This disclosure is related to solvents, monomer, polymers, crosslinking agents and other additives, particularly those useful in the paints and coatings industry that are derived from renewable resources.
FIELD OF THE DISCLOSURE

This disclosure is related to the field of renewable resourced materials. Specifically, the disclosure relates to solvents, intermediates and other chemical products that are produced from renewable resources and are useful for displacing those materials that are currently derived from petroleum feedstocks. Of particular interest are solvents, monomers, polymers and additives that can be used in the field of paints and coatings, especially automotive coatings.

DESCRIPTION OF THE RELATED ART

The production of chemical intermediates, solvents for chemical reactions, monomers and the polymers produced from monomers is an important industry. The chemical industry supplies many of the raw materials and finished products that are in use today. Many of the components that are supplied by the chemical industry are produced using petroleum feedstock as the initial source. Some of these components can be refined or otherwise purified directly from the petroleum. Other components need to be subject to further processes or chemical reactions to produce to the desired chemical/intermediate.

With a growing world population, the demand for products produced in the chemical industry is also increasing. This growing demand places a high burden on the remaining petroleum feedstock, a non-renewable resource. The increasing demand, dwindling supplies and the ever increasing instability in some of the regions that produce petroleum feedstock is causing raw material prices to rise sharply. These price increases are ultimately passed onto the consumer who purchases the products that are made from these raw materials.

A need exists to produce chemical products and chemical intermediates from resources other than petroleum. There have been attempts in the past to produce chemicals wherein at least part of the molecule is renewably resourced. An example of this is polytrimethylene terephthalate. In this polyester, the trimethylene portion of the molecule can be derived from 1,3-propane diol that is derived from bio-sources. However,
the terephthalic acid comes from a petroleum source, so the polyester is only partially derived from renewable resources.

A need exists to produce products from renewable resources that have the same or better performance attributes. There also exists a need in the chemical industry to incorporate renewable resources into the chemical processes that make products and/or intermediates.

**SUMMARY OF THE DISCLOSURE**

Disclosed herein is a melamine resin of the formula;

\[
\begin{align*}
R_3R_4N & \quad N(R_3)CH_2OH \\
N & \quad NR_3R_4
\end{align*}
\]

wherein each \( R_1 \) and \( R_2 \) are independently selected from the group of \( H \) and \( CH_2OH \) and wherein the carbon atoms of each \( CH_2OH \) present in the molecule is derived from bio-formaldehyde.

Also disclosed herein is a melamine resin of the formula;

\[
\begin{align*}
R_3R_4N & \quad N(R_5)CH_2OR_5 \\
N & \quad NR_3R_4
\end{align*}
\]

wherein each of \( R_3 \) and \( R_4 \) is independently selected from the group \( H \) and \( CH_2OR_5 \);

each \( R_5 \) is independently selected from an alkyl group having from 1 to 4 carbon atoms;

the carbon atoms of each \( CH_2O \) present in the molecule is derived from bio-formaldehyde; and

wherein each of the carbon atoms of each \( R_5 \) present is derived from a bio-alcohol.

**DETAILED DESCRIPTION**

The features and advantages of the present disclosure will be more readily understood, by those of ordinary skill in the art, from reading the
following detailed description. It is to be appreciated that certain features of the disclosure, which are, for clarity, described above and below in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the disclosure that are, for brevity, described in the context of a single embodiment, may also be provided separately or in any sub-combination. In addition, references in the singular may also include the plural (for example, "a" and "an" may refer to one, or one or more) unless the context specifically states otherwise.

The use of numerical values in the various ranges specified in this application, unless expressly indicated otherwise, are stated as approximations as though the minimum and maximum values within the stated ranges were both preceded by the word "about". In this manner, slight variations above and below the stated ranges can be used to achieve substantially the same results as values within the ranges. Also, the disclosure of these ranges is intended as a continuous range including every value between the minimum and maximum values.

