bondlines 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 and which bonds well to itself.

This disclosure ~~invention~~ is in one ~~aspect~~ embodiment a cured syntactic polyurethane elastomer which is a reaction product of a reaction mixture comprising at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 and wherein the polyether polyol(s) contain no more than 60 microequivalents per gram (μeq/g) of terminal unsaturation, 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 polyether polyol having a number average hydroxyl equivalent weight of at least 800 wherein the polyether polyol(s) contain no more than 60 μeq/g of terminal unsaturation, 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 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.

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

a) forming a reaction mixture containing at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 wherein the polyether polyol(s) no more than 60 μeq/g of terminal unsaturation, 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 non-mercury catalyst, and 0.1 to 0.25% of a ß-diketone compound based on the combined weight of all components of the reaction mixture except the polyisocyanate(s), 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.

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 and 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 at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 wherein the polyether polyols contain no more than 60 μeq/g of terminal unsaturation, 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 surface of the substrate 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 at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 wherein the polyether polyol(s) contain no more than 60 μeq/g of terminal unsaturation, 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 surface 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 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 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 at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 wherein the polyether polyols(s) contain no more than 60 μeq/g of terminal unsaturation, 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, 0.1 to 0.25% of a ß-diketone compound based on the combined weight of all components of the reaction mixture except the polyisocyanate(s), and a non-mercury catalyst to at least a portion of the surface of the substrate 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 at least one polyether polyol having a number average hydroxyl equivalent weight of at least 1000 wherein the polyether polyol(s) contain no more than 60 μeq/g of terminal unsaturation, 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, 0.1 to 0.25% of a ß-diketone compound based on the combined weight of all components of the reaction mixture except the polyisocyanate(s), and a non-mercury catalyst to at least a portion of the surface 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 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.

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.

WHAT IS CLAIMED IS:

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

a) forming a reaction mixture containing at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 wherein the polyether polyol(s) no more than 60 μeq/g of terminal unsaturation, 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 non-mercury catalyst, and 0.1 to 0.25% of a ß-diketone compound based on the combined weight of all components of the reaction mixture except the polyisocyanate(s), 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 at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 wherein the polyether polyols(s) contain no more than 60 μeq/g of terminal unsaturation, 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, 0.1 to 0.25% of a ß-diketone compound based on the combined weight of all components of the reaction mixture except the polyisocyanate(s), and a non-mercury catalyst to at least a portion of the surface of the substrate 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 at least one polyether polyol having a number average hydroxyl equivalent weight of at least 1000 wherein the polyether polyol(s) contain no more than 60 μeq/g of terminal unsaturation, 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, 0.1 to 0.25% of a ß-diketone compound based on the combined weight of all components of the reaction mixture except the polyisocyanate(s), and a non-mercury catalyst to at least a portion of the surface 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 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.

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

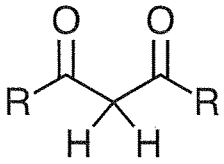
7. The process of any of claims 2-6 wherein the substrate is an undersea pipe or undersea architecture.

8. The process of claim 7 wherein the undersea pipe or undersea architecture is branched, curved or has another non-linear configuration.

9. The process of claim 7 or 8 wherein the undersea pipe or undersea architecture has one or more external features that protrude partially or completely through the applied syntactic polyurethane elastomer.

~~10. The process of any preceding claim, wherein the reaction mixture contains a ß-diketone compound.~~

1011. The process of claim 10 or claim 3, wherein the ß-diketone is a compound having the structure:



wherein each R is independently hydrocarbyl or inertly substituted hydrocarbyl.

1112. The process of claim 10, wherein the ß-diketone compound is one or more of acetylacetone (pentane-2,4-dione), hexane-2,4-dione, heptane-3,5-dione and 2,2,6,6-tetramethyl-3,5-heptanedione.

~~13. The process of any of claims 10-12, wherein the ß-diketone compound constitutes 0.1 to 0.25% of the combined weight of all components of the reaction mixture except the polyisocyanate(s).~~

1214. The process of ~~any of claims 10-13~~claim 10 or 11, wherein the non-mercury catalyst is one or more metal catalyst(s), and the weight of the ß-diketone compound 2 to 5 times that of the metal non-mercury catalyst(s).

1315. The process of ~~any preceding claim~~claim 10, wherein the polyether polyol is in each instance (A) prepared by adding propylene oxide and ethylene oxide to a difunctional or trifunctional initiator to produce a polyol having a hydroxyl equivalent weight of 1500 to 2500 and containing 5 to 30% by weight polymerized ethylene oxide, wherein the polymerized ethylene oxide is randomly polymerized with the propylene oxide, forms one or more internal blocks and/or forms terminal blocks that result in primary hydroxyl groups or (B) made by homopolymerizing propylene oxide or randomly copolymerizing 75-99.9 weight percent propylene oxide and 0.1 to 25 weight percent ethylene oxide onto a trifunctional initiator, and optionally capping the resulting polyether with up to 30% by weight (based on total product weight) ethylene oxide to form a polyether polyol having an equivalent weight of 1500 to 2500.

1417. The process of ~~any preceding claim~~claim 13, wherein the chain extender is 1,4-butanediol.

1518. The process of ~~any preceding claim~~claim 13, wherein the catalyst includes a zinc carboxylate.

~~19. The process of any of claims 8-12 wherein each of the first and second reaction mixtures contains 15 to 30 weight percent microspheres.~~

~~20. A cured syntactic polyurethane elastomer which is a reaction product of a reaction mixture comprising at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 wherein the polyether polyol(s) contain no more than 60 microequivalents per gram of terminal unsaturation, 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 organomercury compounds.~~