

Aqueous system curable resin composition and method of forming a film or multilayer films using same

FIELD OF THE INVENTION

5 The present invention relates to an aqueous system curable resin composition and a method of forming a film and, more particularly, to an aqueous system curable resin composition excellent in film forming ability and adhesion to
10 substrates in a low temperature and/or high humidity environment, and, further, in adhesion to topcoats when a topcoating composition is applied, as well as a method of forming a film or multilayer films using the same.

PRIOR ART

15 The use of aqueous system curable resin compositions has begun in various fields owing to the possibility of minimizing the amount of volatile organic solvents and of coping with the recent environmental problems.

 Generally known as aqueous system curable resin
20 compositions are acrylic resin curing systems and epoxy resin/amine resin curing systems. Recently, urethane curing systems using an aqueous system self-emulsifiable polyisocyanate resin have also been used.

 However, such aqueous system curable resin compositions,
25 when applied to substrates in a low temperature and/or high humidity environment, show poor film forming ability, and the possibility that the strength and adhesion to substrates of films obtained might decrease have been a matter of concern. For removing all apprehensions regarding such possibility,
30 equipment is required for modifying the working environment and maintaining and controlling an appropriate environment for a certain period of time. Thus, the problem is that much labor and cost are required for securing the required quality of resulting films.

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SUMMARY OF THE INVENTION

It is an object of the present invention to provide an aqueous system curable resin composition excellent in film forming ability and adhesion to substrates in a low temperature and/or high humidity environment, and, further, in adhesion to topcoats when a topcoating composition is applied, as well as a method of forming a film or multilayer films using said composition.

The present invention is related to an aqueous system curable resin composition

wherein an epoxy resin (A) and a self-emulsifiable polyisocyanate resin (B) are dispersed in an aqueous system. Here, the epoxy resin (A) has at least two epoxy groups per molecule and an epoxy equivalent, on the resin solid basis, of 150 to 5,000, for instance, and is a self-emulsifiable epoxy resin. The self-emulsifiable polyisocyanate resin (B) has an aliphatic polyisocyanate skeleton, for instance, and has at least two isocyanate groups per molecule and an isocyanate equivalent, on the resin solid basis, of 170 to 700, for instance. Further, the ratio of isocyanate equivalent, on the resin solid basis, of said self-emulsifiable polyisocyanate resin (B) to the epoxy equivalent, on the resin solid basis, of said epoxy resin (A) is not less than 0.7, for instance.

The present invention is also related to a method of forming a film which comprises applying a curable resin composition to a substrate, followed by topcoating.

said curable resin composition is an aqueous system curable resin composition. Said aqueous system curable resin composition is prepared just before application to the substrate by mixing the epoxy resin (A) with the self-emulsifiable polyisocyanate resin (B).

The present invention is further related to a method of forming multilayer films which comprises applying a curable resin composition to a substrate, followed by topcoating, said curable resin composition being the aqueous system

curable resin composition mentioned above. Here, a coating composition used for topcoating may be a polyurea resin composition.

5 DETAILED DESCRIPTION OF THE INVENTION

Aqueous system curable resin composition

 The aqueous system curable resin composition of the present invention comprises (A) an epoxy resin and (B) a self-emulsifiable polyisocyanate resin, both dispersed in an aqueous system.

 From the viewpoint of film forming ability and of adhesion to substrates on the occasion of film formation, said epoxy resin (A) preferably has at least two epoxy groups per molecule and an epoxy equivalent, on the resin solid basis, of 150 to 5,000.

 Usable as such epoxy resin are, for example, reaction products from a novolak type phenol resin and epichlorohydrin, reaction products from a bisphenol resin (e.g. type A, type B, type F) and epichlorohydrin, reaction products from a novolak type phenol resin, a bisphenol resin (e.g. type A, type B, type F) and epichlorohydrin, and reaction products from a cresol novolak or like cresol compound and epichlorohydrin. The epoxy resin (A) may have a substituent not causing side reactions when said resin is used in the aqueous system curable resin composition, inclusive of, for example alkyl, allyl, ether and like groups.

