[0024] It is an object of the invention to provide an alternative plasticizer for use in a reactive polyurethane formulation, which achieves comparable or improved compatibility, color, exudation, optical properties, MVTR, hardness, tensile strength, tear strength, modulus, rebound, compression, and solvent swell, as compared to traditional plasticizers, including benzoate esters, used in polyurethane formulations, wherein the plasticizer comprises a low hydroxyl dibenzoate plasticizer.

[0025] It is another object of the invention to provide a reactive polyurethane formulation comprising a low hydroxyl non-phthalate plasticizer for property modifications, wherein the hydroxyl number is lower than that of currently available and utilized plasticizers in polyurethane systems, including other benzoate esters.

[0026] It is yet another object of the invention to provide a method to improve on yellowing, among other properties, encountered with the use of traditional plasticizers used in polyurethane formulations.

[0027] Still another object of the invention is to provide a low hydroxyl plasticizer for use in polyurethane, which may be substituted for traditional polyurethane TPU plasticizers known in the art.

[0028] Other objects of the invention will be apparent to one skilled in the art.

SUMMARY

[0029] In one aspect, the present invention refers to the use of a dibenzoate plasticizer in a reactive polyurethane composition prepared from the reaction of an isocyanate and a polyol, wherein the dibenzoate plasticizer consists of a low hydroxyl 1,2-propylene glycol dibenzoate having a hydroxyl number of less than 2 mg KOH/g when measured by the ASTM E222 method and less than 4 mg KOH/g when measured by the ASTM E1899 method, wherein the dibenzoate plasticizer is added to the polyurethane composition at the same time or close to the time that the isocyanate and polyol are mixed together to form a polyurethane polymer, and wherein the dibenzoate plasticizer achieves comparable or improved properties of compatibility, color, exudation, optical properties, MVTR, hardness, tensile strength, tear strength, rebound, compression set, and solvent swell, as compared to that achieved with traditional plasticizers known for use in polyurethanes. In another aspect, the present invention refers to a reactive thermoplastic

polyurethane composition, comprising a. a thermoplastic polyurethane, and b. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein. In yet another aspect, the present invention refers to a method of preventing yellowing of a polyurethane composition comprising the step of adding the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined herein to a reactive polyurethane formulation during manufacture. In yet another aspect, the present invention refers to thermoplastic polyurethane composition comprising a. an isocyanate; b. a polyol; c. a diol; d. the low hydroxyl dibenzoate plasticizer of as defined herein; and e. a stabilizer. In another aspect, the present invention refers to an adhesive comprising a. a polyurethane polymer; and b. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein. In another aspect, the present invention refers to a sealant comprising a. a polyurethane polymer; and b. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein. In another aspect, the present invention refers to a reactive thermoset polyurethane comprising a. a polyurethane polymer; and b. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein. In another aspect, the present invention refers to a 1K or 2K polyurethane adhesive or sealant comprising the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein. In another aspect, the present invention is directed to a method for reducing or eliminating yellowing associated with the use of traditional plasticizers in polyurethane compositions, comprising the steps of a. substituting the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein for the traditional plasticizer in the polyurethane composition, and b. incorporating the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer at the same time or close to the time that the isocyanate and polyol are mixed together to form a polyurethane polymer. In another aspect, the present invention refers to a method for improving the properties of articles made from a polyurethane composition, comprising the steps of aa. substituting the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein for the traditional plasticizer in the polyurethane composition, and b. incorporating the low hydroxyl 1,2-propylene glycol dibenzoate plasticizers at the same time or close to the time that the isocyanate and polyol are mixed together to form a polyurethane polymer. In yet another aspect, the present invention refers to a reactive polyurethane composition, comprising a. an

