Title: BIODEGRADABLE POLYMER COMPOSITIONS

Abstract

There is disclosed a composition comprising the combination, under conditions sufficient to ensure uniform melt formation, of: (a) starch and/or a starch derivative, and (b) at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group. The invention further relates to methods of making the composition, to articles made from said composition, and to the use of at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group, as a processing aid in the preparation and/or processing of a starch-based composition.
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Biodegradable Polymer Compositions

Field of the Invention

The present invention relates to biodegradable compositions capable of being formed by heat and pressure into articles having good dimensional stability and physical properties. These compositions comprise a starch and/or a derivative of starch and at least one compound, preferably obtainable from a natural source, which compound comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group. In a preferred embodiment of the present invention said composition further contains one or more compounds selected from the group consisting of hydrophilic and/or hydrophobic polymers.

Background of the Invention

It is known that natural starch which is found in vegetable products as well as derivatives thereof and which contain various amounts of different plasticizers can be treated at elevated temperatures to form a melt. The plasticizer generally used is water. It is also known that said starch under these conditions can be mixed with synthetic thermoplastic polymers to form a uniform melt which can be formed into various shaped articles. Such articles formed by different techniques such as injection molding, extrusion, coextrusion, blow molding or foaming have found numerous applications.

In humid air, however, these articles tend to absorb and/or adsorb water thereby increasing their moisture content which may lead to a diminution in their hitherto good physical properties. Alternatively, they may dry out under conditions of low humidity and thus become brittle. The known starch blends further require a relatively high pressure and temperature during processing which, for example, excludes the presence in the blend of certain
highly-temperature sensitive components. Moreover, the transparency of the obtained solidified blend is often insufficient for many applications.

It is an object of the present invention at least to reduce the disadvantages mentioned above and to provide a biodegradable material with improved processability and transparency.

**Summary of the invention**

According to the present invention there is provided a composition comprising the combination, under conditions sufficient to ensure uniform melt formation, of: (a) starch and/or a starch derivative, and (b) at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group.

It is preferred that said compound is obtained from a natural source.

By a compound obtainable from a "natural source" is meant a biosynthesised material which is extracted, secreted or otherwise obtained from prokaryotic or eukaryotic organisms including micro-organisms, plants, animals and insects. Such definition embraces also the products obtained from the processing (biological or otherwise), of such material. Thus, it will be appreciated that oils, for example, are compounds obtainable from a natural source according to this present definition.

Said composition preferably further contains item (c) - viz one or more compounds selected from the group consisting of hydrophilic and/or hydrophobic polymers.

Item (a) of the composition is preferably a native starch as derived from potatoes, rice, tapioca, corn, pea, rye, oats, wheat, maize or barley or a derivative of such a
starch, for example an ether or ester derivative, preferably an ester derivative, as described herein below.

The starch ester may be a mixed ester, i.e. having different kinds of ester groups attached to the same molecule, as are obtained for example by reaction of starch with a mixed acid anhydride or a mixture of different acid anhydrides. Such a mixed acid anhydride may be for example an acid anhydride made from acetic acid and propionic acid; a mixture of different acid anhydrides may be for example a mixture of acetic acid anhydride and propionic acid anhydride.

The degree of substitution (DS) of the starch derivative of item (a) is preferably between 0.1 and 3.0, preferably about 0.8 to about 2.1 and most preferably from about 0.8 to about 1.5. The equilibrium moisture content at about 25°C and at a relative humidity of about 50% is preferably less than about 12% by weight of the moistened starch derivative.

The compound (item b of the composition) may be present in the composition in an amount of up to about 10% by weight with respect to that of the total composition.

The at least one component present in the compound may have between about 3 and about 25 carbon atoms, and may comprise between 1 and about 10 carboxyl groups and between 1 and about 10 hydroxyl groups. In a particularly preferred embodiment of the compound, at least two such components are present, at least one of which may be alicyclic and comprise a methanoazulene ring.

A preferred embodiment of the present invention includes a composition comprising item (a) and item (b) as defined above, and item (c) - viz at least one polymer selected from the group consisting of hydrophilic and/or hydrophobic polymers.
Item (a) and item (b) and optionally item (c) when combined provide a composition which yields products with enhanced transparency.

The composition may contain further additives.

In one aspect, the present invention refers to compositions comprising the combination, under conditions sufficient to ensure uniform melt formation, of: (a) starch and/or a starch derivative, and (b) at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group.

