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 even when cast in confined complex geometries and which bonds well to itself.

This disclosure ~~invention~~ is in one embodiment ~~aspect~~ a cured syntactic polyurethane elastomer which is a reaction product of a reaction mixture comprising an alkylene glycol chain extender, 5 to 50 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, and (iii) 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 an alkylene glycol chain extender, 5 to 50 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, and (iii) 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 an alkylene glycol chain extender, 5 to 50 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, (iii) wherein the non-mercury catalyst is a zinc carboxylate or a mixture of 98-99.99 weight percent of one or more zinc carboxylates and 0.01 to 2 weight percent of one or more zirconium carboxylates and (iv) the reaction mixture is essentially devoid of mercury compounds, and

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

Surprisingly, the syntactic polyurethane elastomer of the disclosure~~invention~~ is morphologically very similar to conventional syntactic polyurethane elastomers made in a one-step process (*i.e.*, without first forming a prepolymer by reacting

the starting polyisocyanate with the polyol) using a mercury catalyst. These morphological similarities are seen using microscopic methods such as atomic force microscopy (AFM) as described more fully below. The syntactic polyurethane elastomer contains small discrete morphological domains of the order of 0.1 to 3 μm in diameter and is substantially free of discrete morphological domains on the order of 5 to 30 μm in diameter. These small discrete morphological domains are believed to represent regions rich in "hard segment", *i.e.,* the reaction product of the polyisocyanate and chain extender. Similarly sized discrete morphological domains are seen in conventional processes, using a mercury catalyst and without forming the prepolymer. When using a non-mercury catalyst without forming the prepolymer, the polyurethane often contains many large discrete morphological domains that are of the order of 5 to 30 μm across. It is believed that the morphological differences account at least in part for the difference in performance of elastomers made using mercury catalysts vs. non-mercury catalysts. The morphology of the Hg-GSPU systems correlates to better residual stress and shrinkage profile with acceptable application properties. The ability to simulate the morphology obtained with mercury-catalyzed systems without using a mercury catalyst is unexpected and quite advantageous.

The syntactic polyurethane elastomer of this disclosure ~~invention~~ also exhibits mechanical properties quite similar to those of conventional syntactic polyurethane elastomers made in the conventional one-step process with a mercury catalyst.

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 subsea architecture are substrates of particular interest.

An important advantage of this disclosure ~~invention~~ is that the syntactic polyurethane elastomer bonds well to itself and to other cured polyurethane elastomers. Thus, in certain embodiments, the disclosure ~~invention~~ is a process for producing a substrate having an applied syntactic polyurethane elastomer to a substrate. This process comprises the steps of

a) forming a section of a syntactic polyurethane elastomer on at least a portion of the substrate by (1) applying a first reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the

reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, and (iii) the reaction mixture is essentially devoid of mercury compounds, to at least a portion of the substrate and (2) 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 (1) applying a second reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, and (iii) the reaction mixture is essentially devoid of mercury compounds 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 and (2) 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, there is provided a process for producing a substrate having an applied syntactic polyurethane elastomer, comprising

a) forming a section of a syntactic polyurethane elastomer on at least a portion of the substrate by (1) applying a first reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is

sufficient to provide an isocyanate index of 80 to 130, (iii) wherein the non-mercury catalyst is a zinc carboxylate or a mixture of 98-99.99 weight percent of one or more zinc carboxylates and 0.01 to 2 weight percent of one or more zirconium carboxylates and (iv) the reaction mixture is essentially devoid of mercury compounds, to at least a portion of the substrate and (2) 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 (1) applying a second reaction mixture containing an alkylene glycol chain extender, 5 to 35 weight percent, based on the weight of the reaction mixture, of microspheres, an isocyanate-terminated prepolymer having an isocyanate content of 3 to 12% by weight, and a non-mercury catalyst, wherein (i) the prepolymer is the reaction product of at least one polyether polyol having a number average hydroxyl equivalent weight of at least 800 with an excess of an aromatic polyisocyanate, (ii) the amount of prepolymer provided to the reaction mixture is sufficient to provide an isocyanate index of 80 to 130, (iii) wherein the non-mercury catalyst is a zinc carboxylate or a mixture of 98-99.99 weight percent of one or more zinc carboxylates and 0.01 to 2 weight percent of one or more zirconium carboxylates and (iv) the reaction mixture is essentially devoid of mercury compounds 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 and (2) 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 dynamic mechanical analysis curve for an embodiment of the invention.

Figure 2a) is a micrograph of a syntactic polyurethane elastomer of the invention.

Figure 2b) is a micrograph of a prior art syntactic polyurethane elastomer.

Figure 2c) is a micrograph of a prior art syntactic polyurethane elastomer.

For purposes of this invention, a chain extender is one or more compounds having two to three hydroxyl groups and a hydroxyl equivalent weight of up to 125. A preferred type of chain extender is an aliphatic glycol or glycol ether. The aliphatic glycol is a straight-chain or branched alkane having two hydroxyl