent undesirable for environmentally friendly coatings and products.

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A need exists for alternate water borne polyurethane coating systems capable of minimizing or eliminating the factors that promote tannin extraction and migration from tannin containing substrates.

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#### Summary of the Invention

In work leading up to the present invention, the inventors have developed a new class of cationic polyurethane dispersions (PUD) that retard tannin migration when in a cationic, wet state and are effective tannin blockers following dry film formation and conversion to a non-ionic polymer state. The polyurethane dispersions of the invention are useful in forming tannin blocking coating compositions for tannin containing substrates and can be used in a number of applications including undercoat primers, sealers and as topcoats on tannin containing substrates.

25

30 In a first aspect, the present invention is directed to a cationic polyurethane dispersion which comprises a reaction product of:

- a) a di-functional polyol,
- b) an isocyanate monomer or a polyisocyanate pre-polymer, and
- c) a tertiary amine containing diol,

35 in the presence of:

d) a solvent having a boiling point in the range of about 140 - 260°C selected from the group consisting of glycol ethers, glycol acetates, glycol ether acetates and mixtures thereof;

e) a weak, volatile acid in an amount sufficient to ensure the cationic polyurethane dispersion has a low pH; and

40 f) water.

It will be understood that aqueous polyurethane dispersions are formed in a wet stage and then allowed to dry to form a solid polymer. The cationic polyurethane dispersion (PUD) according to the first aspect of the invention is in a cationic state whilst in the wet stage and upon drying, converts to a non-ionic state in a dry polymer form.

According to the present invention, the cationic PUD in the aqueous state is effective in retarding tannin extraction from a wood substrate and upon drying, the resultant non-ionic polyurethane polymer is able to block further tannin migration from a tannin containing wood substrate.

According to the present invention, the presence of an external surfactant is not required in the formation of the cationic polyurethane dispersion. Accordingly, in one embodiment, the cationic polyurethane dispersion according to the invention is formed in the absence of an external surfactant.

Preferably, the cationic polyurethane dispersion as referred to in the first aspect of the invention consists essentially of a reaction product of a) - f).

In a second aspect, the present invention is directed to a tannin blocking coating composition comprising the cationic polyurethane dispersion of the first aspect together with one or more coating excipients.

The coating composition may also include known epoxy emulsions, latex emulsions, anionic and cationic acrylic emulsions, cationic and anionic polyurethane dispersions and/or other compatible water borne polymers.

In a third aspect, the present invention is directed to a tannin blocking, non-ionic polyurethane polymer formed by drying the cationic polyurethane dispersion of the first aspect or the coating composition of the second aspect of the invention.

In a fourth aspect, the present invention is directed to a method of preparing a cationic polyurethane dispersion comprising the steps of reacting:

- i) a di-functional polyol,
  - ii) isocyanate monomers or a polyisocyanate pre-polymer, and
  - iii) a tertiary amine containing diol,
- in the presence of a solvent to form a polyurethane pre-polymer, and
- iv) dispersing the polyurethane pre-polymer in water in the presence of a weak, volatile acid, wherein the solvent has a boiling point in the range of about 140 - 260°C and is selected from the group consisting of glycol ethers, glycol acetates, glycol ether acetates and mixtures thereof.

In one embodiment, the cationic polyurethane dispersion is as defined in the first aspect of the invention.

5 In a fifth aspect, the present invention is directed to a method of blocking or retarding tannin migration from a tannin-containing substrate comprising:

- i) applying a cationic polyurethane dispersion according to the first aspect or a coating composition according to the second aspect of the invention to the tannin-containing substrate; and
- ii) drying the cationic polyurethane dispersion or coating composition so as to convert the cationic polyurethane dispersion into a non-ionic polyurethane polymer.

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In a sixth aspect, the present invention is directed to a cationic polyurethane dispersion according to the first aspect or a coating composition according to the second aspect when used to retard tannin migration from a tannin containing surface.

15 In a seventh aspect, the present invention is directed to a cationic polyurethane dispersion according to the first aspect or a coating composition according to the second aspect when used as a coating sealer or as a topcoat for tannin containing surfaces.

20 In another aspect there is provided a tannin blocking, non-ionic polyurethane polymer according to the third aspect when used to block tannin migration from a tannin containing surface.

In yet another aspect, there is provided a tannin blocking, non-ionic polyurethane polymer according to the third aspect when used as a coating sealer or a topcoat for a tannin containing surface.

25 Tannin containing surfaces include but are not limited to wood, particleboard and leather.

Throughout the specification the phrase "consisting essentially of" is intended to exclude features that materially effect the properties/characteristics of the invention described and defined herein.

30 Throughout this specification, the word "comprise", or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated element, integer or step, or group of elements, integers or steps, but not the exclusion of any other element, integer or step, or group of elements, integers or steps.

35

### Brief Description of the Drawings

Figure 1 shows a general reaction scheme for the formation of a cationic polyurethane dispersion according to one embodiment of the first aspect of the present invention.

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Figure 2 shows a general reaction scheme for the formation of the non-ionic polyurethane resin according to one embodiment of the third aspect of the present invention.

### Detail Description of Embodiments

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According to the present invention, the cationic polyurethane dispersion has the following unique molecular features: a urethane containing backbone, tertiary amine containing moieties, weak acid counter ions that originate from weak volatile acids, and specific counter coalescence solvents selected from group consisting of glycol ethers, glycol acetates, glycol ether acetates and mixtures thereof. These unique cationic PUD's are useful in retarding tannin migration from a tannin containing substrate. The cationic PUD'S of the invention are environmentally friendly, specifically because they do not contain NMP.

15

The new series of cationic polyurethane dispersions of the present invention have performance attributes which include:

20

- N-methyl pyrrolidone (NMP) free;
- surfactant free;
- a low pH;

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cationic PUD molecular design which is capable of remaining in cationic state in dispersion form or the wet state (contributing to the stability of the dispersion) and yet capable of converting to a non-ionic state upon dry film formation capable of forming a tight and water impermeable film matrix which results in continued blocking of tannin migration after dry film formation. This unique molecular feature makes the dry film less water sensitive, thus making it capable of blocking the continuous tannin extraction upon contact with water or moisture.