In a further aspect, the present invention relates to finished articles made from said compositions or said melts.

In a still further aspect, the present invention refers to the use of a compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group as a processing aid in the manufacture of a composition comprising (a) a starch and/or a derivative of a starch, and optionally (c) one or more compounds selected from the group consisting of hydrophilic and/or hydrophobic polymers.

The compositions according to the present invention may be powdery mixtures of their components or in the form of a melt or in the form of solid shaped articles or, for example, in pre-extruded forms such as granulates or pellets.

When in the form of a melt, the compositions may be further processed into shaped articles by use of any known process, such as: injection molding, compression molding, filming, blow molding, vacuum forming, thermoforming, extrusion, co-extrusion, foaming, and combinations thereof.
The present invention further refers to a method of preparation of a melt of a composition according to this invention, comprising:

(i) forming a melt from a composition comprising (a) a starch and/or a derivative of a starch, and optionally (c) one or more compounds selected from the group consisting of hydrophilic and/or hydrophobic polymers;

(ii) admixing thereto before, during or after melt formation, at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group;

(iii) plasticising the mixture until a uniform melt is obtained and optionally drying the mixture during melt formation and/or plastification to a moisture content of less than 15% by weight of the total composition.

The invention will be further apparent from the following description, in conjunction with the following examples and the appended claims.

**Detailed Description of the Invention**

Specifically the present invention refers to compositions comprising the combination, under conditions sufficient to ensure uniform melt formation, of: (a) starch and/or a starch derivative, and (b) at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group.

The present invention also refers to compositions comprising the combination, under conditions sufficient to ensure uniform melt formation, of (a) a starch and/or a derivative of a starch, (b) at least one compound which comprises at least one component having a molecular weight
of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group, and (c) at least one polymer selected from the group consisting of hydrophilic and/or hydrophobic polymers.

The starch which is present in the composition of the present invention is of vegetable origin and may be obtained, for example, from potatoes, rice, tapioca, corn, pea, rye, oats, wheat, maize and barley.

In one embodiment of the composition of the present invention, the starch has an amylose content, by weight, of up to about 65%, more preferably of up to about 45%, and most preferably between about 30% and about 35%. The lower limit for the amylose content of the starch preferably is about 10 to about 15%, likewise by weight.

In another embodiment of the invention, the starch is a high amylose variety having an amylose content, by weight, of between about 70% and about 95%, and more preferably of between about 75% and about 85%.

Item (a) may also be a derivative of a starch whereby the starch to be derivatized may be obtained for example from potatoes, rice, tapioca, corn, pea, rye, oats, and/or wheat. Said derivative of starch may have an amylose content, by weight, of up to about 65%, more preferably of up to about 45%, and most preferably between about 30% and about 35%. The lower limit for the amylose content of the starch derivative preferably is about 10 to about 15%, likewise by weight.

For certain applications it is preferred that the starch from which the derivative is obtained is a high amylose starch having an amylose content, by weight, of between about 70% and about 95%, preferably between about 75% and about 85%.

Item (a) of the composition, when in the form of a starch
derivative, may be an ether or ester, and preferably is an ester derivative.

The starch ester may be a mixed ester comprising at least two different types of alkylcarbonyl groups (i.e. of different lengths) in the same molecule and as such may be of the kind as obtained by reaction of starch with a mixed anhydride or with a mixture of different acid anhydrides.

It is most preferred that such mixed starch esters comprise at least two members selected from the group consisting of acetate, propionate, butyrate, pentanoate, hexanoate, heptanoate and octanoate residues bound to a common starch molecule.

Particularly preferred starch diesters comprise both acetate and propionate groups or both acetate and butyrate groups or both propionate and butyrate groups or both pentanoate and butyrate groups bound to a common starch molecule.

In the case of starch diesters, the ratio of the types of ester groups comprised by the starch ester may vary greatly, but preferably is in the range of about 1:1 to about 1:20.

Examples of ether derivatives are alkyl ethers or hydroxyalkylethers of starch, such as the methyl ether, propyl ether, butyl ether, hydroxyethyl ether or hydroxypropyl ether wherein the starch is substituted to a degree of about 0.1 to about 3, and preferably is substituted to a degree of between 0.1 and 2.1.