 The above epoxy resin (A) may be a self-emulsifiable epoxy resin. This self-emulsifiable epoxy resin is derived from the above-mentioned epoxy resin (A) by introducing at least one hydrophilic moiety thereinto. Examples are epoxy resins intramolecularly having a hydrophilic moiety. As the hydrophilic moiety, there may specifically be mentioned ionic hydrophilic moieties and nonionic polyalkylene oxide skeletons, among others.

 From the viewpoint of stability in aqueous dispersion,

the epoxy resin (A) to be contained in the aqueous system curable resin composition of the present invention is preferably a self-emulsifiable one as mentioned above, or a non-self-emulsifiable epoxy resin dispersed in water by emulsification using an emulsifier well known in the art. From the viewpoint of adhesion upon application to substrates, the self-emulsifiable epoxy resin is more preferred. Such self-emulsifiable epoxy resin is not particularly restricted but, from the viewpoint of adhesion, a self-emulsifiable epoxy resin intramolecularly having a polyalkylene oxide skeleton as a hydrophilic moiety is preferred.

Said self-emulsifiable epoxy resin intramolecularly having a polyalkylene oxide skeleton can be prepared, for example, by reacting the above epoxy resin with a polyalkylene glycol in the conventional manner under conditions such that the epoxy equivalent is in excess. Such epoxy resin may be a mixture of two or more species.

The polyalkylene glycol is not particularly restricted but includes, among others, alkylene glycols such as ethylene glycol, propylene glycol and butylene glycol, and polyethylene glycols (e.g. diethylene glycol, triethylene glycol) and polypropylene glycols with a degree of polymerization of 2 to 10.

As commercial grades of such epoxy resin intramolecularly having a polyalkylene oxide skeleton, there may be mentioned, for example, "WEX-5001" and "WEX-5002", which are reaction products from a bisphenol A-based resin having an alkylene oxide skeleton and epichlorohydrin, and "WEX-5100", which is a reaction product from an o-cresol novolak type phenol resin and epichlorohydrin (all products of Tohto Resin Kako).

The self-emulsifiable polyisocyanate resin (B) to be contained in the aqueous system curable resin composition of the present invention is not particularly restricted but, from the viewpoint of film forming ability and adhesion to topcoat, it is preferably one having at least two isocyanato groups per

molecule and an isocyanate equivalent, on the resin solid basis, of 170 to 700.

The above self-emulsifiable polyisocyanate resin (B) can be prepared, for example, by reacting an isocyanato-containing
5 compound with a compound having a hydrophilic moiety capable of reacting with the isocyanate group in the conventional manner under conditions such that the isocyanate equivalent is in excess. As the isocyanato-containing compound, there may specifically be mentioned polyisocyanates, for example
10 aliphatic polyisocyanates such as 1,6-hexamethylene diisocyanate and 1,4-tetramethylene diisocyanate, alicyclic polyisocyanates such as isophoronediiisocyanate and hydrogenated tolylene diisocyanates, and aromatic polyisocyanates such as 2,4-tolylene diisocyanates, among
15 others.

As the compound having a hydrophilic moiety capable of reacting with the isocyanate group, there may specifically be mentioned such polyalkylene glycols as mentioned above in relation to the epoxy resin.

20 As the self-emulsifiable polyisocyanate resin (B) to be contained in the aqueous system curable resin composition of the present invention, there may further be mentioned, in addition to a monomeric isocyanato-containing compound as mentioned above, a dimer or trimer thereof or and those derived
25 from an isocyanato-terminated prepolymer prepared by reacting a substoichiometric amount of such an isocyanato-containing compound as mentioned above with a compound having an active hydrogen-containing compound reactive with the isocyanato group.

30 From the viewpoint of adhesion in the step of applying a topcoating composition following the film formation using the aqueous system curable resin composition of the present invention, the self-emulsifiable polyisocyanate resin (B) to be contained in said resin composition is preferably one having
35 an aliphatic polyisocyanate skeleton. Among examples thereof

which are commercially available, there may be mentioned "Aquanate 200" and "Aquanate 210" (products of Nippon Polyurethane Industry).