The phrases "renewable resource" and "renewably resourced" mean that the material or process described comprise components that can be derived from plant or animal material, commonly called bio-mass. The components may be naturally occurring in the bio-mass or may be the transformation product of natural or genetically engineered organisms or other chemical transformation processes. Suitable examples for the transformation of bio-mass include, for example, chemical processes, biological fermentation; anaerobic yeast, fungal or bacterial processes; aerobic yeast, fungal or bacterial process; and chemical enzyme process. The components may be produced in their pure form or they may require a step or steps of isolation and/or purification prior to use. While the components may be capable of being derived from petroleum feedstock, the phrases are intended to exclude components that specifically derive 100 percent of their carbon atoms from petroleum feedstock.

The term "bio-" placed as a prefix means that at least a portion of the carbon atoms of the component are derived from a renewable resource. Also included within this definition are those components that are produced naturally in plants. For example, bio-limonene and bio-isobomyl alcohol can be harvested from various plants. While the component may be capable of being derived from petroleum feedstock, the prefix is intended to exclude
those components that specifically derive all of their carbon atoms from petroleum feedstock. As an example, "bio-ethanol" means ethanol that is formed from renewable resources. All of the carbon atoms in bio-ethanol derived from, for example, fermentation, are from renewable resources. If a component is the reaction product of two or more intermediates, then to be described as a bio-component, at least a portion of the carbon atoms that form a part of the final component must be derived from biomass sources. Catalysts, solvents or other adjuvants that are used to facilitate the reaction, but do not form a part of the final bio-component, do not necessarily need to be derived from biomass.

In one embodiment of the disclosure, a bio-component derives all of its carbon content from renewable resources. For example, a bio-monomer produced from the esterification reaction between bio-acrylic acid and bio-ethanol to form bio-ethyl acrylate derives 100 percent of its carbon from renewable resources.

In a second embodiment, a bio-component derives greater than 1 percent of its carbon from renewable resources. For example, a bio-monomer produced from the esterification reaction between petroleum based acrylic acid (containing 3 carbon atoms) and bio-ethanol (containing 2 carbon atoms) to form bio-ethyl acrylate derives 40 percent of its carbon from renewable resources.

In a third embodiment, a bio-component derives greater than 10 percent of its carbon from renewable resources.

In a fourth embodiment, a bio-component derives greater than 20 percent of its carbon from renewable resources.

These bio-based components differ from petroleum-based components. Petroleum-based components do not have the carbon 14 isotope present. Bio-based products have an identifiable amount of carbon 14. Carbon 14 is present in bio-mass as a result of carbon dioxide that is formed when nitrogen is struck by an ultra-violet light produced neutron, causing the nitrogen to lose a proton and form carbon of molecular weight 14 which is immediately oxidized to carbon dioxide. This radioactive isotope represents a small but measurable fraction of atmospheric carbon. Atmospheric carbon dioxide is cycled by green plants to make organic molecules during the process known as photosynthesis. The cycle is completed when the green plants or other forms of life metabolize the organic
molecules producing carbon dioxide which is released back to the atmosphere. Virtually all forms of life on Earth depend on this green plant production of organic molecule to produce the chemical energy that facilitates growth and reproduction. Therefore, the carbon 14 that exists in the atmosphere becomes part of all life forms, and their biological products. These renewably based organic molecules that biodegrade to carbon dioxide do not contribute to global warming as there is no net increase of carbon emitted to the atmosphere. In contrast, petroleum-based carbon does not have the signature radiocarbon ratio of atmospheric carbon dioxide.

Assessment of the renewably based carbon in a material can be performed through standard test methods. Using radiocarbon and isotope ratio mass spectrometry analysis, the bio-based content of materials can be determined. ASTM International, formally known as the American Society for Testing and Materials, has established a standard method for assessing the bio-based content of materials. The ASTM method is designated ASTM-D6866.

The application of ASTM-D6866 to derive a "bio-based content" is built on the same concepts as radiocarbon dating, but without use of the age equations. The analysis is performed by deriving a ratio of the amount of radiocarbon (carbon 14) in an unknown sample to that of a modern reference standard. The ratio is reported as a percentage with the units "pMC" (percent modern carbon). If the material being analyzed is a mixture of present day radiocarbon and fossil carbon (containing no carbon 14), then the pMC value obtained correlates directly to the amount of biomass material present in the sample.