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More specifically, the cationic charge of the cationic polyurethane dispersion of the present invention in the wet stage is desirable for dispersion stability and the low pH of the cationic dispersion retards the migration of the acidic tannin upon application to a tannin containing substrate, such as a wood surface, when the coating is still in the wet stage on the wood surface. Further, the desirable feature of the resulting non-ionic dry film following drying of the cationic polyurethane dispersion, is that the lack of charge effectively blocks the continuous extraction of tannin from the wood substrate upon contact with water.

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The formation of the polyurethane dispersion of the invention involves reacting a di-functional polyol and isocyanate monomer or polyisocyanate pre-polymer with a tertiary amine containing diol in the presence of a particular solvent to form a pre-polymer of polyurethane having a tertiary amine containing moiety. The pre-polymer of polyurethane is then dispersed in water under elevated  
5 temperature, as specified below, in the presence of a weak volatile acid and a solvent. The acid may be added before the addition of water or in conjunction with the water. In one embodiment, the acid is added before addition of water.

The di-functional polyol that is used in the present invention for the preparation of the urethane pre-  
10 polymer includes known polyols compounds conventionally used for the preparation of polyurethanes and include having greater than one function hydroxyl group and include but are not limited to any polyhydroxylated polymers or oligomers and alkylene oxide and caprolactone adducts. Examples of suitable di-functional polyols include polyethers, polyesters, polyesteramides, polyacetals, polythioethers, polycarbonates and polybutadienne. Particularly preferred di-functional  
15 polyols include polyether polyol, polyester polyol, polycarbonate polyol, neopentyl glycol adipate and combinations thereof. Most preferably, the di-functional polyol is polycarbonate polyol. When the cationic PUD is formed using polycarbonate polyol, the inventors have found that the resulting non-ionic PUD polymer is impermeable to water.

20 Preferably, the amount of di-functional polyol used to form the cationic PUD is in the range of 5 - 50 wt%, more preferably 10 - 40 wt%, even more preferably, about 19 - 30 wt%.

The isocyanate monomers used in the present invention include but are not limited to aromatic isocyanates including but not limited to 2,4-toluene diisocyanate, 2,6 toluene diisocyanate, xylene  
25 diisocyanate and methylene-4,4'-phenyl diisocyanate; aliphatic isocyanates including but not limited to isophorone diisocyanate, hexamethylene diisocyanate, tetramethyl hexamethylene diisocyanate, methylene-4,4'-bis(hydroxypropyl) diisocyanate, 4,4' methylene dicyclohexyl diisocyanate; and mixtures thereof. As discoloration of the finished film may occur using aromatic isocyanate, the aliphatic isocyanates are preferred. Preferably, the isocyanate is 4,4' methylene dicyclohexyl  
30 diisocyanate. When the cationic PUD is formed using 4,4' methylene dicyclohexyl diisocyanate, the inventors have found that the resulting non-ionic PUD polymer has the desirable properties of being tough and flexible.

Preferably, the polyisocyanate pre-polymer in the present invention is prepared from any isocyanate  
35 monomers with at least two cross-linkage isocyanate functional groups. Suitable isocyanate monomers are as indicated above.

The polyisocyanate pre-polymers that may be used in the present invention include but are not limited to those formed from combinations of the above isocyanate monomers.

Preferably, the amount of isocyanate monomers used to form the cationic PUD is in the range of 3 - 20 wt%, more preferably 4 - 15 wt%, even more preferably, about 5 - 7 wt%.

The tertiary amine containing diol used in the present invention include any compound that contains both a tertiary amine group and a diol. The tertiary amine containing diol include but are not limited to N-methyl diethanol amine, N-ethyl diethanol amine, N-propyl diethanol amine, N-methyl dipropanol amine, N-ethyl dipropanol amine, N-methyl dibutanol amine, N-ethyl dibutanol amine, N-propyl dipropanol amine, 3-(diethylamino)-1,2-propanediol, 2-(dimethylamino)-1,3-propanediol, 2-(diethylamino)-1,3-propanediol, 2-(dimethylamino)-1,4-butanediol, 2-(diethylamino)-1,4-butanediol and mixtures thereof. Preferably, the tertiary amine containing diol is N-methyl diethanol amine. When the cationic PUD is formed using N-methyl diethanol amine, the inventors have found that it reacts readily with polyisocyanate without the need of high temperature and catalyst.

Preferably, the amount of tertiary amine containing diol used to form the cationic PUD is in the range of 0.5 - 15 wt%, more preferably 1 - 10 wt%, even more preferably, about 2 - 4 wt%.

The cationic PUD of the present invention is formed using a weak, volatile acid in an amount sufficient to ensure the cationic polyurethane dispersion has a low pH. Preferably, the pH is <7, more preferably the pH is in the range of about 3 - 6.5, even more preferably, in the range of about 4 - 5.5. The presence of weak acidic counterions facilitates the formation of a stable dispersion.

The weak volatile acid used in the present invention are weak organic acids that are able to evaporate under ambient conditions. The weak volatile acid includes but is not limited to formic acid, acetic acid, propanoic acid, carbonic acid or combinations thereof. Preferably, the weak volatile acid is acetic acid. When the cationic PUD is formed using the above weak volatile acids, preferably acetic acid, the inventors have found that a stable low pH solution is able to be maintained. In one embodiment, a pH in the range of about 4.5 - 5.5 is maintained.

Preferably, the amount of acid used to form the cationic PUD is in the range of 0.1 - 10 wt%, more preferably 0.3 - 5 wt%, even more preferably, 0.5 - 3 wt%.

It is essential to the present invention that the weak acid is volatile. Non-volatile acids such as 0.1 N HCl, methane sulfonic acid or p-toluene sulfonic acid would result in a positive charge remaining on the dry film, making formation of a non-ionic dry film impossible.

The term "ambient conditions" is intended to mean a standard ambient temperature of about 25°C and atmospheric pressure.

