Polyurethane Reactive Hot Melt Adhesives Comprising Hydroxy Terminated Resin Ester Modifiers

Executive summary
A new polyol family for the manufacture of novel polyurethane systems, preferably of polyurethane reactive hot melt adhesives is disclosed. The polyol(s) are reactive modifiers that enhance the properties of polyurethane systems. The inventive polyols are the reaction product of a monocarboxylic acid, a polycarboxylic acid and a polyhydric alcohol. The polyol of the present invention is used to produce urethane polymers, preferably polyurethane reactive hot melt adhesives by reacting the polyol with polyfunctional isocyanates. These adhesives provide good green strength and longer open time.

Background
In conventional hot melt adhesives, typically a polymer, a tackifier, and a selection of other additives such as antioxidants, are mixed together to produce an adhesive composition. These materials tend to form bonds through their rapid solidification from the melt. These materials have the advantage of being relatively easy to apply. However hot melt adhesives are typically not reactive in nature and therefore do not develop sufficient strength and sufficient heat and chemical resistance for certain applications. In order to impart sufficient structural, heat and chemical resistance to adhesive formulations, reactive or curable compositions are conventionally used. These materials tend to form durable bonds through a chemical reaction and as such are the adhesives of choice for various applications and substrates. However, reactive or curable compositions are typically lacking in versatility on the combined property characteristics of "green" strength and "open" time. This lack of process versatility makes the compositions handling characteristics poor and limits the composition's utility in some assembly operations.

In polyurethane reactive hot melt adhesives (polyurethane Rhma), an isocyanate terminated urethane polymer is produced through the polymerization of polyols and excess polyisocyanate compounds.

Polyurethane Rhma(s) typically are cured in the presence of moisture. Moisture, which is present in the ambient atmosphere, reacts with the isocyanate end groups to cause chain extension and or crosslinking. As a result of this curing reaction, polyurethane Rhma develop temperature and chemical resistance. A typical cured polyurethane Rhma would generally exhibit a degree of stiffness as well as toughness. Toughness of polyurethane Rhma is attributed to long chain polyols called "soft segments". Stiffness of the polyurethane Rhma is attributed to relatively short chain, high Tg, regions called "hard segments".

Typically, polyurethane Rhma(s) do not exhibit sufficient combined green strength and open time for many manufacturing processes. Also, while moisture cured polyurethane Rhma exhibit good temperature resistance when compared to typical hot melt adhesives, a need exists for a polyurethane Rhma that exhibit a desirable balance of processing, thermal and mechanical attributes.

Those skilled in the art of formulating polyurethane Rhma(s) have used so-called "modifiers" in an
attempt to improve the balance of processing, thermal and mechanical attributes of polyurethane Rhma(s). These conventional modifiers have included rosin glycerol ester, polycaprolactone diol and terpene phenolic resins. These modifiers have not provided a viable solution to the formulators' needs and hence a need still exists for a modifier that can provide a useful balance of processing, thermal and mechanical attributes to polyurethane Rhma(s).

**Eastman addresses a need**
The polyester polyols made in accordance with the present invention have resin acids incorporated therein through an esterification reaction. It is believed that the rosin acid brings advantages to the polyol of the present invention. First, the rosin’s monocarboxylic acid controls the hydroxyl functionality of the polyol, which allows use of polyhydric alcohols such as pentaerythritol, and improves structural performance of the adhesive. Second, the rosin may serve to increase the glass transition temperature. Moreover, presence of the rosin in combination with the other components used to make the polyol enhances the peel strength of adhesives made therefrom. For example, incorporation of an effective amount of the polyols made in accordance with the present invention into a urethane adhesive enhances such physical properties as modulus, elongation, tensile strength and heat resistance.

The isocyanate functional urethane polymers of this invention and or their blends with conventional isocyanate functional urethane polymers and or other thermoplastic and or elastomeric polymers may be used advantageously as moisture curable adhesives with excellent physical properties, including improved heat resistance. The inventive polyurethane Rhma(s) display a heretofore unattainable balance of processing, mechanical and thermal properties. Particularly surprising and beneficial is the ability of the inventive polyurethane Rhma to attain Shear Adhesion Failure Temperatures in excess of 200 degrees Centigrade.

Adhesives of the present invention are of use in many end uses, particularly in assembly operations. Among the assembly operations are transportation uses such as; carpet bonding, door panels, instrument panel assembly, recreation vehicles, over the road trailers, heavy-duty trucks and marine uses. Also among the assembly operations that adhesives of the present invention are of use in construction uses such as; window assembly, garage door assembly and structural insulated panels. Also among the assembly operations that adhesives of the present invention are of use in other assembly applications such as; shoe soles, non-wovens, and profile wrapping including edge banding.

**Technology highlights**
The present invention relates to new polyols, urethane polymers made from these polyols and reactive hot melt adhesive compositions which include the urethane polymers.

The present invention particularly relates to polyols comprising the reaction products of a polyesterification process employing monocarboxylic acids, polyhydric alcohols and dicarboxylic acids as reactants.

The polyols of this invention have utility in polyurethane compositions and confer upon such compositions a desirable balance of processing, mechanical and thermal attributes, particularly when such compositions are used as reactive hot melt adhesives.
Technology details
The present invention relates to new polyols, new urethane polymers made from these polyols and reactive hot melt adhesive compositions based on the new urethane polymers. In one embodiment, the present invention particularly relates to polyester polyols which include the reaction products of a polyesterification process employing monocarboxylic acids, polyhydric alcohols and polycarboxylic acids as reactants.

The preferred monocarboxylic acid reactants are rosin acids including wood, gum and tall oil rosin acids. Particularly preferred rosin acids are tall oil rosin acids. The rosin acids may be a mixture of rosin acids obtained by a distillation process. Such distillates will comprise a mixture of various rosin acids including abietic acid and its isomers.

The polyhydric alcohol reactants preferably have more than two hydroxyl functional groups per molecule. Particularly preferred are polyhydric alcohols having three or more hydroxyl functional groups per molecule. Preferred polyhydric alcohols include pentaerythritol cyclohexane dimethanol, trimethylol propane, dipropylene glycol, and combinations thereof.

The preferred polycarboxylic acid reactants have an acid functionality of about two and may be aliphatic or aromatic dicarboxylic acids. Preferred aliphatic dicarboxylic acids include adipic acid and preferred aromatic dicarboxylic acids include phthalic and isophthalic acids. Phthalic acid is preferably used as its anhydride. Particularly preferred are aliphatic dicarboxylic acids and especially adipic acid. When the particularly preferred aliphatic dicarboxylic acid, adipic acid, is utilized, aromatic dicarboxylic acids such as phthalic acid and isophthalic acids may be optionally and advantageously used as well in the reactant mixture provided the moles of aromatic dicarboxylic acid does not exceed about twice the moles of aliphatic dicarboxylic acid.

Intellectual property portfolio
US Patent No. 6,525,162: Polyols, polyurethane systems and polyurethane reactive hot melt adhesives produced therefrom

Other technology and service offerings
Eastman’s Technology Licensing and Alliances group focuses on the licensing, sale, donation and disposition of intellectual capital for the enterprise. The scope of our offerings can begin with the simplistic granting of rights from the Eastman patent portfolio and progress through the transfer of proprietary skills, design specifications and knowledge captured in our confidential know-how.

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