5 The equivalent ratio of the isocyanate equivalent, on the resin solid basis, of the above self-emulsifiable polyisocyanate resin (B) to the epoxy equivalent, on the resin solid basis, of the above epoxy resin (A) in the aqueous system curable resin composition of the present invention is not particularly restricted but may be not less than 0.7. When said
10 equivalent ratio is less than 0.7, the effects of the present invention may not be obtained, as the case may be. From the viewpoint of adhesion to substrates, it is preferably 0.7 to 3.0, more preferably 1.0 to 2.5.

 From the viewpoint of water dispersibility, film forming
15 ability and workability, the aqueous system curable resin composition of the present invention preferably has a coating solid content of 20 to 60% by weight. In cases where the coating solid content is less than 20% by weight, the film forming ability and workability may possibly decrease while, when it
20 is higher than 60% by weight, the water dispersibility and workability may decrease, as the case may be.

 The aqueous system curable resin composition of the present invention may contain, in addition to the above epoxy resin (A) and self-emulsifiable polyisocyanate resin (B), one
25 or more of such additives as organic solvents, surfactants, antifoaming agents, flame retardants, plasticizers, dyes, color pigments, fillers, fungicides, bactericides, antioxidants, ultraviolet absorbers and light stabilizers, as necessary.

30 The aqueous system curable resin composition of the present invention can be prepared by mixing together the above epoxy resin (A), self-emulsifiable polyisocyanate resin (B) and other ingredients. When, on that occasion, the epoxy resin (A) is not self-emulsifiable, its dispersion in water is preferably
35 effected by using an emulsifier, for instance. This emulsifier

improves the stability of the dispersion and therefore can effectively be used also when the above epoxy resin (A) is a self-emulsifiable one.

From the viewpoint of storage stability, the aqueous system curable resin composition of the present invention is preferably used as the so-called two component system, namely the components are stored separately and mixed together just prior to application. From the viewpoint of applicability and adhesion, the time period referred to by the phrase "just prior to application" is preferably about 7 hours.

Method of forming a film

The method of forming a film according to the present invention comprises applying a curable resin composition to substrates, wherein the curable resin composition is the above-mentioned aqueous system curable resin composition.

The substrate to be used for the film forming method of the present invention is not particularly restricted but specifically includes concrete, mortar, slates and like building materials, iron or steel panels, and wood, among others. It is judicious, however, to apply the method to porous materials such as concrete, mortar, slates and the like.

The curable resin composition to be used in the film forming method of the present invention is the above-mentioned aqueous system curable resin composition comprising the above epoxy resin (A) and the above self-emulsifiable polyisocyanate resin (B).

In cases where the above aqueous system curable resin composition is not the so-called one-component system but the so-called two-component system in which the above epoxy resin (A), the above self-emulsifiable polyisocyanate resin (B), and water are separated from each other, the aqueous system curable resin composition is prepared by mixing up these prior to application to such substrates as mentioned above. The mixing ratio between the epoxy resin (A) and self-emulsifiable

polyisocyanate resin (B) can be selected based on the equivalent ratio mentioned above in relation to the aqueous system curable resin composition. The method of mixing is not particularly restricted but includes, for example, the one comprising
5 stirring and mixing using such mechanical means as Disper, and the one comprising manually stirring and mixing using a spatula or the like. From the viewpoint of homogeneity, the method comprising stirring and mixing using mechanical means is preferred.

10 Considering the applicability and adhesion, the period from mixing up of the above materials to the time of application is preferably about 7 hours, for instance.

In practicing the film forming method of the invention, a required amount of the above aqueous system curable resin
15 composition is applied to substrates using a brush, roller, sprayer or the like and dried, whereby a film can be obtained on the substrates. The time required for dry to touch, i.e. tack-free time, is hardly influenced by the application environment and other factors, and is about 10 to 30 minutes,
20 for instance.