The solvent used in the present invention has a boiling point in the range of about 140 - 260°C and is selected from the group consisting of glycol ethers, glycol acetates, glycol ether acetates and mixtures thereof. The solvent used in the present invention functions as both a coalescence solvent and a co-solvent for the dispersion. To reduce environmental contamination, the solvent used to form the cationic PUD is not N-methyl pyrrolidone (NMP).

Accordingly, the solvent is water miscible, contains no hydroxyl groups, is not strongly alkaline and is less toxic to the environment than NMP.

The solvent used in the present invention is selected from one or more of the group consisting of glycol ethers, glycol acetates, glycol ether acetates. Preferably, the solvent is selected from the group including but not limited to diethylene glycol dimethyl ether, propylene glycol methyl ether, propylene glycol ethyl ether, dipropylene glycol methyl ether, propylene glycol diacetate, propylene glycol methyl ether acetate, dimethyl dipropylene glycol ether and combinations thereof. Most preferred are solvents with low tannin extracting properties. Preferably, the solvent is selected from the group consisting of propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol diacetate, propylene glycol methyl ether acetate and combinations thereof. Most preferred is dimethyl dipropylene glycol ether because it has the highest solubility value in water and has low tannin extracting properties.

The presence of solvent is essential to the formation of the cationic PUD's of the present invention and it is not removed during the entire polymerisation process. The solvent essentially acts as a coalescence solvent and assists in film formation when the non-ionic PUD is formed following evaporation of the water.

The amount of solvent used in the cationic PUD dispersion may be in the range of about 5 - 40 %w/w, preferably about 5 - 25 %w/w. More preferably, the amount of solvent is in the range of about 10 - 15 %w/w. Most preferably, the maximum amount of solvent is about 15 %w/w.

The formation of the pre-polymer according to the invention is carried out by reaction of a mixture of the di-functional polyol, isocyanate monomer/polyisocyanate pre-polymer and the tertiary amine containing diol in the presence of a solvent.

The formation of the polyurethane pre-polymer is characterized by the hydroxyl group being reacted in a concentration of between about 0 and 15% in excess of the stoichiometric concentration required to completely react with the isocyanate monomer/polyisocyanate. Accordingly, the formation of the prepolymer occurs until there are substantially no free isocyanate groups detected resulting in a pre-polymer with no free isocyanate groups. The concentration of tertiary amine containing diol present is sufficient to provide adequate stability to the polyurethane dispersion in water.

Preferably, polymerization of the above mixture to form the polyurethane pre-polymer occurs at a temperature in the range of about 35°C to 95°C, preferably over a period of between about half an hour and about 5 hours. Preferably polymerization occurs at a temperature in the range 50 - 90°C, more preferably about 70 - 90°C. In one embodiment, the mixture is heated to about 90°C. In another embodiment, the mixture is heated to about 85°C. The reaction continues until the free isocyanate content reaches or is close to the theoretical value, as determined by standard titration with dibutylamine. Preferably, the mixture is held at the desired temperature for a period until the measured % NCO content is less than about 0.1%. This corresponds to the amount of free isocyanate being less than 0.4%. In one embodiment of the invention, the mixture is held at the desired temperature for up to about 2 hours until the measured % NCO content is less than about 0.1%. In another embodiment, the mixture is held at the desired temperature for up to about 3 hours until the measured % NCO content is less than about 0.1%.

15 The polyurethane pre-polymer is then dispersed in water in the presence of a weak volatile acid to form the cationic polyurethane dispersion of the present invention.

Following heating, the resulting reaction mixture (polymerised polyurethane pre-polymer) is adjusted to a temperature suitable for dispersion formation. Generally, the resulting reaction mixture is cooled, as the initial reaction temperature is usually about 10 - 20°C higher than the dispersion temperature. Preferably the reaction mixture is cooled below 70°C, more preferably below 60°C, even more preferably below 50°C. In one embodiment, the reaction mixture is cooled to a temperature in the range of about 35 - 70°C. The dispersion of the invention may be formed by agitation, preferably vigorous agitation of the mixture, and the addition of water and weak volatile acid. The acid may be added to the mixture in conjunction with the water or the acid or water may be added first followed by the addition of the other.

Figure 1 depicts a general reaction for the formation of a cationic polyurethane dispersion according to a preferred embodiment of the invention. The di-functional polyol, as hereinbefore defined, is represented by the general formula HO-P-OH. The isocyanate, as hereinbefore defined, is represented by OCN-R'-NCO. The amine diol is represented by N-methyl diethanol amine.

Figure 2 depicts a general reaction scheme for the drying of the cationic polyurethane dispersion from Figure 1 to form the dry polymer film according to one preferred embodiment of the present invention.

The resulting dispersion is the cationic PUD of the present invention. The present inventors have found that the cationic PUD of the present invention retards tannin migration when used on a tannin containing surface prior to drying to form the non-ionic PUD.

According to the present invention, drying of the cationic PUD results in formation of a non-ionic PUD which has tannin blocking properties. Drying may be achieved in air at room temperature, preferably in the range of 25 - 28°C, over an extended period which may range from a few hours to a few days or a few weeks. Accelerated drying times may be achieved with increased temperatures, using known methods including mechanical dryers.

More specifically, the advantages of having a non-ionic PUD in the dry state are firstly, the non-ionic film is much less water sensitive (not hydrophilic) than an ionic film (e.g. the cationic), and thus upon contact with water or moisture, the dry film can maintain its polymeric integrity, mechanical strength and other physical properties, making the tight film less permeable to stains and other molecules, thus making continuous extraction of the ionic tannin from the wood substrate much less likely. Secondly, there will not be any formation of salt on the film upon contact with charged materials (either organic or inorganic). Thirdly, since tannin materials are polar substances, a non-ionic dry film is less likely to attract tannin from the core of the wood substrate.

The new series of polyurethane dispersions made by the new process of this invention has many applications, including coatings, adhesives, and sizing agents for glass fibers and minerals. The dispersions are particularly suitable for coating applications for substrate surfaces such as wood, metal, plastic, and cement/concrete, textiles, leather etc. For these applications, the new series of polyurethane dispersions can be blended with other systems including but not limited to epoxy emulsions, latex emulsions, anionic and cationic acrylic emulsions, cationic and anionic polyurethane dispersions or other compatible water borne polymers to achieve certain cost performance objectives.

