bondlines can form when the reaction mixture divides into multiple flow fronts as it flows around the part and the separate flow fronts meet. When the polyurethane does not adhere to itself very strongly, cracks appear at the bondlines. This leads to a loss of thermal insulation efficiency and can expose the underlying substrate to the corrosive effects of seawater.

What is needed in the art is a method of making a syntactic polyurethane elastomer, which does not contain a mercury catalyst, which is resistant to cracking even when cast in confined complex geometries and which bonds well to itself.

This ~~invention~~ disclosure is in one ~~aspect~~ embodiment a cured syntactic polyurethane elastomer which is a reaction product of a reaction mixture comprising one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of based on the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst, wherein the reaction mixture is essentially devoid of mercury compounds.

The disclosure~~invention~~ is also a method for making a syntactic polyurethane elastomer, comprising

a) forming a reaction mixture containing at least one polymer polyol having a continuous phase containing one or more polyether polyols including a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst, wherein the reaction mixture is essentially devoid of mercury compounds, and

b) curing the reaction mixture to form the syntactic polyurethane elastomer.

The process of the disclosure~~invention~~ is suitable for applying a syntactic polyurethane elastomer to a substrate. Substrates of interest are parts that require thermal insulation. Subsea pipe and architecture is a substrate of particular interest.

In one aspect, the present disclosure provides a process for making a syntactic polyurethane elastomer, comprising

forming a reaction mixture containing at least one polymer polyol having a continuous phase containing one or more polyether polyols including a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), 0.10 to 0.25% based on the combined weight of all components of the reaction mixture except the polyisocyanate(s) of a ß-diketone compound, an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst, wherein the reaction mixture is essentially devoid of mercury compounds, and

b) curing the reaction mixture to form the syntactic polyurethane elastomer.

An important advantage of this disclosure~~invention~~ is that the syntactic polyurethane elastomer adheres well to itself and to other cured polyurethane elastomers. This is an especially important advantage when multiple sections of the syntactic polyurethane elastomer are applied to a substrate, these sections are in contact with each other, and good bonding between the sections is wanted. Thus, in certain embodiments, the disclosure~~invention~~ is a process for producing a substrate having an applied syntactic polyurethane elastomer. This process comprises the steps of

a) forming a first section of syntactic polyurethane elastomer on at least a portion of the substrate by (i) applying a first reaction mixture containing one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting

1 to 50 wt.-% of the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst to at least a portion of the substrate, wherein the first reaction mixture is substantially devoid of mercury compounds, and (ii) at least partially curing the first reaction mixture to form the first section of syntactic polyurethane elastomer, and then

b) forming a second section of syntactic polyurethane elastomer on at least a portion of the substrate by (i) applying a second reaction mixture containing one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of the combined the weight of particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of

microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst to at least a portion of the substrate and in contact with the first section of syntactic polyurethane elastomer to form at least one bondline between the first section of syntactic polyurethane elastomer and the second reaction mixture, wherein the second reaction mixture is substantially devoid of mercury compounds, and (ii) at least partially curing the second reaction mixture to form the second section of syntactic polyurethane elastomer adherent to the first section of syntactic polyurethane elastomer.

In another aspect, the present disclosure provides a process for producing a substrate having an applied syntactic polyurethane elastomer, comprising the steps of

a) forming a first section of syntactic polyurethane elastomer on at least a portion of the substrate by (i) applying a first reaction mixture containing one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), 0.10 to 0.25% based on the combined weight of all components of the reaction mixture except the polyisocyanate(s) of a ß-diketone compound, an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst to at least a portion of the substrate, wherein the first reaction mixture is substantially devoid of mercury compounds, and (ii) at least partially curing the first reaction mixture to form the first section of syntactic polyurethane elastomer, and then

b) forming a second section of syntactic polyurethane elastomer on at least a portion of the substrate by (i) applying a second reaction mixture containing one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer

particles constituting 1 to 50 wt.-% of the combined the weight of particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), 0.10 to 0.25% based on the combined weight of all components of the reaction mixture except the polyisocyanate(s) of a ß-diketone compound, an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst to at least a portion of the substrate and in contact with the first section of syntactic polyurethane elastomer to form at least one bondline between the first section of syntactic polyurethane elastomer and the second reaction mixture, wherein the second reaction mixture is substantially devoid of mercury compounds, and (ii) at least partially curing the second reaction mixture to form the second section of syntactic polyurethane elastomer adherent to the first section of syntactic polyurethane elastomer.

In another aspect, the present disclosure provides a cured syntactic polyurethane elastomer which is a reaction product of a reaction mixture comprising one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of based on the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), 0.10 to 0.25% based on the combined weight of all components of the reaction mixture except the polyisocyanate(s) of a ß-diketone compound, an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst, wherein the reaction mixture is essentially devoid of mercury compounds.