The modern reference standard used in radiocarbon dating is a NIST (National Institute of Standards and Technology) standard with a known radiocarbon content equivalent approximately to the year AD 1950. AD 1950 was chosen since it represented a time prior to thermo-nuclear weapons testing which introduced large amounts of excess radiocarbon into the atmosphere with each explosion (termed "bomb carbon"). The AD 1950 reference represents 100 pMC.

Bomb carbon in the atmosphere reached almost twice normal levels in 1963 at the peak of testing and prior to the treaty halting the testing. Its distribution within the atmosphere has been approximated since its appearance, showing values that are greater than 100 pMC for plants and
animals living since A.D. 1950. It's gradually decreased over time with today's value being near 107.5 pMC. This means that a fresh biomass material such as corn could give a radiocarbon signature near 107.5 pMC.

Combining fossil carbon with present day carbon into a material will result in a dilution of the present day pMC content. By presuming 107.5 pMC represents present day biomass materials and 0 pMC represents petroleum derivatives, the measured pMC value for that material will reflect the proportions of the two component types. A material derived 100% from present day biomass would give a radiocarbon signature near 107.5 pMC. If that material was diluted with 50% petroleum derivatives, it would give a radiocarbon signature near 54 pMC.

A biomass content result is derived by assigning 100% equal to 107.5 pMC and 0% equal to 0 pMC. In this regard, a sample measuring 99 pMC will give an equivalent bio-based content result of 93%.

**RENEWABLY RESOURCED SOLVENTS**

In one embodiment of this disclosure, a bio-solvent is produced from renewable resources. The bio-solvent may not be directly available from the renewable resource. In cases where the bio-solvent is not directly available from the renewable resource, the component that can be derived from the renewable resource may need to undergo one or more chemical reactions and/or purification steps to form the desired bio-solvent. In one embodiment, two or more chemical components, at least one of which is derived from bio-mass sources, are used to produce the desired bio-solvent. In another embodiment, two or more chemical components, each of which is derived from bio-mass sources, are used to produce the desired bio-solvent. As an example, the esterification of bio-acetic acid with bio-butanol, can form bio-butyl acetate.

In another embodiment, a bio-solvent derives greater than 10 percent of its carbon from renewable resources.

In a further embodiment, a bio-solvent derives greater than 20 percent of its carbon from renewable resources.

The renewably resourcing of solvents is an area of the chemical industry that has a large potential for displacing petroleum-derived solvents. Commonly used solvents include alcohols, esters, ketones, ethers and hydrocarbons. Many of these materials are not available as pure compounds
from bio-mass sources, but the reaction of two or more compounds available via bio-transformation processes can result in useful solvents.

**ALCOHOLS**

Suitable alcohols that can be produced via renewable resources include mono-, di-, tri- and higher alcohols having 1 or more carbon atoms. For example, bio-methanol, bio-ethanol, isomers of bio-propanol, isomers of bio-butanol, isomers of bio-pentanol, isomers of bio-hexanol, cyclopentanol, bio-ethylene glycol, bio-1,3-propane diol, bio-1,2-propane diol, bio-1,4-butane diol, bio-2-methyl-1,4-butane diol, bio-1,5-pentane diol, bio-glycerol, bio-isobomyl alcohol, and others. Bio-methanol, bio-ethanol and bio-butanol can be formed by well-known fermentation process. Other alcohols can be produced as well, see for example, US 4,536,584.

**ESTERS**

Ester-based solvents can be produced from the reaction of a bio-carboxylic acid and a bio-alcohol. Suitable acids that can be produced via renewable resources include, for example, formic acid, acetic acid, propionic acid, butyric acid, lactic acid, malonic acid, and adipic acid. See US 5,874,263, WO 95/07996, Biotechnology Letters Vol. 11(3), pages 189-194, 1989 and Green Chemistry 2008, DOI: 10.1039/b802076k.