According to one aspect of the invention, there is provided a tannin blocking composition comprising the cationic polyurethane dispersion of the invention together with one or more excipients.

The one or more excipients included in the composition will depend on the application of the composition. Different excipients may be used for different applications such as for coatings (e.g. sealers), adhesives, sizing agents etc. The excipient includes but is not limited to defoamers, pigments, extenders, dispersing agents, wetting agents, anti-freeze agent (including but not limited to propylene glycol) and water.

Examples of defoamers include but are not limited to BYK 011, BYK-012, BYK-014, BYK-015, BYK-020, BYK-022, BYK-023, Rhodeline DF681F, Surfynol DF-58, Surfynol DF-62, Surfynol DF-66 and Surfynol DF-110.

Examples of pigments and extenders include but are not limited to titanium dioxide, different colours of iron(II) oxides, carbon black, all sizes of calcium carbonate, talc powder and fibres and fused silica powder.

Examples of dispersing agents include but are not limited to Orotan 850, Anti-Terra U, BYK 105, Zetaspheres 1200, Zetaspheres 1600, Zetaspheres 2100, Zetaspheres 2300, Zetaspheres 2500, Zetaspheres 3100, Zetaspheres 3400 and Zetaspheres 3700.

5

Examples of wetting agents include BYK 333, BYK 303, Carbowet 100, Carbowet 106, Carbowet 109, Carbowet 125, Carbowet 13-40, Carbowet 144, Carbowet 300, Carbowet 76, Carbowet DC01, Carbowet DC11, BYK 304 etc.

10 When the tannin blocking composition is intended as a tannin blocking clear sealer, for instance, the composition may comprise the cationic PUD of the present invention together with propylene glycol, BYK 304 and water. For a pigmented (e.g. white) tannin blocking sealer it may additionally comprise anti-Terra U (dispersing agent) , talc powder (extender), silica flour (extender), titanium dioxide (white pigment), RM 2020 (rheology modifier).

15

The cationic PUDS of the present invention are compatible with other systems including but not limited to epoxy emulsions, latex emulsions, anionic and cationic acrylic emulsions, cationic and anionic polyurethane dispersions. Testing for compatibility of the PUD's of the invention with other systems was carried out by mixing the PUD'S with for example a latex emulsion, leaving the  
20 resulting solution for about 30 - 60 minutes and observing for particle settlement.

The presence of a non-ionic or ionic state of the polymer in the dry film is easily determined according to known methods based on their water sensitivity. This involves applying a PUD dispersion to a glass panel and drying for about 1 week to form a dry film. The dry film is then wet  
25 with water. Whitening of the polymeric film indicates dry film damage including loss of mechanical properties such as hardness. This indicates the presence of an ionic polymer rather than a non-ionic polymer. The polymeric film produced by the present invention is non-ionic, thus it is not hydrophilic and not sensitive to water. Films that have a cationic charge are hydrophilic and water sensitive and result in whitening of the film when water is applied.

30

## EXAMPLES

The following examples are intended to illustrate the invention, and should not be construed as limiting the invention in any way.

35

### Example 1

The solvents listed below in Table 1 were examined for their tannin extracting properties.

A drop of solvent was added to the surface of Merbau wood and left for 1 minute. A clean white paper was used to wipe the liquid off. The degree of red staining on the paper by the extracted tannin was observed.

5. The following table (Table 1) illustrates the tannin extracting properties of a number of solvents.

**Table 1:**

Solvent used	Result
Water	4
N-methyl pyrrolidone (NMP)	5
Dimethyl dipropylene glycol ether (DMDPG)	1
Mixture of ratio of NMP: Water : 5: 95	3
Mixture of ratio of DMDPG ether : Water : 5:95	2
Mixture of ratio of NMP: Water : 10:90	4
Mixture of ratio of DMDPG ether : Water : 10:90	1~2

- 10 Score ratings:

0 no stain found  
5 Very red stain found

- The above table shows that the use of NMP can extract a large degree of tannin from the wood  
15 while the use of DMDPG ether shows a low degree of tannin extraction.

The following examples 2 to 4 illustrate the process of preparing the polyurethane polymer:

**Example 2:** Preparation of Polypropylene Glycol Based Cationic Polyurethane Dispersion

20

Substance Used	Supplier	Weight/g	%w/w	Function
Polypropylene Glycol of Mw 2000	Dow Chemical	90	26.34	di-functional polyol
Isophorone Diisocyanate	Evonik Degussa	18.67	5.46	isocyanate monomer
N-methyl dibutanol amine	Taminco	10	2.93	tertiary amine
Propylene Glycol Ethyl Ether	Dow Chemical	50.86	14.88	solvent
Formic acid	Sigma aldrich	2.63	0.77	Weak volatile organic acid
Deionised Water		169.52	49.61	
<b>Total</b>		<b>341.69</b>		

Polypropylene Glycol of Mw 2000, isophorone diisocyanate, N-methyl dibutanol amine and propylene glycol ethyl ether were loaded into a round bottom reactor equipped with an overhead stirrer and a temperature controller.

5

The mixture was heated to 85°C and it was held for 2 hours until the measured % NCO content was less than 0.1%.

10 The mixture was then cooled to below 60°C. With vigorous agitation, formic acid followed by water was added to enable a good dispersion.

**Example 3: Preparation of Polyester Based Cationic Polyurethane Dispersion**

Substance Used	Supplier	Weight / g	%w/w	Function
RSP-2163 (neopentyl glycol adipate)	PCTS	180	23.67	di-functional polyol
Hexamethylene diisocyanate	Bayer AG	43.34	5.70	Isocyanate monomer
N-Ethyl diethanol amine	Taminco	20	2.63	tertiary amine
Propylene glycol methyl ether acetate (Dowanol PMA)	Dow Chemical	91.26	12.05	solvent
Glacial Acetic Acid	Sigma aldrich	20.18	2.65	Weak volatile organic acid
Deionised Water		405.66	53.35	
<b>Total</b>		<b>760.44</b>		

15 RSP-2163, hexamethylene diisocyanate, N-ethyl diethanol amine and Dowanol PMA were loaded into a round bottom reactor equipped with an overhead stirrer and a temperature controller.

