CLAIMS

What is claimed is:

1. A method of forming a coating composition, said method comprising the steps of:

A. introducing an organoborane-amine complex, a radical polymerizable compound, and optionally an amine onto a substrate to form a coating composition;

B. introducing carbon dioxide into the coating composition in a molar ratio of at least 1:1 of the carbon dioxide to free amine groups present in the coating composition;

C. reacting the carbon dioxide and the free amine groups to form a carbamic zwitterion *in-situ* and to dissociate the organoborane-amine complex thereby forming a radical; and

D. polymerizing the radical polymerizable compound using the radical, optionally in the absence of external heating, or optionally at a temperature of from 20°C to 30°C.

2. A method as set forth in claim 1 wherein the substrate is further defined as an automobile component and the step of polymerizing is further defined as polymerizing to cure the coating composition on the automobile component, and optionally wherein the method further comprises the step of electrocoating the automobile component with a first composition wherein the coating composition is applied to the first composition on the automobile component.

3. A method as set forth in claim 1 or claim 2 wherein a molar ratio of the free amine groups to the amine of the organoborane-amine complex is about 1:1, optionally from about 0.5:1 to 1:1, or optionally less than about 1:1.

4. A method as set forth in any one of claims 1 to 3 wherein the step of reacting is further defined as reacting the carbamic zwitterion with a bound amine of the organoborane-

amine complex thereby dissociating the organoborane-amine complex into an organoborane initiator and the reaction product of the amine and the carbamic zwitterion.

5. A method as set forth in any one of claims 1 to 4 wherein the coating composition further comprises water and the step of reacting is further defined as transferring a proton from the carbamic zwitterion to the water to form an acidic species which protonates the bound amine of the organoborane-amine complex causing dissociation of the organoborane-amine complex.

6. A method as set forth in any one of claims 1 to 4 wherein the step of reacting is further defined as transferring a proton from a nitrogen atom of the carbamic zwitterion to an oxygen atom of the carbamic zwitterion thereby forming an unstable carbamic acid type compound which protonates the bound amine of the organoborane-amine complex causing dissociation of the organoborane-amine complex.

7. A method as set forth in any one of claims 1 to 6 further comprising the step of limiting an amount of oxygen introduced into the coating composition, optionally in a molar ratio of from 1:1 to 5:1 with the organoborane of the organoborane-amine complex, or optionally in an amount of 0.5 to 5 parts by weight of the oxygen per 100 parts by weight of the carbon dioxide present in the coating composition.

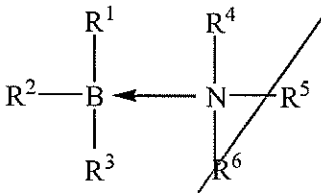
8. A method as set forth in any one of claims 1 to 7 wherein the step of introducing the organoborane-amine complex, the radical polymerizable compound, and optionally the amine, is further defined as spraying the organoborane-amine complex, the radical polymerizable compound, and optionally the amine onto the substrate.

9. A method as set forth in any one of claims 1 to 8 wherein the step of introducing the carbon dioxide is further defined as spraying the carbon dioxide from a nozzle of a spray gun, and optionally wherein the step of spraying the carbon dioxide is further defined as shaping the

organoborane-amine complex, the radical polymerizable compound, and optionally the amine with the carbon dioxide as the organoborane-amine complex, the radical polymerizable compound, and optionally the amine are being sprayed.

10. A method as set forth in any one of claims 1 to 9 further comprising the step of introducing a second gas to the coating composition wherein the second gas is sulfur dioxide.

11. A method as set forth in any one of claims 1 to 10 wherein the organoborane-amine complex has the following formula:



wherein each of R^1, R^2, R^3, R^4, R^5, and R^6 is independently selected from the group of a hydrogen atom, an alkyl group, an alkoxy group, an arylalkyl group, an alkylene group, halogenated homologs thereof, and combinations thereof and at least one of R^4, R^5, and R^6 is optionally nitrogen or sulfur functional.

12. A method as set forth in any one of claims 1 to 11 wherein the radical polymerizable compound is selected from the group of unsaturated acrylic and methacrylic ester resins, functional acrylic and methacrylic ester monomers, and combinations thereof.

13. A method as set forth in any one of claims 1 to 12 wherein the radical polymerizable compound is present in an amount of from 50 to 80 parts by weight per 100 parts by weight of the coating composition and the organoborane-amine complex is present in an amount of from 2 to 5 parts by weight per 100 parts by weight of the coating composition.

14. A method as set forth in any one of claims 1 to 13 wherein the step of introducing the organoborane-amine complex, the radical polymerizable compound, and optionally the amine occurs before, or simultaneously with, the step of introducing the carbon dioxide.

15. A method as set forth in any one of claims 1 to 14 wherein the step of introducing the carbon dioxide is further defined as exposing the coating composition to an atmosphere of carbon dioxide in a gas sink.