isocyanate; b. a diol; c. a polyol; d. a stabilizer; and e. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein, present in an amount ranging from 20 phr to 60 phr, based on 100 parts of polyurethane polymer formed by the reaction of the isocyanate and the polyol, wherein components are blended in the polymer formation steps at the same time or very close to the point where the isocyanate and polyol components react to form the polyurethane polymer and not when the polyurethane polymer is fully formed. In yet another aspect, the present invention refers to a reactive polyurethane system, comprising a. an isocyanate; b. a diol; c. a polyol; d. a stabilizer; and e. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer of as defined herein, wherein components are blended in the polymer formation steps at the same time or very close to the point where the isocyanate and polyol components react to form the polyurethane polymer and not when the polyurethane polymer is fully formed. This disclosure is directed to reactive polyurethane systems comprising an isocyanate and polyol in combination with a non-phthalate plasticizer. In particular, the present disclosure is directed to improved polyurethane formulations wherein 1,2-propylene glycol dibenzoate (plasticizer) is added at or near the time at which the isocyanate and polyol are mixed to react and form the resulting polyurethane polymer and not after the polyurethane polymer is formed. The invention is directed to use of a special grade of a low hydroxyl dibenzoate plasticizer that is 1,2-propylene glycol dibenzoate (PGDB), having a lower hydroxyl content than dibenzoate plasticizers currently used in polyurethane systems. The inventive PGDB also has a lower half-ester content than typical dibenzoate plasticizers used in polyurethane systems.

[0030] In one example, the disclosure refers to a reactive polyurethane system comprising the inventive PGDB as a plasticizer.

[0031] In another example, the disclosure refers to a polyurethane based adhesive or sealant comprising PGDB as a plasticizer.

[0032] In yet another example, the disclosure refers to an article or part made by utilizing the thermoset or thermoplastic polyurethane comprising PGDB.

[0033] The PGDB plasticizer is characterized by low hydroxyl content as compared to traditional dibenzoate plasticizers, specifically DPGDB, used in polyurethane formulations currently and in the past.

[0034] Potential applications of the reactive formulations of the invention include luxury footwear and luxury accessories, reactive floor adhesives and construction sealants, and casted parts such as wheels, rollers, and conveyor belts, among others. Other applications will be evident to one skilled in the art. It is expected that the improved reactive polyurethane formulations of the invention may be used in any applications where polyurethanes are suitable.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035] FIG. 1(a) shows Pot Life @ 90°C results for TPU samples utilizing different plasticizers evaluated against an unplasticized control.

[0036] FIG. 1(b) shows Pot Life @ 150°C results for TPU examples utilizing different plasticizers against an unplasticized control.

[0037] FIG. 2(a) and FIG. 2(b) show initial and 10 second hardness, respectively, achieved for TPU samples utilizing different plasticizers evaluated against an unplasticized control.

[0038] FIG. 2(c) and FIG. 2(d) show initial and 10 second hardness at 7 days achieved for TPU samples utilizing different plasticizers evaluated against an unplasticized control.

[0039] FIG. 3(a) and FIG. 3(b) shows yellowing of TPU samples utilizing different plasticizers evaluated against an unplasticized control.

[0040] FIG. 4(a) and FIG. 4(b) shows tensile strength (@ 600% Nominal Strain) achieved for TPU samples utilizing different plasticizers evaluated against an unplasticized control.

[0041] FIG. 5(a) and FIG. 5(b) shows 100% modulus achieved for TPU samples utilizing different plasticizers evaluated against an unplasticized control.

WHAT IS CLAIMED IS:

1. Use of a dibenzoate plasticizer in a reactive polyurethane composition prepared from the reaction of an isocyanate and a polyol,

wherein the dibenzoate plasticizer consists of a low hydroxyl 1,2-propylene glycol dibenzoate having a hydroxyl number of less than 2 mg KOH/g when measured by the ASTM E222 method and less than 4 mg KOH/g when measured by the ASTM E1899 method,

wherein the dibenzoate plasticizer is added to the polyurethane composition at the same time or close to the time that the isocyanate and polyol are mixed together to form a polyurethane polymer, and

wherein the dibenzoate plasticizer achieves comparable or improved properties of compatibility, color, exudation, optical properties, MVTR, hardness, tensile strength, tear strength, rebound, compression set, and solvent swell, as compared to that achieved with traditional plasticizers known for use in polyurethanes.