Ester-based solvents are widely used in the chemical industry, especially as polymerization solvents and reducers in the paint and coating industry. Bio-esters can be formed from a bio-acid and a bio-alcohol via the well-known esterification industrial process of these generic components. In one embodiment of the present disclosure, bio-acetic acid can be reacted under esterification reaction conditions with bio-butanol to form bio-butyl acetate. Bio-butyl acetate can be used in the synthesis of polyacrylates and as a reducer for many paint and coating applications. In another embodiment, bio-tert-butyl acetate can be produced using Indium catalysts, see Journal of Molecular Catalysis, volume 235, page 150-153, 2005.

**KETONES AND ALDEHYDES**

Ketone-based and aldehyde-based solvents can be produced by the oxidation of many of the above listed bio-alcohols. Bio-acetone, bio-methyl
ethyl ketone, bio-cyclopentanone, bio-cyclohexanone, bio-2-pentanone, bio-2,5-hexanediione, and the various isomers of 4 to 6 carbon bio-ketones are useful as solvents in many chemical reactions, such as, for example, free radical polymerization and they can also be used as a reducer in paint and coating applications. See for example, US 4,536,584.

**ETHERS**

Bio-ethers, including bio-polyethers, can be produced from bio-mass or via the condensation of bio-alcohols with bio-ketones and bio-aldehydes according to known ether forming reaction processes. Examples include, bio-diethoxymethane and bio-tetrahydrofuran. See for example, US 4,536,584. Other methods to produce bio-polyethers can include, the polymerization of bio-ethylene oxide. Bio-ethylene oxide can be produced from the epoxidation of bio-ethylene. Low molecular weight polyethers, especially alkyl capped-polyethers, are commonly used as solvents.

**ALKANES**

Alkane hydrocarbon solvents are commonly used in free radical polymerizations. Bio-hydrocarbons having in the range of from 1 to 15 carbon atoms can be produced from bio-mass according to the procedures given in US 6,180,845 or Chemistry and Sustainable Chemistry, Volume 1, pages 417-424, 2008. Distillation or other purification procedures can provide pure fractions of bio-hydrocarbons, such as, for example, bio-hexane that can be used in, for example, free radical polymerization processes.

**AROMATICs**

Aromatics, such as, toluene and xylene, are also commonly used in polymerization reactions and as reducers in coatings formulations. Using fast-pyrolosis techniques and certain zeolites, it is possible to produce bio-aromatics that can be used for polymerization solvents and as reducers for the paint and coatings industry. See for example, Chemistry and Sustainable Chemistry, Volume 1, pages 397-400, 2008.

**RENEWABLY RESOURCED MONOMERS AND POLYMERS**

Acrylic and methacrylic monomers represent a large portion of the monomers that are used to produce the acrylic polymers in the paint and
coating industry. Both bio-3-hydroxypropionic acid and bio-2-hydroxyisobutyric acids are available via bio-transformation pathways, see for example, Biotechnology Journal, volume 1, pages 756-769, 2006 and Applied Microbiological Biotechnology, volume 66, pages 131-142, 2004. These bio-acids can be dehydrated to form bio-acrylic acid and bio-methacrylic acid.

The bio-acrylic acid and bio-methacrylic acid monomers can be used to form numerous bio-alkyl acrylate and bio-alkyl methacrylate esters as well as bio-acrylamides, bio-methacrylamides, bio-acrylonitrile and bio-methacrylonitrile. Bio-acrylate and bio-methacrylate esters can be produced, via esterification reactions with bio-alcohols. By incorporating an excess of bio-diols into the esterification reaction, hydroxy functional bio-acrylate and bio-methacrylate esters can be formed. Using at least two equivalents excess of the bio-acrylic acid and bio-methacrylic acid with bio-diols, bio-diacylates and bio-dimethacrylates can be formed. These types of monomers find widespread use in the acrylic polymers used in the paint and coatings industry.