Figure 1 is a front view, in section, of a mold for making samples for bond strength testing.

Figure 2 is a front view of a tripartite elastomer for bond strength testing.

Figure 3 is a front view of a test sample for bond strength testing.

Figure 4 is a micrograph of a prior art syntactic polyurethane elastomer.

Figure 5 is a micrograph of a prior art syntactic polyurethane elastomer.

Figure 6 is a micrograph of a syntactic polyurethane elastomer of the invention.

The polymer polyol has a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 dispersed polymer particles. The dispersed polymer particles constitute, 1 to 50 wt.-%, preferably 5 to 25 wt.-%, of, the combined weight of the particles and all polyether polyol(s) in the reaction mixture.

The hydroxyl equivalent weight of the polyether polyol preferably is at least 1500 and is preferably up to 3000.

The polyether polyol(s) preferably have a nominal functionality of 2 to 6, preferably 2 to 4 and more preferably 2 to 3. The "nominal functionality" of a polyether polyol refers to the average number of oxyalkylatable groups per molecule on the initiator compound(s) used to make the polyether polyol. Actual functionalities may be somewhat lower than nominal functionalities in some instances.

Initiators that are useful for producing the polyether polyol(s) include, for example, water, ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propane diol, dipropylene glycol, tripropylene glycol, glycerin, trimethylolpropane,

WHAT IS CLAIMED IS:

1. A process for making a syntactic polyurethane elastomer, comprising

forming a reaction mixture containing at least one polymer polyol having a continuous phase containing one or more polyether polyols including a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), 0.10 to 0.25% based on the combined weight of all components of the reaction mixture except the polyisocyanate(s) of a ß-diketone compound, an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst, wherein the reaction mixture is essentially devoid of mercury compounds, and

b) curing the reaction mixture to form the syntactic polyurethane elastomer.

2. The process of claim 1 wherein in step b) is performed on the surface of a substrate to form a coating of the syntactic polyurethane elastomer on the substrate.

3. A process for producing a substrate having an applied syntactic polyurethane elastomer, comprising the steps of

a) forming a first section of syntactic polyurethane elastomer on at least a portion of the substrate by (i) applying a first reaction mixture containing one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), 0.10 to 0.25% based on the combined weight of all components of the reaction mixture except the polyisocyanate(s) of a ß-diketone compound, an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst to at least a portion of the substrate, wherein the first reaction

mixture is substantially devoid of mercury compounds, and (ii) at least partially curing the first reaction mixture to form the first section of syntactic polyurethane elastomer, and then

b) forming a second section of syntactic polyurethane elastomer on at least a portion of the substrate by (i) applying a second reaction mixture containing one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of the combined the weight of particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), 0.10 to 0.25% based on the combined weight of all components of the reaction mixture except the polyisocyanate(s) of a ß-diketone compound, an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst to at least a portion of the substrate and in contact with the first section of syntactic polyurethane elastomer to form at least one bondline between the first section of syntactic polyurethane elastomer and the second reaction mixture, wherein the second reaction mixture is substantially devoid of mercury compounds, and (ii) at least partially curing the second reaction mixture to form the second section of syntactic polyurethane elastomer adherent to the first section of syntactic polyurethane elastomer.

4. The process of claim 3 wherein the reaction mixtures are essentially devoid of mercury compounds.

5. The process of claim 3 or 4 wherein the bondline has a bond strength of at least 8.0 MPa, as measured according to ATSM D638.

6. The process of claim 3, 4 or 5 wherein the bondline has no visible defects when visualized microscopically at a magnification of 100X.

7. The process of any of claims 2-6 wherein the substrate is an undersea pipe or undersea architecture.

15. A cured syntactic polyurethane elastomer which is a reaction product of a reaction mixture comprising one or more polyether polyols including at least one polymer polyol having a continuous phase of a liquid polyether polyol having a hydroxyl equivalent weight of at least 800 and dispersed polymer particles, the dispersed polymer particles constituting 1 to 50 wt.-% of based on the combined weight of the particles and all polyether polyol(s) in the reaction mixture, 5 to 50 weight percent of microspheres based on the total weight of the reaction mixture, 1 to 30 parts by weight of a hydroxyl-terminated chain extender per 100 parts by weight of the polyether polyol(s), 0.10 to 0.25% based on the combined weight of all components of the reaction mixture except the polyisocyanate(s) of a ß-diketone compound, an aromatic polyisocyanate in amount to provide an isocyanate index of 80 to 130 and a non-mercury catalyst, wherein the reaction mixture is essentially devoid of mercury compounds.