Method of forming multilayer films

The multilayer film forming method of the present invention comprises applying a curable resin composition to
25 substrates and then further applying a topcoating composition, wherein the curable resin composition is the above-mentioned aqueous system curable resin composition. As the substrates and the method of applying the aqueous system curable resin composition thereto, there may be mentioned those mentioned
30 hereinabove referring to the method of forming a film.

The topcoating composition to be used in the step of topcoating in the above method may be, for example, a polyurea resin composition, a polyurethane/urea resin composition, a polyurethane resin composition, an epoxy resin composition or
35 the like. A polyurea resin composition is suited for use.

Specifically, the polyurea resin composition is, for example, one comprising an amine-terminated polyoxyalkylenepolyamine, an amine terminal chain extending agent and a polyisocyanate. As examples of such polyurea resin composition which are
5 commercially available, there may be mentioned "Toughguard R-G" and "Toughguard R-P" (both products of Nippon Paint), among others.

The method of applying the above topcoating composition is not particularly restricted but a necessary amount of the
10 topcoating composition employed can be applied by any method adequate for the composition. When the polyurea resin coating composition, for instance, is used, the method comprising spraying components while causing collision and mixing thereof using a high pressure two liquid collision mixing type sprayer
15 or the method comprising spreading the composition using a trowel or spatula, for instance, can be selectively employed according to the species of resin.

The application of the above topcoating composition can be carried out after drying of the surface layer of the film
20 obtained by the above-mentioned film forming method. On that occasion, it is not always necessary that the whole film be found set. The drying of the surface layer can be confirmed by touching with a finger. Drying at ordinary temperature or forced drying following application gives a multilayer film.
25 An adequate drying time can be selected depending on the application environment.

From the viewpoint of adhesion, the interval between the application of the above aqueous system curable resin composition to a substrate and the application of the topcoating
30 composition in the process of multilayer film formation according to the present invention may be generally at most 7 days. From the viewpoint of shortening the term of construction, about 1 to 2 hours, for instance, may be selected as the interval.

The time required for obtaining sufficient film quality
35 using the multilayer film forming method of the invention is

about 16 hours after topcoating when the above polyurea resin composition is used as the topcoating, for instance.

The aqueous system curable resin composition of the present invention contains the epoxy resin (A), the self-emulsifiable polyisocyanate resin (B) and water and, therefore, is excellent in film forming ability. In particular, even in a low temperature (e.g. 5°C) or high humidity (e.g. 100% relative humidity) environment, the rate of film forming is high and the tack-free time is short, and the film strength, adhesion to substrates, and adhesion to the topcoat in case of application of a topcoating composition can be secured.

Although the mechanisms of these effects are unknown, they are presumably produced by an improvement in adhesion as brought about by the substrate being impregnated with the epoxy resin contained in the aqueous system curable resin composition of the present invention and, on the other hand, by an improvement in film forming ability of the film surface layer as brought about by the urea forming reaction of the self-emulsifiable polyisocyanate resin and, further, by an improvement in adhesion to the topcoat as brought about by the urethane bond and/or urea bond formed.

The film forming method of the present invention, which uses the above-mentioned aqueous system curable resin composition, makes it no more necessary to modify the working environment and maintain and control an adequate environment for a certain period of time by expending much labor and cost, which is usual in the prior art. Thus, for example, films of stable and high quality can be provided in a short period of time even in a low temperature environment (e.g. 5 °C) or in a high humidity environment (e.g. 100% relative humidity), for instance.

Further, when a topcoating composition is provided on the film formed by the film forming method of the present invention, the time until application of a topcoating composition can be

shortened since the tack-free time is very short with the above aqueous system curable resin composition. In particular when a urea resin composition is used for topcoating, the working time can be further reduced and multilayer films of stable and high quality can be obtained in about 16 hours following application of the urea resin composition.

Since the aqueous system curable resin composition of the present invention gives films of excellent quality, it is also possible to use coated articles without topcoating.