The mixture was heated to 90°C and it was held for 3 hours until the measured % NCO content is less than 0.1%.

20

The mixture was then cooled to below 50°C. With vigorous agitation, water and acetic acid were added to enable a good dispersion.

**Example 4:** Preparation of Polycarbonate based Cationic Polyurethane Dispersion

Substance Used	Supplier	Weight / g	%w/w	Function
Oxymer M-56 (Poly(oxy-carbonyloxy 2-butyl-2-ethyl-1,3-propanedioyl))	Perstorp	85	19.87	di-functional polyol
Methylene-4,4'-bis(cyclohexyl) diisocyanate	Evonik Degussa	25.80	6.03	isocyanate monomer
N-ethyl dipropanol amine	Taminco	15	3.51	tertiary amine
Diethylene glycol dimethyl ether	Dow Chemical	62.90	14.71	solvent
Propanoic acid	Sigma Aldrich	8.35	1.95	Weak volatile organic acid
Deionised Water		230.63	53.93	
<b>Total</b>		<b>427.68</b>		

The procedures were similar to that of Example 2.

5

The following examples 5 to 7 illustrate the cationic polyurethane dispersion based, tannin blocking, water borne wood coating sealer.

**Example 5:** Clear coat tannin blocking sealer for wood surfaces and substrates

10

Various wood such as cedar and Merbau, comprise relatively high levels of extractive that include oil, rosins and tannin. These extractive content can migrate to the surface of the wood over time and it can accelerate upon application of heat. This migration of extractable, especially tannin, to the surface of the wood, often leads to adhesion problems between the coating and the wood, and staining or discoloration of the coating.

15

Currently available tannin blocking primers are solvent-based coating systems including two component urethanes composition and oil modified urethane systems. Waterborne coatings with similar performance are particularly desirable because of safety, health and environment concerns on the solvent primers.

20

**Illustrative Example** of Clear-coat Tannin Blocking Sealer (Formula 1)

Substance Used	Supplier	Weight / g	Function
Dispersion as stated in Example 4	Ex 4	100	Cationic PUD
Propylene Glycol	Dow Chemical	1	Anti-freezing agent
BYK 304	BYK	0.30	Wetting agent
Deionised Water		73.2	
<b>Total</b>		<b>175</b>	

All the stated materials stated are mixed thoroughly to give a final coating system of 20% solid  
 5 content and 220 cps.

**Comparative Example** of Clear-coat Tannin Blocking Sealer using Acrylic Emulsion (Formula 2)

Substance Used	Supplier	Weight / g	Function
Acrylic Emulsion of MFT 8°C – developed for tannin blocking	BASF	100	Binder
Propylene Glycol	Dow Chemical	1	Anti-freezing agent
BYK 304	BYK	0.30	Wetting agent
Deionised Water		73.2	
<b>Total</b>		<b>175</b>	

10 Methods and results of evaluation for tannin blocking property:

The Merbau wood panels were sanded smoothly by the use of 220 sanding paper. A clear sealer coat (Formula 1 or 2 - see below) was applied onto the wood panels. After allowing the clear coat tannin blocking sealer to air dry at room temperature (25~28°C) for 3 to 5 hours, a coat (about 75  
 15 micro-mil wet thickness) of a commercial white latex based paint was applied over the clear coat tannin blocking sealers. Then these painted wood panels were placed in a humidity chamber with relative humidity of 90% for 16 hours. After that, the degree of tannin staining was evaluated and graded.

20

**Results of tannin blocking evaluation:**

Tannin blocking sealers	Tannin Blocking properties
Formula 1 based on resin obtained from dispersion of Example 4	5
Formula 2 based on acrylic Emulsion MFT 8	2

**Tannin score:**

- 5: Best (no tannin stain on panel surface)  
 4: Slight amount of stain covering less than 5% of panel surface  
 3: Moderate amount of stain covering less than 30% of panel surface  
 2: Large amount of tannin stain covering less than 50% of the panel surface  
 1: Worst (tannin stain cover more than 70% of panel)

10

The above results have demonstrated that the tannin blocking sealer Formula 1 (based on a cationic PUD as described in Example 4) has much better tannin blocking ability than the blocking sealer Formula 2 (based on an acrylic emulsion).

- 15 **Example 6:** Application as pigmented (white) tannin blocking sealer in wood coating applications

**Illustrative Example of Pigmented Tannin Blocking Sealer (Formula 3)**

Substance Used	Supplier	Weight / g	Function
Water		6.67	
Anti-Terra U	BYK	3.04	Dispersing agent
Talc Powder	Dhirajlah & Co	8.33	Extender
Silica Flour	Evonik Degussa	6.48	Extender
Titanium dioxide	Dupont	15.47	Pigment
Cationic PUD resin stated in Example 2		40.74	Binder
RM 2020	Rohm & Haas	1.10	Rheology Modifier
Water		17.97	
<b>Total</b>		<b>100</b>	

20

**Comparative Example of Pigmented Tannin Blocking Sealer using Acrylic Emulsion (Formula 4)**

Substance Used	Supplier	Weight / g	Function
Water		6.67	
Anti-Terra U	BYK	3.04	Dispersing agent
Talc Powder	Dhirajlah & Co	8.33	Extender
Silica Flour	Evonik Degussa	6.48	Extender
Titanium dioxide	Dupont	15.47	Pigment
Acrylic Emulsion of MFT 8°C – developed for tannin blocking	BASF	40.74	Binder
RM 2020	Rohm & Haas	1.10	Rheology Modifier
Water		17.97	
<b>Total</b>		<b>100</b>	

Water, Anti-Terra U, Talc Powder, Silica Flour and Titanium dioxide were mixed together with a high disperser until the fineness was less than 50 um.

Resin obtained from the dispersion formed in Example 2, RM 2020 and water were added when the agitation speed was reduced to only mixing speed. The resultant coating had a viscosity of 70 KU.

10 Methods and results of evaluation for tannin blocking property:

The methods are the same as those stated for the clear-coat tannin blocking sealer.