Examples of ester derivatives are the methyl esters, butyl esters or propyl esters of starch wherein the starch is substituted to a degree of about 0.1 to about 2.1. Particularly preferred are the ester derivatives of starch such as the acetates and propionates, and most particularly preferred are the starch propionates. In respect of starch
esters, the degree of substitution (DS) of the starch is from about 0.1 to about 2.1. Preferred is a DS of about 0.5 to about 1.8, and preferably from about 0.8 to about less than 1.5 which preferably is 1.4. The preferred DS for starch acetates is from about 0.7 to about 1.8 and most preferred is a DS of from about 0.9 to about 1.5. Likewise, the preferred DS for starch propionates is from about 0.5 to about 1.6 and preferably from about 0.7 to about 1.4.

Methods for making the starch derivatives of item (a) are known per se and are described, for example, at pages 311 to 366 in Starch Chemistry and Technology (1984) (Academic Press), edited by R. L. Whistler et al.

The compound (item b) may be present in the composition in an amount of up to 10% by weight with respect to that of the total composition, and more preferably is likewise present in an amount of between about 1% and 5%. The compound is most preferably present in the composition in an amount of about 2 to 3% by weight with respect to that of the total composition.

The at least one component present in the compound may have the general formula: A(OH)\(_y\)(COOH)\(_z\); wherein:

\[
A \quad \text{is a saturated or unsaturated aliphatic or alicyclic moiety comprising at least 3 and preferably less than about 25 carbon atoms;}
\]
\[
y \quad \text{is greater than or equal to 1 and less than or equal to about 10; and-}
\]
\[
z \quad \text{is greater than or equal to 1 and less than or equal to about 10.}
\]

In one embodiment of the component, it is preferred that A comprises from about 10 to about 20 carbon atoms, and it is more preferred that it comprises from about 11 to about 15 carbon atoms.

The component may comprise 2 or more hydroxyl groups and/or two or more carboxyl groups. It is more preferred that the
component comprises 2 or 3 hydroxyl and 2 or 3 carboxyl groups, and it is most preferred that the sum of the carboxyl and hydroxyl groups in the compound does not exceed about 8, being typically between about 4 and about 6.

Suitable such components include lactic acid, citric acid, 2-hydroxy valeric acid, 2-hydroxy caprylic acid, 16-hydroxy palmitic acid; 9,10-dihydroxy palmitic acid; 9,10-dihydroxy stearic acid; 2,3-dihydroxy stearic acid; 2-hydroxy stearic acid; 3-hydroxy stearic acid; 10-hydroxy stearic acid; 11-hydroxy stearic acid; 12-hydroxy stearic acid; and 9,10,12-trihydroxy stearic acid. In a particularly preferred embodiment of the compound, at least two components are present, each of which may have a molecular weight of from about 100 to about 1000.

At least one of the components present in the compound may be alicyclic. Such an alicyclic component may comprise a methanoazulene ring.

It is most preferred that the compound comprises dodecahexanoic acid, such as aleuritic acid, and an hydroxylated-methanoazulene-containing carboxylic acid, such as shellolic acid, jalaric acid or laksholic acid, and preferably a mixture of such compounds. A compound which comprises shellolic acid and aleuritic acid is shellac, obtainable from MHP Shellac GmbH of Repsoldstrasse 4, D-2000, Hamburg, Germany. Where shellac is present in the composition as item (b) it is preferred that it is substantially 100% micronised and possesses an average particle size of below about 80um.

The composition according to this invention may further comprise in an amount of up to 50%, and preferably up to 30% by weight of the total composition one or more compounds selected from the group consisting of hydrophilic polymers. As used herein, the term "hydrophilic polymers" includes water-soluble and/or water-swellable polymers.
This group includes a large number of known polymers such as water-soluble celluloses such as: alkylcelluloses, hydroxyalkylcelluloses and hydroxyalkylalkylcelluloses, such as: methylcellulose, hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, hydroxyethylmethylcellulose, hydroxypropylmethylcellulose, hydroxybutylmethylcellulose, cellulose esters and hydroxyalkylcellulose esters such as: cellulose acetylphthalate (CAP), Hydroxypropylmethyl-cellulose (HPMCP); carboxyalkylcelluloses, carboxyalkyl-alkylcelluloses, carboxyalkylcellulose esters such as: carboxymethylcellulose and their alkali-metal salts; water-soluble or water-swelling synthetic polymers such as: poly(acrylic acids) and their salts and essentially water soluble poly(acrylic acid) esters, poly(methacrylic acids) and their salts and essentially water-soluble poly(methacrylic acid) esters, essentially water soluble poly(vinyl acetates), poly(vinyl alcohols), poly(vinyl acetate phthalates) (PVAP), poly(vinyl pyrrolidone), poly(crotonic acids); cationically modified acrylates and methacrylates possessing, for example, a tertiary or quaternary amino group, such as the diethylaminoethyl group, which may be quaternized if desired; and mixtures of such polymers. Preferred from the group of poly(vinylalcohols) are alkenol homopolymers and alkenol copolymers.