What is claimed is:

1. A method of forming a coating composition, said method comprising the steps of:

A. introducing an organoborane-amine complex, a radical polymerizable compound, and optionally an amine onto a substrate to form a coating composition;

B. introducing carbon dioxide into the coating composition in a molar ratio of at least 1:1 of the carbon dioxide to free amine groups present in the coating composition;

C. reacting the carbon dioxide and the free amine groups to form a carbamic zwitterion in-situ and to dissociate the organoborane-amine complex thereby forming a radical; and

D. polymerizing the radical polymerizable compound using the radical.

2. The method as set forth in claim **1**, wherein the substrate is an automobile component and the step of polymerizing is further defined as polymerizing to cure the coating composition on the automobile component, and optionally wherein the method further comprises the step of electrocoating the automobile component with a first composition wherein the coating composition is applied to the first composition on the automobile component.

3. The method as set forth in claim **1**, wherein a molar ratio of the free amine groups to the amine of the organoborane-amine complex is about 1:1.

4. The method as set forth in claim **1**, wherein the step of reacting is reacting the carbamic zwitterion with a bound amine of the organoborane-amine complex thereby dissociating the organoborane-amine complex into an organoborane initiator and the reaction product of the amine and the carbamic zwitterion.

5. The method as set forth in claim **1**, wherein the coating composition further comprises water and the step of reacting is transferring a proton from the carbamic zwitterion to the water to form an acidic species which protonates the bound amine of the organoborane-amine complex causing dissociation of the organoborane-amine complex.

6. The method as set forth in claim 1, wherein the step of reacting is transferring a proton from a nitrogen atom of the carbamic zwitterion to an oxygen atom of the carbamic zwitterion thereby forming an unstable carbamic acid compound which protonates the bound amine of the organoborane-amine complex causing dissociation of the organoborane-amine complex.

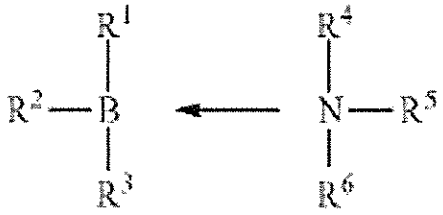
7. The method as set forth in claim 1, further comprising the step of limiting an amount of oxygen introduced into the coating composition, in a molar ratio of from 1:1 to 5:1 with the organoborane of the organoborane-amine complex.

8. The method as set forth in claim 1, wherein the step of introducing the organoborane-amine complex, the radical polymerizable, and optionally the amine, is further defined as spraying the organoborane-amine complex, the radical polymerizable compound, and optionally the amine onto the substrate.

9. The method as set forth in claim 1, wherein the step of introducing the carbon dioxide is as spraying the carbon dioxide from a nozzle of a spray gun, and optionally wherein the step of spraying the carbon dioxide is combining the organoborane-amine complex, the radical polymerizable compound, and optionally the amine with the carbon dioxide as the organoborane-amine complex, the radical polymerizable compound, and optionally the amine are being sprayed.

10. The A method as set forth in claim 1, further comprising the step of introducing a second gas to the coating composition wherein the second gas is sulfur dioxide.

11. The method as set forth in claim **1**, wherein the organoborane-amine complex has the following formula:



wherein each of R^1, R^2, R^3, R^4, R^5, and R^6 is independently selected from the group of a hydrogen atom, an alkyl group, an alkoxy group, an arylalkyl group, an alkylene group, halogenated homologs thereof, and combinations thereof and at least one of R^4, R^5, and R^6 is optionally a functional group containing nitrogen or sulfur.

12. The method as set forth in claim **1**, wherein the radical polymerizable compound is selected from the group consisting of a) unsaturated acrylic and methacrylic ester, resin, b) functional acrylic and methacrylic ester monomer and combinations thereof.

13. The method as set forth in claim **1** wherein the radical polymerizable compound is present in an amount of from 50 to 80 parts by weight per 100 parts by weight of the coating composition and the organoborane-amine complex is present in an amount of from 2 to 5 parts by weight per 100 parts by weight of the coating composition.

14. The method as set forth in claim **1**, wherein the step of introducing the organoborane-amine complex, the radical polymerizable compound, and optionally the amine occurs before the step of introducing the carbon dioxide.

15. The method as set forth in claim **1**, wherein the step of introducing the carbon dioxide is exposing the coating composition to an atmosphere of carbon dioxide in a gas sink.

16. The method as set forth in claim **1**, wherein in step D is carried out in the absence of external heating.

17. The method as set forth in claim **1**, wherein in step D is carried out at a temperature of from 20° C. to 30° C.

18. The method as set forth in claim **1**, wherein a molar ratio of the free amine groups to the amine of the organoborane-amine complex is from about 0.5:1 to 1:1.

19. The method as set forth in claim **1**, wherein a molar ratio of the free amine groups to the amine of the organoborane-amine complex is less than about 1:1.

20. The method as set forth in claim **1**, further comprising the step of limiting an amount of oxygen introduced into the coating composition, in an amount of 0.5 to 5 parts by weight of the oxygen per 100 parts by weight of the carbon dioxide present in the coating composition.

21. A method of forming a coating composition, said method comprising the steps of:

A. introducing an organoborane-amine complex, a radical polymerizable compound, carbon dioxide and optionally an amine onto a substrate to form a coating composition and wherein a molar ratio of at least 1:1 of the carbon dioxide to free amine groups present in the coating composition;

B. reacting the carbon dioxide and the free amine groups to form a carbamic zwitterion in-situ and to dissociate the organoborane-amine complex thereby forming a radical; and

C. polymerizing the radical polymerizable compound using the radical.