**Resultsof tannin blocking evaluation**

15

Tannin blocking sealers	Tannin Blocking properties
Formula 3 based on resin from Example 2	5
Formula 4 based on acrylic Emulsion MFT 8	3

**Tannin scores:**

- 5: Best (no tannin stain on panel surface)
- 4: Slight amount of stain covering less than 5% of panel surface
- 20 3: Moderate amount of stain covering less than 30% of panel surface
- 2: Large amount of tannin stain covering less than 50% of the panel surface
- 1: Worst (tannin stain cover more than 70% of panel)

The above results have demonstrated that the tannin blocking sealer of Formula 3 (based on cationic PUD as described in Example 2) has much better tannin blocking ability than the blocking sealer of Formula 4 (based on an acrylic emulsion).

5 The following examples 7 and 8 illustrate blending compatibility with latex emulsions.

**Example 7:** Blending compatibility of cationic PUD with regular pure acrylic latex emulsion

Methods and evaluation of compatibility:

10

Weigh the amount of latex emulsion into the beaker. Place this beaker onto a magnetic stirrer plate. With low speed agitation, add the required polyurethane dispersion into the beaker. After stirring for 10 minutes, the physical appearance for the blended mixture was inspected and its viscosity measured by cup method.

15

**Results:**

	PUD stated in Example 2	PUD stated in Example 3	PUD stated in Example 4
Acrylic Latex Emulsion (Non-ionic, %N.V~35% and MFT 40°C)	Mixable and no increase in viscosity	No gelation and no settling	Mixable without any settlements
Acrylic Latex Emulsion (Anionic, % N.V~45%, MFT 20°C)	No increase in viscosity and no settlement found	Mixable	Mixable without settling found

The above results have demonstrated that the cationic PUD prepared according to this invention is compatible with some anionic latexes in blending.

20

**Example 8:** Blending compatibility with cationic latex emulsions

Methods and evaluation of compatibility

25 The method is the same as the one stated in Example 7.

**Results:**

	PUD stated in Example 2	PUD stated in Example 3	PUD stated in Example 4
Cationic Latex (% N.V~30% and MFT 0°C)	Extremely mixable	Mixable	Extremely mixable
Latex Emulsion (% N.V ~37% and MFT 4°)	Mixable	Mixable	Mixable

The above results have demonstrated that the cationic PUD prepared according to this invention is compatible with cationic latexes in blending.

**Example 9:** Test for determining whether or not a non-ionic polymeric dry film has formed after  
5 drying a PUD

A simple experiment can determine if a dry film is ionic or non-ionic on the basis of their difference in water sensitivity:

10 Apply the film produced according to the present invention onto a glass panel, and apply another film that is neutralised by 0.1 M HCl onto another glass panel. Allow these two films to dry for 7 days; after the 7 days of dry film formation, wet the films with tap water.

The polymeric film according to the present invention does not show any whitening (an indicator of  
15 dry film damage) or visible damages, while the other film neutralised by 0.1 HCl turns white and loses most of its mechanical properties such as hardness. The film produced by the present invention is non-ionic, thus it is not very hydrophilic; but the dry film produced by the other system still contains cationic charge, thus making it very hydrophilic and water sensitive.

20 This test was carried out to verify the formation of a non-ionic dry film in the above Examples.

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all  
25 respects as illustrative and not restrictive.

CLAIMS

The claims defining the invention are:

- 5 1. A cationic polyurethane dispersion which comprises a reaction product of:  
a) a di-functional polyol,  
b) an isocyanate monomer or a polyisocyanate pre-polymer, and  
c) a tertiary amine containing diol,  
in the presence of:  
10 d) a solvent having a boiling point in the range of about 140 - 260°C selected from the group consisting of glycol ethers, glycol acetates, glycol ether acetates and mixtures thereof;  
e) a weak, volatile acid in an amount sufficient to ensure the cationic polyurethane dispersion has a low pH; and  
f) water.
- 15 2. The cationic polyurethane dispersion according to claim 1 wherein the di-functional polyol is selected from the group consisting of polyhydroxylated polymers or oligomers and alkylene oxide and caprolactone adducts.
- 20 3. The cationic polyurethane dispersion according to claim 1 or 2 wherein the di-functional polyol is selected from the group consisting of polyethers, polyesters, polyesteramides, polyacetals, polythioethers, polycarbonates and polybutadienne glycols.
4. The cationic polyurethane dispersion according to any one of claims 1-3 wherein the di-  
25 functional polyol is selected from the group consisting of polyether polyol, polyester polyol, polycarbonate polyol, neopentyl glycol adipate and combinations thereof, preferably polycarbonate polyol.
5. The cationic polyurethane dispersion according to any one of claims 1-4 wherein the di-  
30 functional polyol is in the range of 5 – 50 wt%, more preferably 10 - 40 wt%, even more preferably, about 19 - 30 wt%.
6. The cationic polyurethane dispersion according to any one of claims 1-5 wherein the  
isocyanate monomer is selected from the group consisting of aromatic isocyanates including 2,4-  
35 toluene diisocyanate, 2,6 toluene diisocyanate, xylene diisocyanate and methylene-4,4'-phenyl diisocyanate; aliphatic isocyanates including isophorone diisocyanate, hexamethylene diisocyanate, tetramethyl hexamethylene diisocyanate, methylene-4,4'-bis(hydroxypropyl) diisocyanate, 4,4' methylene dicyclohexyl diisocyanate; or mixtures thereof, preferably 4,4' methylene dicyclohexyl  
diisocyanate