The alkenol homopolymer is preferably a polyvinyl alcohol which has a degree of hydrolysis of from about 80 mol% to about 100 mol% and preferably from about 88 mol% to about 99 mol% and most preferably from about 96 mol% to about 98 mol%. The number average molecular weight ranges preferably are from about 15,000 to about 250,000, and more preferably from about 26,000 to about 120,000. Most preferred is a molecular weight ranging from about 40,000 to about 80,000.

It is particularly preferred that the composition contains pre-treated polyvinyl alcohol in the form of a melt,
obtained previously by adding sufficient energy to polyvinyl alcohol to melt it and substantially eliminate crystallinity in the melt. It is particularly preferred that such crystallinity is substantially completely eliminated.

Alkenol copolymers as mentioned above are preferably synthetic copolymers containing vinyl alcohol units as well as aliphatic units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate with monomers preferably ethylene, propylene, isobutylene and/or styrene with subsequent partial or complete hydrolysis of the vinyl ester group. These polymers comprise a sufficient hydroxyl group content such that they remain at least water-swellable within the definition as given herein.

The composition according to this invention may further comprise in an amount up to 60 %, preferably in an amount up to 35% and most preferably in an amount up to 25% by weight of the total composition one or more hydrophobic thermoplastic polymers as item (c), which is a substantially water-insoluble thermoplastic polymer.

Such a water-insoluble polymer dissolves in water in an amount of less than 25 grams per 100 grams of the dry polymer, preferably in an amount of less than 15 grams per 100 grams of dry polymer when immersed in water at room temperature.

Examples of hydrophobic thermoplastic polymers are polyolefines, such as polyethylene, polyisobutylene, polypropylene, vinylpolymers such as poly(vinyl chloride), poly(vinyl acetates), polystyrenes; polyacrylonitriles; polyvinylcarbazoles; substantially water-insoluble poly(acrylic acid) esters or poly(methacrylic acid) esters; polyacetals (POM); polycondensates such as polyamides, thermoplastic polyesters, polycarbonates, polyurethanes, poly(alkylene terephthalates); polyarylethers; thermoplastic polyimides; but also poly(hydroxybutyrate) (PHB),
poly(hydroxybutyrate-co-hydroxyvalerate) and high molar-mass, substantially water-insoluble poly(alkylene oxides) such as polymers of ethylene oxide and propylene oxide as well as their copolymers are included.

Further included are hydrophobic thermoplastic copolymers of the different kinds known such as ethylene/vinyl acetate-copolymers (EVA); ethylene/vinyl alcohol-copolymers (EVOH); ethylene/ethyl acrylate-copolymers (EEA); ethylene-acrylic acid copolymers (EAA); ethylene/methyl acrylate-copolymers (EMA); ABS - copolymers; styrene/acrylonitrile-copolymers (SAN); as well as their mixtures.

Preferred from these hydrophobic thermoplastic polymers are those with a set processing temperature within the range of about 95°C to about 210°C, preferably within the range of about 95°C to about 190°C.

Preferred from these are further those polymers containing polar groups such as hydroxyl, ether-, acid, ester or urethane groups. Such polymers include, for example, copolymers of ethylene, propylene or isobutylene such as ethylene/vinyl acetate-copolymers (EVA), ethylene/vinyl alcohol-copolymers, ethylene/ethyl acrylate-copolymers (EEA), ethylene/methacrylate- copolymers (EMA), polyurethane-copolymers, styrene/acrylonitrile-copolymers (SAN); polyacetals (POM) and their mixtures as mentioned above. The synthetic polymer may contain the usual known additives for processing.

The composition according to the present invention may have a relatively low water content. Said water content is preferably below 15%, more preferably below 12% and most preferably below 8% by weight of the total composition. Accordingly, if necessary, the moisture content of the composition is reduced either before mixing the components or during the melt formation process. It is possible for example to initiate melt formation of the composition in a
vented extruder and to evaporate the moisture from the melt by vacuum just before the melt is extruded.