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BEST MODE FOR CARRYING OUT THE INVENTION

Example 1 Aqueous system curable composition 1

15	WEX-5001	20.0 weight parts
	(product of Tohto Resin Kako; bisphenol A type epoxy resin having a polyalkylene oxide skeleton; resin solid-based epoxy equivalent 530; resin solid content 50% by weight)	
	Aquanate 200	6.5 weight parts
20	(product of Nippon Polyurethane Industry; self-emulsifiable polyisocyanate resin having an aliphatic polyisocyanate skeleton; resin solid-based isocyanate equivalent 347; resin solid content 100% by weight)	
	Water	27.1 weight parts

25 The above materials were mixed together and the mixture was stirred at 1,000 rpm for 5 minutes using a table type Disper mixer to give an aqueous system curable resin composition 1 in which the ratio of resin solid-based isocyanate equivalent to resin solid-based epoxy equivalent was 1.0 and the solid content was 30% by weight.

30 JIS mortar pieces, 70 × 70 × 20 mm in size, ground beforehand on one side using a disk sander and stored under environmental conditions of 5 °C and 85% (relative humidity; hereinafter, "RH"), 25 °C and 85% RH, or 25 and 100% RH were used (two pieces for each set of environmental conditions; a

total of 6 pieces). The aqueous system curable resin composition 1 obtained as mentioned above (each 0.5 g) was applied to the ground face of each piece using a brush to give a test specimen. The test specimens thus obtained were stored again under the corresponding respective set of environmental conditions. The test specimens were taken out one by one so that the interval amounted to 1 hour or 16 hours, and 10 g of "Toughguard R-G" (product of Nippon Paint; solvent-free polyurea resin composition) was applied to each surface portion coated with the aqueous system curable resin composition using a spraying apparatus for exclusive use, followed by one day storage under the respective environmental conditions to give test specimens for adhesion testing.

Example 2 Aqueous system curable resin composition 2

WEX-5002	20.0 weight parts
(product of Tohto Resin Kako; bisphenol A type epoxy resin having a polyalkylene oxide skeleton; resin solid-based epoxy equivalent 710; resin solid content 50% by weight)	
Aquanate 200	9.8 weight parts
(product of Nippon Polyurethane Industry; self-emulsifiable polyisocyanate resin having an aliphatic polyisocyanate skeleton; resin solid-based isocyanate equivalent 347; resin solid content 100% by weight)	
Water	36.2 weight parts

An aqueous system curable resin composition 2 with a ratio of resin solid-based isocyanate equivalent to resin solid-based epoxy equivalent of 2.0 and a solid content of 30% by weight was prepared in the same manner as in Example 1 except that the above materials were used. Thereafter, test specimens and test specimens for adhesion testing were obtained in the same manner as in Example 1.

Example 3 Aqueous system curable resin composition 3

An aqueous system curable resin composition 3 with a ratio of resin solid-based isocyanate equivalent to resin solid-based epoxy equivalent of 1.0 and a solid content of 30% by weight was prepared in the same manner as in Example 2 except that "Aquanate 200" was used in an amount of 4.9 weight parts and water in an amount of 24.8 weight parts. Thereafter, test specimens and test specimens for adhesion testing were obtained in the same manner as in Example 1.

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Comparative Example 1 Aqueous system curable resin composition 4

An aqueous system curable resin composition 4 with a ratio of resin solid-based isocyanate equivalent to resin solid-based epoxy equivalent of 0.6 and a solid content of 30% by weight was prepared in the same manner as in Example 2 except that "Aquanate 200" was used in an amount of 2.9 weight parts and water in an amount of 20.1 weight parts. Thereafter, test specimens and test specimens for adhesion testing were obtained in the same manner as in Example 1.

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Comparative Example 2 Aqueous system curable resin composition 5

Using 2.8 weight parts of "EH-623W" (product of Clariant Japan; modified aliphatic amine resin; resin solid-based amine equivalent 160; resin solid content 80% by weight) in lieu of 9.8 weight parts of "Aquanate 200" and using water in an amount of 18.0 weight parts, an aqueous system curable resin composition 5 with a ratio of resin solid-based amine equivalent to resin solid-based epoxy equivalent of 1.0 and a solid content of 30% by weight was prepared in the same manner as in Example 2. Thereafter, test specimens and test specimens for adhesion testing were obtained in the same manner as in Example 1.