7. The cationic polyurethane dispersion according to any one of claims 1-5 wherein the isocyanate pre-polymer is formed from a combination of the isocyanate monomers of claim 6.
- 5 8. The cationic polyurethane dispersion according to any one of claims 1-6 wherein the isocyanate monomer is present in an amount in the range of 3 - 20 wt%, more preferably 4 - 15 wt%, even more preferably, about 5 - 7 wt%.
9. The cationic polyurethane dispersion according to any one of claims 1-6 wherein the tertiary  
10 amine containing diol is selected from the group consisting of N-methyl diethanol amine, N-ethyl diethanol amine, N-propyl diethanol amine, N-methyl dipropanol amine, N-ethyl dipropanol amine, N-methyl dibutanol amine, N-ethyl dibutanol amine, N-propyl dipropanol amine, 3-(diethylamino)-1,2-propanediol, 2-(dimethylamino)-1,3-propanediol, 2-(diethylamino)-1,3-propanediol, 2-(dimethylamino)-1,4-butanediol, 2-(diethylamino)-1,4-butanediol and mixtures thereof, preferably N-  
15 methyl diethanol amine.
10. The cationic polyurethane dispersion according to any one of claims 1-9 wherein the tertiary amine containing diol is present in an amount in the range of 0.5 - 15 wt%, more preferably 1 - 10 wt%, even more preferably, about 2 - 4 wt%.
- 20 11. The cationic polyurethane dispersion according to any one of claims 1-10 wherein the weak, volatile acid is present in an amount sufficient to ensure the cationic polyurethane dispersion has a pH <7, more preferably a pH in the range 3 - 6.5, even more preferably, a pH in the range 4 - 5.5.
- 25 12. The cationic polyurethane dispersion according to any one of claims 1-11 wherein the weak volatile acid is selected from the group consisting of formic acid, acetic acid and propanoic acid, carbonic acid or combinations thereof, preferably acetic acid.
- 30 13. The cationic polyurethane dispersion according to any one of claims 1-12 wherein the weak volatile acid is present in an amount in the range of 0.1 - 10 wt%, more preferably 0.3 - 5 wt%, most preferably 0.5 - 3 wt%.
- 35 14. The cationic polyurethane dispersion according to any one of claims 1-13 wherein the solvent is selected from the group consisting of glycol ethers, glycol acetates, glycol ether acetates and mixtures thereof.

15. The cationic polyurethane dispersion according to any one of claims 1-14 wherein the solvent is selected from one or more of the group consisting of diethylene glycol dimethyl ether, propylene glycol methyl ether, propylene glycol ethyl ether, dipropylene glycol methyl ether, 5 propylene glycol diacetate, propylene glycol methyl ether acetate, dimethyl dipropylene glycol ether and combinations thereof, preferably from the group consisting of propylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol diacetate, propylene glycol methyl ether acetate and combinations thereof, most preferably dimethyl dipropylene glycol ether.
- 10 16. The cationic polyurethane dispersion according to any one of claims 1-15 wherein the solvent is present in a range of about 5 – 40 %w/w, preferably about 5 - 25 %w/w, more preferably about 10 – 15 %w/w.
- 15 17. A tannin blocking coating composition comprising the cationic polyurethane dispersion according to any one of claims 1-16 together with one or more coating excipients.
18. The tannin blocking coating composition according to claim 17 wherein the one or more excipients is selected from the group consisting of defoamers, pigments, titanium dioxide, talc powder, talc fibre, silica flour, fumed silica, dispersing agents, wetting agents, propylene 20 glycol, BYK 304 and water.
19. The coating composition according to claim 17 or 18 further comprising one or more of: an epoxy emulsions, latex emulsion, anionic acrylic emulsions, cationic acrylic emulsions, cationic polyurethane dispersion, anionic polyurethane dispersion and/or a compatible water borne polymer. 25
20. The coating composition according to any one of claims 17-19 when used to retard tannin migration from a tannin containing surface.
21. The coating composition according to any one of claims 17-19 when used as a coating 30 sealer for a topcoat on a tannin containing surface.
22. A tannin blocking, non-ionic polyurethane polymer formed by drying the cationic polyurethane dispersion according to any one of claims 1-16 or the coating composition according to any one of claims 17-19. 35
23. The tannin blocking, non-ionic polyurethane polymer according to claim 22 when used to block tannin migration from a tannin containing surface.

24. The tannin blocking, non-ionic polyurethane polymer according to claim 22 when used as a coating sealer or a topcoat for a tannin containing surface.

5 25 A method of preparing a cationic polyurethane dispersion comprising the steps of reacting:  
i) a di-functional polyol,  
ii) isocyanate monomers or a polyisocyanate pre-polymer, and  
iii) a tertiary amine containing diol,  
in the presence of a solvent to form a polyurethane pre-polymer, and  
10 iv) dispersing the polyurethane pre-polymer in water and a weak, volatile acid,  
wherein the solvent has a boiling point in the range of about 140 - 260°C and is selected from the group consisting of glycol ethers, glycol acetates, glycol ether acetates and mixtures thereof.

26. The method according to claim 34 wherein the cationic polyurethane dispersion is as defined  
15 in any one of claims 1-16.

27. The method of claim 25 or 26 wherein the steps of reacting i) the di-functional polyol, ii) the isocyanate monomer or polyisocyanate pre-polymer and iii) the tertiary amine containing diol occur at a temperature in the range of about 35°C to 95°C, preferably 50 - 90°C, more preferably 70 -  
20 90°C.

28. The method of any one of claims 25-27 wherein in step iv), dispersing the pre-polymer in water and the weak, volatile acid occurs at a temperature below 70°C, more preferably below 60°C, even more preferably below 50°C.

25

29. The method of any one of claims 25-28 wherein agitation is included in step iv).

30 The method of any one of claims 25-29 wherein in step iv) the acid is added in conjunction with the water.

30

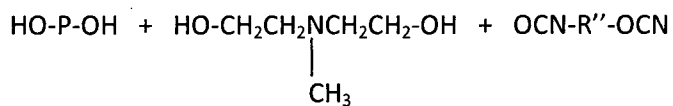
31. The method of any one of claims 25-29 wherein in step iv) the acid is added before the water.

32. The method of any one of claims 25-31 wherein the steps of reacting i), ii) and iii) occurs  
35 until the isocyanate monomer content is less than about 0.1%.

33. The method of any one of claims 25-32 wherein the steps of reacting i), ii) and iii) occurs over a period of between about half an hour to about 5 hours.