The present invention further refers to a method of preparation of a melt of a composition according to this invention, comprising:

(i) forming a melt from a composition comprising (a) a starch and/or a derivative of a starch, and optionally (c) one or more compounds selected from the group consisting of hydrophilic and/or hydrophobic polymers;

(ii) admixing thereto before, during or after melt formation, at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group;

(iii) plasticising the mixture until a uniform melt is obtained and optionally drying the mixture during melt formation and/or plastification to a moisture content of less than 15% by weight of the total composition.

Item (a) may be mixed with item (b) and optionally with item (c) and further additives as defined herein in any desired sequence. It is preferred to mix all the components of the composition with all the intended additives to form the final composition, which may then be heated to form a uniform melt. Of course, other sequences may be more appropriate.

Preferably, all the composition components are mixed together in a form as to obtain a free flowing powder, which is useful for continuous processing. This powder is fed to the hopper of an extruder and is processed to form a melt which may subsequently be dried. The melt may then be either granulated or further processed into shaped articles.
In order to melt the composition according to the invention, it is suitably heated in a screw and barrel of an extruder for a time sufficient to enable uniform melt formation. The temperature is preferably within the range of 100°C to 220°C, and more preferably within the range of from 160 to 200°C, the precise temperature being dependent up on the type and nature of the composition used. For thermoplastic melt formation of the composition according to the invention, the composition preferably is heated in an extruder, and preferably in a vented extruder for optionally drying the composition as explained above.

Pressures created in such a volume correspond to the vapour pressure of the most volatile material present which may be water at the used temperature. It will be appreciated that pressures may be applied or generated, as is known to be possible in the use of said screw and barrel.

The preferred applied and/or generated pressures are in the range of pressures which occur in extrusion and are known per se, being up to about 150 x 10^5 N/m^2, preferably up to about 75 x 10^5 N/m^2 and most preferably up to about 50 x 10^5 N/m^2.

Within the screw the granular mixture is heated to a temperature which is generally within the range of about 120 to 220°C, preferably within the range of about 120 to 190°C and most preferably within the range of about 130 to 190°C.

The minimum pressures under which the melts are formed correspond to the vapour pressures produced by the compositions at said temperatures. These pressures are recommended even if a substantially anhydrous composition is used. Ranges of pressures suitable for extrusion processes are from zero to about 150 x 10^5 N/m^2, preferably from zero to about 75 x 10^5 N/m^2 and most preferably from zero to about 50 x 10^5 N/m^2. Pressures used in injection molding may exceed 150 x 10^5 N/m^2.
Optionally the composition comprises at least one member selected from the group consisting of extenders, fillers, lubricants, mold release agents, other plasticisers, flame-retardants, stabilisers and colouring agents.

Examples of extenders are gelatin, vegetable proteins such as sunflower protein, soybean proteins, cotton seed proteins, peanut proteins or rape seed proteins. Such extenders may optionally be added in any desired amount up to and including 20%, preferably within the range of 3% to 10% based on the total weight of the composition.

Suitable fillers include, for example, oxides of magnesium, aluminum, silicon, and titanium. The fillers are present in the composition at a concentration of up to about 20% by weight, and preferably between about 3.0 and about 10%, by weight, based on the total weight of the composition.

The lubricants include stearates of aluminum, calcium, magnesium, and tin, as well as the free acid and magnesium silicate, silicones and substances such as lecithin, and mono and diglycerides, which for the purpose of the present invention function in like manner. The particularly preferred lubricants are stearic acid or lecithin, which are present in the composition in amounts of up to 3%, preferably in an amount of 1%, and most preferably are present in the composition in an amount 0.6% by weight with respect to that of the composition.

Other plasticisers include low molecular weight poly(alkylene oxides), such as, for example, poly(ethylene glycols), poly(propylene glycols), poly(ethylene-propylene glycols), such as, for example, glycerol; pentaerythritol; propylene glycol; sorbitol; sodium diethylsulphosuccinate; phosphatides of which lecithin is preferred. These plasticisers are preferably present in the composition at a concentration of between about 0.5% and about 15% by weight, and more preferably between about 0.5% and about 5% by weight, based on the weight of all of the components,
including the water therein.

Preferably the sum of all the plasticisers in the composition does not exceed about 25% by weight, and most preferably does not exceed about 20% by weight, based on the total weight of the composition.

The composition may further comprise flame retardants which, for example, comprise phosphorous, sulphur and halogens, or mixtures thereof.