A representative sample of bio-alkyl acrylate and bio-alkyl methacrylate esters are shown in TABLE 1. This table is meant to provide a sample of the commercially important bio-acrylate and bio-methacrylate esters that can be produced from bio-sources.
Bio-epichlorhydrin is also available from glycerol, a renewable resource, via the EPICEROL™ process developed by Solvay. Bio-epichlorohydrin allows the formation of bio-glycidyl acrylate and bio-glycidyl methacrylate monomers, which are two monomers that find use in the paints and coatings industry.

While acrylic and methacrylic esters monomers make up the majority of the monomers that are used to produce acrylic polymers, other monomers can be copolymerized with these ester monomers to modify the properties of the polymer. This is especially useful for producing acrylic polymers used in the paint and coatings industry. These monomers can include, for example,

<table>
<thead>
<tr>
<th>Bio-alcohol</th>
<th>Bio-acrylic acid</th>
<th>Bio-methacrylic acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio-methanol</td>
<td>bio-methyl acrylate</td>
<td>bio-methyl methacrylate</td>
</tr>
<tr>
<td>Bio-ethanol</td>
<td>bio-ethyl acrylate</td>
<td>bio-ethyl methacrylate</td>
</tr>
<tr>
<td>Bio-1-propanol</td>
<td>bio-propyl acrylate</td>
<td>bio-propyl methacrylate</td>
</tr>
<tr>
<td>Bio-2-propanol</td>
<td>bio-isopropyl acrylate</td>
<td>bio-isopropyl methacrylate</td>
</tr>
<tr>
<td>Bio-1-butanol</td>
<td>bio-butyl acrylate</td>
<td>bio-butyl methacrylate</td>
</tr>
<tr>
<td>Bio-2-butanol</td>
<td>bio-isobutyl acrylate</td>
<td>bio-isobutyl methacrylate</td>
</tr>
<tr>
<td>Bio-ethylene glycol</td>
<td>bio-2-hydroxyethyl acrylate</td>
<td>bio-2-hydroxyethyl methacrylate</td>
</tr>
<tr>
<td>Bio-1,2-propylene glycol</td>
<td>bio-2-hydroxypropyl acrylate</td>
<td>bio-2-hydroxypropyl methacrylate</td>
</tr>
<tr>
<td>Bio-1,3-propylene glycol</td>
<td>bio-3-hydroxypropyl acrylate</td>
<td>bio-3-hydroxypropyl methacrylate</td>
</tr>
<tr>
<td>Bio-1,4-butane diol</td>
<td>bio-4-hydroxybutyl acrylate</td>
<td>bio-4-hydroxybutyl methacrylate</td>
</tr>
<tr>
<td>Bio-1,2-butane diol</td>
<td>bio-2-hydroxybutyl acrylate</td>
<td>bio-2-hydroxybutyl methacrylate</td>
</tr>
<tr>
<td>Bio-isobornyl alcohol</td>
<td>bio-isobornyl acrylate</td>
<td>bio-isobornyl methacrylate</td>
</tr>
</tbody>
</table>
acrylamide, methacrylamide, acrylonitrile and methacrylonitrile, styrene and styrene derivatives, or combinations thereof are often used.

Bio-acrylamides and bio-methacrylamides can be derived from the corresponding bio-acrylic acid and bio-methacrylic acid, for example, by the formation of bio-acid chlorides, followed by amination with ammonia or other primary and/or secondary amines.

Bio-acrylonitrile and bio-methacrylonitrile can be produced by the dehydration of bio-acrylamide and bio-methacrylamide using, for example, phosphorus pentoxide.

Bio-styrene can be produced from phenylalanine by the deamination using phenylalanine ammonia lyase, which results in the formation of cinnamic acid. The formed cinnamic acid can then be decarboxylated using a variety of methods, including bio-synthetic pathways. See for example, The Chemical and Pharmaceuticals Bulletin, Volume 49(5), pages 639-641, 2001.