34. A method of blocking or retarding tannin migration from a tannin-containing substrate comprising:
- 5 i) applying a cationic polyurethane dispersion according to any one of claims 1-16 or a coating composition according to any one of claims 17-19 to the tannin-containing substrate; and
  - ii) drying the cationic polyurethane dispersion or coating composition so as to convert the cationic polyurethane dispersion into a non-ionic polyurethane polymer.
35. The method of claim 34 wherein the drying takes place in air at a temperature of about  
10 25~28°C.
36. The method of claim 34 or 35 wherein the coating composition is a clear sealer.
37. The method of any one of claims 34-36 wherein a resin topcoat is applied over the coating  
15 composition.
38. The method of claim 37 wherein the resin topcoat is selected from one or more of the group consisting of: epoxy emulsions, latex emulsions, anionic acrylic emulsions, cationic acrylic emulsions, anionic polyurethane dispersions and cationic polyurethane dispersions.

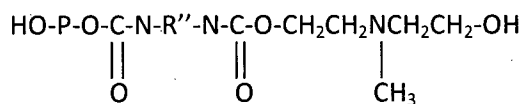
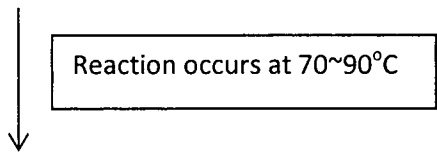
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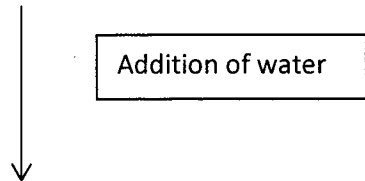
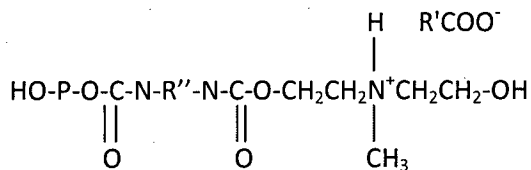
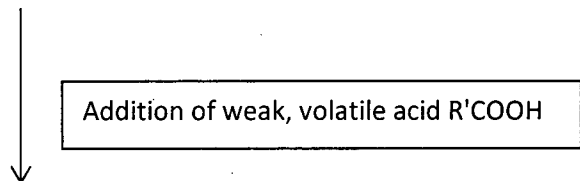
Polyol

Amine diol

Isocyanate



Polyurethane pre-polymer



Cationic Polyurethane Dispersion

**Figure 1**

Cationic Polyurethane Dispersion from Figure 1

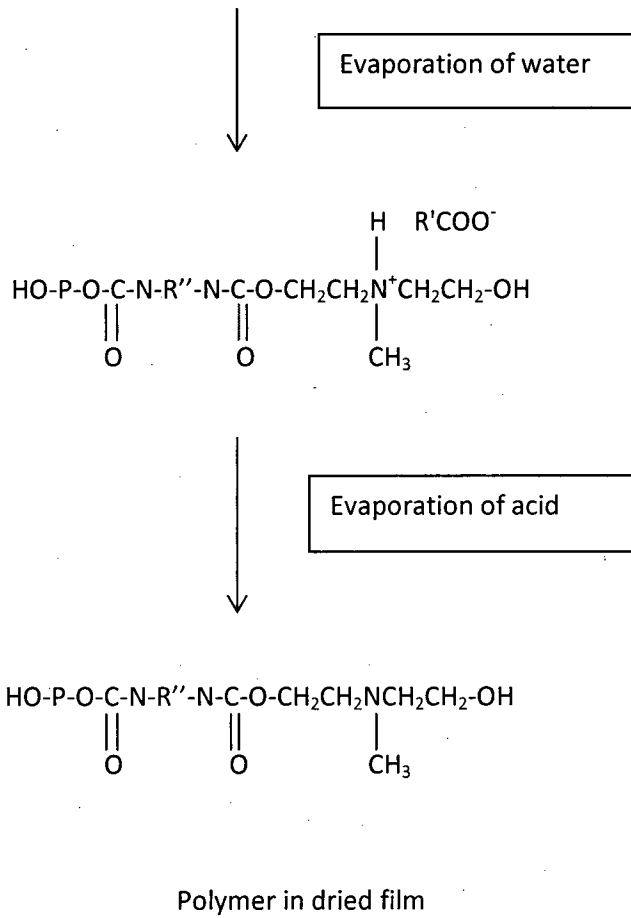


Figure 2

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/SG2012/000109

## A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

*C08G 18/66* (2006.01)      *C08G 18/18* (2006.01)      *C09D 175/04* (2006.01)  
*C08G 18/12* (2006.01)      *C08J 3/09* (2006.01)      *C09D 175/12* (2006.01)

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)

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)

EPODOC, WPI, INSPEC, JAPIO, CAPLUS &amp; keywords: polyurethane, coating, dispersion, sealer, polyol, isocyanate, tertiary amine, glycol ether, glycol acetate, formic acid, acetic acid, carbonic acid, tannin, wood and like terms; Esp@cenet, USPTO and Google Patents using similar keywords.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1158088 A (FARBENFABRIKEN BAYER AKTENGESSELLSCHAFT) 16 July 1969 page 2, lines 1-25; page 3, lines 22-39, 50-58; page 4, lines 10-28; page 5, lines 18-21; page 6, lines 58-62; page 7, lines 51-53, 56-59; page 8, lines 4-5, 48-57; claims 1-2	1-19, 22, 25-33
A	US 2002/0028875 A1 (ANDERLE et al.) 07 March 2002 Abstract; paragraphs [0067], [0076], [0112]; claim 57	1-19, 22, 25-33
A	US 7157120 B2 (NETO et al.) 02 January 2007 Abstract; col. 1, lines 38-46; col. 2, lines 20-26; claims 1-8, 12	1-38

 Further documents are listed in the continuation of Box C See patent family annex

* Special categories of cited documents:		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search  
24 May 2012Date of mailing of the international search report  
30 May 2012Name and mailing address of the ISA/AU  
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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/SG2012/000109**

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
GB	1158088	BE	710181	DE	1694129	FR	1568924
US	2002028875	AU	24549/02	EP	1301564	JP	2004504464
		MX	PA03000515	US	6576702	WO	0208327
US	7157120	US	2005249884				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

**END OF ANNEX**