Suitable phosphorous-containing flame retardants include diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate; dimethyl methylphosphonate; phosphonic acid, methyl-, dimethylester, polymer with oxirane and phosphorous oxide; aliphatic phosphate/phosphonate oligomers; tributyl phosphate; triphenyl phosphate; tricresyl phosphate; 2-ethylhexyl diphenyl phosphate; and tributoxyethyl phosphate. These retardants are available from Akzo Chemicals Inc. of 300 South Riverside Plaza, Chicago, Illinois, USA.

Further suitable phosphorous-containing retardants include: guanidinium phosphate which can be obtained from Chemie Linz GmbH of St Peter strasse 25, A-4021, Linz, Austria; (hydroxypropyl) sec.butyl phosphine oxide which can be obtained from the Chemical Products Group of FMC Corporation, 2000 Market Street, Philadelphia, Pennsylvania 19103, USA; and the following compounds obtainable from Albright and Wilson, Americas Inc, of P.O. Box 26229, Richmond, Virginia, 23260, USA: polypropoxylated dibutyl pyrophosphoric acid; a mixture of phosphonic acid, methyl-, (5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl ethyl ester, P-oxide and phosphonic acid, methyl-, bis [(5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl] ester, P,P'-dioxide as sold under the trade name Amgard V19; ammonium polyphosphate; ethylenediamine polyphosphate; melamine phosphate; dimelamine phosphate; and microencapsulated red phosphorous.
Where ammonium polyphosphate and ethylenediamine polyphosphate are used as flame retardants, it is preferred that they are buffered with disodium orthophosphate so that they are thereby less corrosive to the equipment used for processing the composition comprising them.

Suitable sulphur containing retardants include: guanidinium sulfate obtainable from Chemie Linz GmbH at the address given above; ammonium sulfate; ammonium sulfamate; and tetrakis (hydroxymethyl) phosphonium sulfate; all of which may be obtained from the American Cyanamid Company, of One Cyanamid Plaza, Wayne, New Jersey, 07470, USA.

The particularly preferred flame retardants are ammonium polyphosphate and/or ethylenediamine polyphosphate, guanidinium phosphate, ammonium sulphate and/or guanidinium sulfate.

The above mentioned flame retardants are present in the composition in an amount of from 0.5 to about 15%, preferably from about 1.5 to 8%, and most preferably from 2 to 5%, all percentages being by weight with respect to that of the total composition.

Stabilisers include antioxidants such as thiobisphenols, alkylidenbisphenols, secondary aromatic amines; stabilisers against photo-decomposition, such as, for example, uv absorbers and quenchers; hydroperoxide decomposers; free radical scavengers, and anti-microbial agents.

Colouring agents include known azo dyes, organic or inorganic pigments, or colouring agents of natural origin. Inorganic pigments are preferred, such as the oxides of iron or titanium, these oxides being present in the composition at a concentration of between about 0.01 and about 10% by weight, and preferably present at a concentration of between about 0.05 and about 3% by weight, based on the total weight of the composition. Most preferably the colouring agents are present in the
composition in an amount of about 0.03 to about 0.07% by weight with respect to the total composition.

Still further substances which may be added to the composition include animal or vegetable fats, preferably in their hydrogenated forms, especially those which are solid at room temperature. Such fats preferably have a melting point of at least 50°C and include triglycerides of C12-, C14-, C16- and C18- fatty acids.

The total concentration of said fats, mono-, di- glycerides and phosphatides may be up to 5% by weight, based on the total weight of the composition.

Still further compounds which may be added to, or present in the composition include boron-containing compounds, particularly so when the composition is formed into films, sheets or fibres. The presence of such compounds in the composition yields articles which have improved transparency, Young's modulus and tear strength. The preferred boron-containing compounds are boric acid, metaboric acid, alkali and alkaline earth metal salts, borax and derivatives thereof. Said compounds may be present in the composition in an amount of between 0.002 and 0.4%, by weight with respect to that of the composition, and preferably are present at a concentration of between about 0.01 and 0.3%, likewise by weight.

Inorganic salts of alkali or alkaline earth metals, particularly LiCl and NaCl may be additionally present in the composition in an amount of between 0.1 and 5% by weight with respect to that of the total composition. The presence of such salts in the composition still further improves the Young's modulus, transparency and tear strength of articles made from the composition.