2. The use of a dibenzoate plasticizer according to claim 1, wherein the 1,2-propylene glycol dibenzoate has low acidity of less than 0.1%, water content levels of less than 0.1% and a half-ester content of less than 1%.

3. The use of a dibenzoate plasticizer according to claim 1, wherein the 1,2-propylene glycol dibenzoate has a hydroxyl value of less than 1 mg/KOH/g when measured by the ASTM E222 method.

4. The use of a dibenzoate plasticizer according to claim 1, wherein the 1,2-propylene glycol dibenzoate has a hydroxyl value of 3 or less mg/KOH/g when measured by the ASTM E1899 method.

5. A reactive thermoplastic polyurethane composition, comprising:

a. a thermoplastic polyurethane, and

b. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3 and 4.

6. The reactive thermoplastic polyurethane composition according to claim 5, wherein the dibenzoate plasticizer is present in an amount ranging from about 5 wt.% to about 50 wt.%, based upon the weight of the thermoplastic polyurethane composition.

7. A method of preventing yellowing of a polyurethane composition comprising the step of adding the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3 or 4 to a reactive polyurethane formulation during manufacture.

8. A thermoplastic polyurethane composition comprising:

a. an isocyanate;

b. a polyol;

c. a diol;

d. the low hydroxyl dibenzoate plasticizer as defined in any one of claims 1, 2, 3 or 4; and

e. a stabilizer.

9. The thermoplastic polyurethane composition according to claim 11, wherein the low hydroxyl dibenzoate plasticizer is present in an amount ranging from about 5 wt.% to about 80 wt.%, based upon the total weight of the thermoplastic polyurethane composition.

10. The thermoplastic polyurethane composition according to claim 8,

wherein the isocyanate is a diisocyanate that is methylene diphenyl diisocyanate;

wherein the diol is butanediol; and

wherein the polyol is a polyester or polyether.

11. An adhesive comprising:

a. a polyurethane polymer; and

b. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3 or 4.

12. A sealant comprising:

a. a polyurethane polymer; and

b. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3, or 4.

13. A reactive thermoset polyurethane comprising:

a. a polyurethane polymer; and

b. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3 or 4.

14. A 1K polyurethane adhesive or sealant comprising the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3, or 4.

15. A 2K polyurethane adhesive or sealant comprising the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3 or 4.

16. A method for reducing or eliminating yellowing associated with the use of traditional plasticizers in polyurethane compositions, comprising the steps of:

a. substituting the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3, or 4 for the traditional plasticizer in the polyurethane composition, and

b. incorporating the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer at the same time or close to the time that the isocyanate and polyol are mixed together to form a polyurethane polymer.

17. A method for improving the properties of articles made from a polyurethane composition, comprising the steps of:

a. substituting the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3, or 4 for the traditional plasticizer in the polyurethane composition, and

b. incorporating the low hydroxyl 1,2-propylene glycol dibenzoate plasticizers at the same time or close to the time that the isocyanate and polyol are mixed together to form a polyurethane polymer.

18. A reactive polyurethane composition, comprising:

a. an isocyanate;

b. a diol;

c. a polyol;

d. a stabilizer; and

e. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3 or 4, present in an amount ranging from 20 phr to 60 phr, based on 100 parts of polyurethane polymer formed by the reaction of the isocyanate and the polyol,

wherein components are blended in the polymer formation steps at the same time or very close to the point where the isocyanate and polyol components react to form the polyurethane polymer and not when the polyurethane polymer is fully formed.

19. A reactive polyurethane system, comprising:

a. an isocyanate;

b. a diol;

c. a polyol;

d. a stabilizer; and

e. the low hydroxyl 1,2-propylene glycol dibenzoate plasticizer as defined in any one of claims 1, 2, 3 or 4,

wherein components are blended in the polymer formation steps at the same time or very close to the point where the isocyanate and polyol components react to form the polyurethane polymer and not when the polyurethane polymer is fully formed.