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35 <Evaluation tests>

Tack-free test

The test specimens prepared in Example 1 to 3 and Comparative Example 1 and 2 were stored under the respective conditions, and each coated surface was touched with a finger at timed intervals and whether the fingerprint remained or not was checked by the eye. The time required for the fingerprint to be no more observed was taken as the tack-free time and, when said time was within 30 minutes, the requirement in this respect was regarded as satisfied. The evaluation results are shown in Table 1.

Adhesion testing

The test specimens for adhesion testing as obtained in Examples 1 to 3 and Comparative Examples 1 and 2 were evaluated for adhesion using a Kenken (Building Research Institute) type adhesion tester. The evaluation results are shown in Table 1. The evaluation criteria were as follows:

- : Mortar fracture
- △: Intralayer fracture of the aqueous system curable resin composition
- ×: Mortar/aqueous system curable resin composition film or aqueous system curable resin composition film/Toughguard R-G film delamination

[Table 1]

Environmental conditions	5 °C, 85% RH	Ex. 1	Ex. 2	Ex. 3	Comp.Ex.1	Comp.Ex.2
		25 min	25 min	25 min	30 min	16 hr.
	○	○	○	○	△	×
	○	○	○	○	△	△
	25 °C, 85% RH	10 min	10 min	10 min	15 min	6 hr.
		○	○	○	△	×
	○	○	○	○	△	○
	25 °C, 100% RH	15 min	15 min	15 min	20 min	≥ 16 hr.
		○	○	○	△	×
		○	○	○	△	×

Upper row: Tack-free time.

Middle row: Adhesion of the test specimen for adhesion

testing when the interval was 1 hour.

Lower row: Adhesion of the test specimen for adhesion

testing when the interval was 16 hours.

RH: Relative humidity

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In Examples 1 to 3 in which the aqueous system curable resin composition of the present invention was used, as is evident from Table 1, the tack-free time was short even in a low temperature or high humidity working environment and, even when the interval between the application of the aqueous system curable resin composition to the substrate and the application of the topcoating composition was 1 hour, the adhesion to the substrate was good. In Comparative Example 1 or 2, however, even when the interval until topcoating was 16 hours, the adhesion to the substrate was poor.

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CLAIMS

1. A method of forming multilayer films which comprises applying a curable resin composition to a substrate, followed by topcoating, wherein said curable resin composition is an aqueous system curable resin composition in which an epoxy resin (A) and a self-emulsifiable polyisocyanate resin (B) are dispersed.

2. The method of forming multilayer films according to Claim 1, wherein a coating composition used for topcoating is a polyurea resin composition.

3. A method of forming multilayer films according to Claim 1 or 2, wherein said epoxy resin (A) has at least two epoxy groups per molecule and an epoxy equivalent, on the resin solid basis, of 150 to 5,000.

4. A method of forming multilayer films according to Claim 1 to 3, wherein said epoxy resin (A) is a self-emulsifiable epoxy resin.

5. A method of forming multilayer films according to any of Claims 1 to 4, wherein said self-emulsifiable polyisocyanate resin (B) has an aliphatic polyisocyanate skeleton.

6. A method of forming multilayer films according to any of Claims 1 to 5, wherein said self-emulsifiable polyisocyanate resin (B) has at least two isocyanato groups per molecule and an isocyanate equivalent, on the resin solid basis, of 170 to 700.

7. A method of forming multilayer films according to any of Claims 1 to 6, wherein the ratio of the isocyanate equivalent, on the resin solid basis, of said self-emulsifiable polyisocyanate resin (B) to the epoxy equivalent,

on the resin solid basis, of said epoxy resin (A) is not less than 0.7.

8. A method of forming multilayer films according to any of Claims 1 to 7, wherein the substrate to be used for the method of forming multilayer films is porous material.

9. A method of forming multilayer films according to Claim 8, wherein the porous material is concrete, mortar or slates.

10. An aqueous system curable resin composition, wherein the aqueous system curable resin composition is used for the method of forming multilayer films according to any of claims 1 to 9.