The compositions according to this invention form thermoplastic melts on heating under conditions as described herein. Such melts can be processed like
conventional thermoplastic materials, using, for example, injection molding, blow molding, extrusion and coextrusion (rod, pipe and film extrusion), compression molding, to produce known articles. The articles include bottles, sheets, films, packaging materials, pipes, cups, rods, laminated films, sacks, bags, pharmaceutical capsules, granules or powders.

The compositions according to this invention may also be used as carrier materials for active substances, and may be mixed with active ingredients such as pharmaceuticals and/or agriculturally active compounds such as insecticides or pesticides for sustained release applications of these ingredients. The resulting extruded materials can be granulated or worked to fine powders.

The following Examples further explain the invention.

Example 1

10kg of maize starch, 4.8 kg of polyvinyl alcohol having a number average molecular weight of about 20,000 to 30,000 and degree of hydrolysis of between 80 and 100%, (such as Mowiol 10-98 which has a number average molecular weight of about 25,000 and a degree of hydrolysis of 98%), 200 grams of hydrogenated fat sold as Boeson VP by Boehringer Ingelheim, 100 grams of melt flow accelerator (lecithin), sold as Metarin P by Lucas Meyer, and 1.2kg of glycerol are combined. The moisture content of the combined components is then adjusted to about 12% by weight of the moistened starch mix. The moisture content of the combined components may be adjusted to from about 9 to 17% by weight with similar results to those obtained below. The thus adjusted starch is fed into the entry port of a twin screw extruder (Leistritz model LSM 34) having screws co-rotating in a horizontal cylindrical barrel and an outlet die mounted at the discharge end of the extruder, opposite its entry port.
The starch composition is then heated to a temperature of between 160 and 180°C for about 20 to 120 seconds at a suitable pressure necessary to avoid the formation of water vapour at said temperature.

The thus melted starch is extruded from the outlet die of the extruder, and the extrudate cooled and pelletized.

The pelletized melted starch mix is conditioned to a moisture content of about 12%, and then fed into the entry port of an injection molding machine suitable for the production of tensile test pieces. Said test pieces are injection molded at a pressure is 1,300 bar, and temperature of 175°C. The thus molded test piece has a hazy appearance.

Example 2.

Example 1 is repeated except that shellac is added to the starch composition in an amount of 2% by weight with respect to that of the starch. Test pieces similar to those of Example 1 are produced but at a lower injection molding pressure of 950 bar. The thus produced test piece has a slightly hazy appearance in comparison with that obtained for the test piece from Example 1.

Example 3.

Example 2 is repeated except that the shellac is added to the starch composition in an amount of 8% by weight with respect to that of the starch. Test pieces similar to those of Example 1 are produced at an injection molding pressure of 500 bar. The thus produced test piece has a slightly hazy appearance in comparison with that obtained for the test piece from Example 1.

Example 4

Examples 1 to 3 are repeated except that the maize starch
is replaced by starch acetate wherein the degree of substitution is between 1 and 1.4. Results similar to those of Examples 1-3 are obtained.

The presence of the shellac in the starch blend thus enables articles to be injection molded therefrom at pressures lower than those required in the absence of the shellac for a constant temperature. Alternatively, for a constant pressure articles may be injection molded from the starch compositions comprising shellac at a relatively reduced temperature. This capacity to blend the starch compositions under less energetic conditions is especially advantageous when the starch compositions contains relatively heat labile components, such as flame retardants.

Examples 5 - 7

These Examples demonstrate that the presence of shellac in a melted starch composition facilitates a significant reduction in the water content of the composition for a given injection molding pressure.

The starch compositions of Examples 5 - 7 are given in Table 1 below. All percentages are by weight with respect to that of the composition.

From Example 5 it can be seen that easily de-moldable articles having good dimensional stability are produced when the water content of the composition is relatively low, but only if the injection molding pressure is relatively high (1250 bar).

From Example 6 of the Table, it can be seen that reducing the injection molding pressure to 950 bar by increasing the water content of the composition (to 17%) yields poorly de-moldable articles having poor dimensional stability.

It can be seen from Example 7 of the Table, however, that
the addition of shellac to the composition enables the preparation at relatively low pressures (950 bar) of injection molded articles which are easily de-molded, have a low water content and which exhibit good dimensional stability.