Another group of monomers that are important to the coating industry are the monomers that produce polyesters. These monomers include monoalcohols, diols, triols and higher polyols; monocarboxylic acids, dicarboxylic acids, and higher carboxylic acids; as well as hydroxy-functional carboxylic acids, for example, 12-hydroxy stearic acid. There exists process for many of these monomers to be produced from bio-mass sources, thereby providing a route to bio-monomers that can be used to form bio-polyesters. Bio-alcohols and some bio-acids have been discussed above. Bio-diacids are also available. References can be found to produce bio-adipic acid as well as other diacids; see for example, US 4,400,468 and US 4,965,201.

In one embodiment, all of the carbon atoms of the monomer are derived from bio-mass.

In a second embodiment, greater than 10 percent of the carbon atoms of the monomer are derived from bio-mass.

In a third embodiment, greater than 20 percent of the carbon atoms of the monomer are derived from bio-mass.

In one embodiment, all of the carbon atoms of the polymer are derived from bio-mass.

In a second embodiment, greater than 10 percent of the carbon atoms of the polymer are derived from bio-mass.

In a third embodiment, greater than 20 percent of the carbon atoms of the polymer are derived from bio-mass.
RENEWABLY RESOURCED CROSINGLINKING AGENTS

Melamine resins and polyisocyanate compounds are important to many industries, including the paint and coatings industry where they are often use as crosslinking agents in coating compositions.

Bio-melamine resins can be produced by the reaction of melamine with a bio-aldehyde, typically bio-formaldehyde, to form bio-methylol melamine, bio-dimethylol melamine, bio-trimethylol melamine, up to and including bio-hexamethylol melamine. This class of bio-melamine resins is useful as a crosslinking agent for many coatings and can be represented by compounds of the formula;

\[
\begin{align*}
R_2R_1N & \quad N(R_1)CH_2OH \\
& \quad NR_1R_2
\end{align*}
\]

wherein each \( R_1 \) and \( R_2 \) are independently selected from the group of \( H \) and \( CH_2OH \). In the structure presented above, at least the carbon atom of each \( CH_2OH \) is derived from a renewable resource, via bio-formaldehyde.

Melamine can be produced via the trimerization of cyanamide. Cyanamide is available from urea, which is the dehydration product of ammonium carbonate. Ammonium carbonate can be derived from ammonia and carbon dioxide. If the carbon dioxide were isolated from air, it would be possible that all of the carbon atoms in the above described melamines to have a measurable carbon 14 signature.

Methylol melamine resins are often treated with an alcohol under acidic conditions to form etherated melamine resins. Bio-alcohols, discussed above, can be used to form bio-etherated melamine resins that are derived from renewable resources. Typically, the alcohols used to produce the ether group are low molecular weight alcohols ranging from methanol to isomers of butanol. Etherated melamines typically have a structure according to the formula;
wherein each of $R_3$ and $R_4$ is independently selected from the group $H$ and $CH_2OR_5$;

$R_5$ is independently selected from an alkyl group having from 1 to 4 carbon atoms;

the carbon atoms of each $CH_2O$ present in the molecule is derived from bio-formaldehyde; and

wherein each of the carbon atoms of each $R_5$ present is derived from a bio-alcohol.

Amines and diamines from bio-sources can be used to produce bio-isocyanates and bio-polyisocyanates that are also used in the coatings industry as crosslinking agents. The amine functional group is easily converted to an isocyanate functional group when reacted with phosgene. Diamines can be produced from biomass, as in US 7,189,543, or they can be synthesized from a variety of compounds that are available from bio-sources. For example, bio-alcohols can be oxidized to the corresponding bio-ketones and/or bio-aldehydes and then be subjected to reductive amination procedures. Bio-acids can be converted to bio-nitriles and then hydrogenated to form the desired bio-amines. Other methods are known in the art for producing amine groups from a variety of starting materials, many that are available from renewable resources.

The bio-isocyanate functional compounds can be used in any of the forms that are typically employed in the paint and coating industry. For example, bio-1,6-hexamethylene diisocyanate can be trimerized to form the isocyanurate of 1,6-hexamethylene diisocyanate. Any other bio-polyisocyanate can also be homopolymerized to form any of the known isocyanate adducts, including, for example, carbodiimides, isocyanurates, uretidiones, allophanates, and/or biurets.

Bio-isocyanates such as, for example, bio-1,6-hexamethylene diisocyanate or any other suitable bio-polyisocyanate can be blocked with a blocking agent to form a blocked isocyanate allowing the formation of one-
component coating compositions that unblock and are capable of forming crosslinks with suitable film-forming binders upon the application of heat. Suitable blocking agents include, for example, bio-alcohols and oximes. Bio-alcohols include, for example, bio-methanol, bio-ethanol, isomers of bio-propanol, isomers of bio-butanol. Bio-oximes can be produced by the reaction of a bio-aldehyde or a bio-ketone with hydroxylamine. The oximes can then be reacted with bio-isocyanates and/or bio-polyisocyanates to block the isocyanate groups.

In one embodiment, all of the carbon atoms of the bio-melamine resin are derived from bio-mass.

In a second embodiment, greater than 10 percent of the carbon atoms of the bio-melamine resin are derived from bio-mass.

In a third embodiment, greater than 20 percent of the carbon atoms of the bio-melamine resin are derived from bio-mass.

In one embodiment, all of the carbon atoms of the etherated bio-melamine resin are derived from bio-mass.

In a second embodiment, greater than 10 percent of the carbon atoms of the etherated bio-melamine resin are derived from bio-mass.

In a third embodiment, greater than 20 percent of the carbon atoms of the etherated bio-melamine resin are derived from bio-mass.

In one embodiment, all of the carbon atoms of the bio-isocyanate are derived from bio-mass.

In a second embodiment, greater than 10 percent of the carbon atoms of the bio-isocyanate are derived from bio-mass.

In a third embodiment, greater than 20 percent of the carbon atoms of the bio-isocyanate are derived from bio-mass.

**RENEWABLY RESOURCED COATINGS ADDITIVES**

Additives for coating compositions, that are currently produced, at least in part from petroleum feedstocks could also be prepared from bio-sources. For example, cellulose acetate butyrate (CAB) is a commonly used additive in many coating compositions. Cellulose itself is available from biomass and the reaction of cellulose with bio-acetic acid and bio-butyric acid can form bio-CAB.
RENEWABLY RESOURCED COATINGS

The paint and coatings industry produces many types of coating compositions. For example, the automotive coatings industry produces coatings that are used as primers, basecoats, clearcoats, monocoats and others. Each of these types of coatings utilizes a film-forming polymeric binder to provide a coating composition that provides adhesion to the underlying substrate, chip resistance, protection from ultraviolet radiation, gloss, and other aesthetic attributes according to their specific function. The coating compositions can also include solvents, crosslinking agents, pigments and other additives.

Coating formulations will often use acrylic polymers, polyester polymers, polyesterurethane polymers, polyethers, polyetherurethanes, or combinations thereof as the film-forming binders. These film-forming binders can optionally be crosslinked using any of the previously described crosslinking agents.

To produce film-forming acrylic polymers, a monomer mixture is typically polymerized in a solvent using free radical initiators. The acrylic polymers formed can be linear, graft, comb, crosslinked microgel resins or any of the known acrylic polymers that are typically used in coating compositions. Bio-solvents, are optional during the polymerization and, if used, typically remain as a part of the coating composition and help to produce a coating composition that is able to flow forming a continuous and relatively flat layer of coating composition on the substrate to which it is applied. During the curing step, the bio-solvents can evaporate to give a crosslinked coating that is essentially free from the bio-solvent. Using any of the bio-solvents, bio-monomers and bio-crosslinking agents described herein, one of ordinary skill in the art could produce bio-acrylic coating compositions wherein substantially all of the carbon atoms that form the crosslinked polymer network have come from renewably resourced materials.

Bio-polyesters can be formed that are linear, branched, graft or any other configuration known in the art. Formation of bio-polyesters uses essentially the same procedures as polyesters from non-renewable resources. The bio-polyesters can be formed from neat mixtures of the bio-monomers or bio-solvents can be added. The bio-polyesters can then be
formulated into coating compositions with or without crosslinking agents. Especially useful in a coating composition are those polyesters that are hydroxyl functional. The hydroxyl functional group allows the polyester to react with a crosslinking agent to form a crosslinked network.

Hydroxyl-functional bio-polyesters can also be reacted with bio-isocyanates or bio-polyisocyanates to form bio-polyesterurethanes. The urethane (carbamate) group provides excellent properties in a crosslinked coating, especially in automotive coatings.

Bio-polyethers were previously described in the solvent section. These polymers can be used as film-forming polymers when formulating coating compositions. Star-type polyethers can be formed by initiating the polyether formation with a polyol such as, for example, sorbitol, glycerol, or other bio-polyol. Typically, polyethers used for coating compositions have hydroxyl functional groups to allow the polyether to be crosslinked with the crosslinking agents.

Bio-polyetherurethanes can be formed by the reaction of hydroxyl-functional bio-polyethers with bio-isocyanates or bio-polyisocyanates. The urethane (carbamate) group provides excellent properties in a crosslinked coating, especially in automotive coatings.

While the solvents, monomer, polymers and other additives disclosed herein are described in terms of their use in the paint and coatings industry, they are also suitable for use in many other industries. For example, the solvents, monomer, polymers and additives described can be used in, for example, a pharmaceutical composition, an agricultural composition, an adhesive composition, an ink composition, a lubricant composition, a fuel composition or other industrial composition.
What is claimed is:

1. A melamine resin of the formula:

\[
\begin{align*}
\text{NR}_1\text{R}_2 \\
\text{R}_2\text{R}_1\text{N} \quad \begin{array}{c}
\text{N} \\
\text{N} \quad \text{N} \\
\text{NR}_1\text{R}_2 \\
\text{R}_2\text{R}_1\text{N} \quad \begin{array}{c}
\text{N} \\
\text{N} \quad \text{N} \\
\text{NR}_1\text{R}_2 \\
\text{R}_2\text{R}_1\text{N} \quad \begin{array}{c}
\text{N} \\
\text{N} \quad \text{N} \\
\text{NR}_1\text{R}_2
\end{array}
\end{array}
\end{array}
\end{align*}
\]

wherein each \( R_1 \) and \( R_2 \) are independently selected from the group of \( \text{H} \) and \( \text{CH}_2\text{OH} \) and wherein the carbon atoms of each \( \text{CH}_2\text{OH} \) present in the molecule is derived from bio-formaldehyde.

2. A melamine resin of the formula:

\[
\begin{align*}
\text{NR}_3\text{R}_4 \\
\text{R}_4\text{R}_3\text{N} \quad \begin{array}{c}
\text{N} \\
\text{N} \quad \text{N} \\
\text{NR}_3\text{R}_4 \\
\text{R}_4\text{R}_3\text{N} \quad \begin{array}{c}
\text{N} \\
\text{N} \quad \text{N} \\
\text{NR}_3\text{R}_4 \\
\text{R}_4\text{R}_3\text{N} \quad \begin{array}{c}
\text{N} \\
\text{N} \quad \text{N} \\
\text{NR}_3\text{R}_4
\end{array}
\end{array}
\end{array}
\end{align*}
\]

wherein each of \( R_3 \) and \( R_4 \) is independently selected from the group \( \text{H} \) and \( \text{CH}_2\text{OR}_5 \);

\( R_3 \) is independently selected from an alkyl group having from 1 to 4 carbon atoms;

the carbon atoms of each \( \text{CH}_2\text{O} \) present in the molecule is derived from bio-formaldehyde; and

wherein each of the carbon atoms of each \( R_5 \) present is derived from a bio-alcohol.

3. The melamine resin of claim 1 or 2 used as a crosslinking agent in a coating composition.

4. The melamine resin of claim 1 or 2 wherein greater than 10 percent of the carbon atoms of said melamine are derived from bio-mass.