It will be appreciated that it is not intended to limit the invention to the above examples only, many variations thereto and modifications thereof being possible to one skilled in the art without departing from its scope, which is defined by the appended claims.
<table>
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<th>Formulation</th>
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<td>5</td>
<td>61% Maize Starch; 1.2% Boeson; 0.6% Lecithin; 29% Mowiol 10-98; 7.4% Glycerol.</td>
<td>12.2</td>
<td>1250</td>
<td>good demoldability</td>
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<td></td>
<td></td>
<td></td>
<td>good dimensional stability</td>
</tr>
<tr>
<td>6</td>
<td>61% Maize Starch; 1.2% Boeson; 0.6% Lecithin; 29% Mowiol 10-98; 7.4% Glycerol.</td>
<td>17.0</td>
<td>950</td>
<td>poor demoldability</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>poor dimensional stability</td>
</tr>
<tr>
<td>7</td>
<td>60.6% Maize Starch; 1.2% Boeson; 0.6% Lecithin; 29% Mowiol 10-98; 7.3% Glycerol; 1.2% Shellac.</td>
<td>12.2</td>
<td>950</td>
<td>good demoldability</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>good dimensional stability</td>
</tr>
</tbody>
</table>
What We Claim is:

1. A composition comprising the combination, under conditions sufficient to ensure uniform melt formation, of:
   (a) starch and/or a starch derivative, and (b) at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group.

2. A composition according to claim 1, in which the compound is obtained from a natural source.

3. A composition according to claim 1, in which the compound is present in the composition in an amount of up to about 10% by weight with respect to that of the total composition.

4. A composition according to claim 3, in which the compound is present in the composition in an amount of between about 1 and about 5% by weight with respect to that of the total composition.

5. A composition according to claim 4, in which the compound is present in the composition in an amount of about 2 to about 3% by weight with respect to that of the total composition.

6. A composition according to claim 1, in which the at least one component present in the compound has between about 3 and about 25 carbon atoms.

7. A composition according to claim 1, in which the at least one component comprises between 1 and about 10 carboxyl groups.

8. A composition according to claim 1, in which the at least one component comprises between 1 and about 10 hydroxyl groups.
9. A composition according to claim 3, in which the at least one component present in the compound has the general formula: \( A(OH)_y(COOH)_z \); wherein:
   
   - \( A \) is a saturated or unsaturated aliphatic or alicyclic moiety comprising at least 3 and less than about 25 carbon atoms;
   - \( y \) is greater than or equal to 1 and less than or equal to about 10; and
   - \( z \) is greater than or equal to 1 and less than or equal to about 10.

10. A composition according to claim 9, wherein \( A \) comprises from about 10 to about 20 carbon atoms.

11. A composition according to claim 10, wherein \( A \) comprises from about 11 to about 15 carbon atoms.

12. A composition according to claim 9, wherein the component comprises 2 or more hydroxyl groups and/or two or more carboxyl groups.

13. A composition according to claim 12, wherein the component comprises 2 or 3 hydroxyl and/or 2 or 3 carboxyl groups.

14. A composition according to claim 13, wherein the sum of the carboxyl and hydroxyl groups in the component does not exceed about 8.

15. A composition according to claim 14, wherein the sum of the hydroxyl and carboxyl groups in the component is between about 4 and about 6.

16. A composition according to claim 9, in which the molecular weight of the component present in the compound is from about 100 to about 1000.

17. A composition according to claim 9, in which at least two such components are present in the compound.
18. A composition according to claim 9, in which said component is selected from the group consisting of: aleuritic acid, lactic acid, citric acid, 2-hydroxy valeric acid, 2-hydroxy caprylic acid, 16-hydroxy palmitic acid; 9,10-dihydroxy palmitic acid; 9,10-dihydroxy stearic acid; 2,3-dihydroxy stearic acid; 2-hydroxy stearic acid; 3-hydroxy stearic acid; 10-hydroxy stearic acid; 11-hydroxy stearic acid; 12-hydroxy stearic acid; and 9,10,12-trihydroxy stearic acid.

19. A composition according to claim 17, in which at least one of the components is alicyclic.

20. A composition according to the preceding claim, in which the alicyclic component comprises a methanoazulene ring.

21. A composition according to claim 20, in which the component comprises an hydroxylated-methanoazulene-containing carboxylic acid, selected from the group consisting of: shellolic acid, jalaric acid and laksholic acid.

22. A composition according to claim 1, in which the compound comprises a first member selected from the group consisting of: aleuritic acid, lactic acid, citric acid, 2-hydroxy valeric acid, 2-hydroxy caprylic acid, 16-hydroxy palmitic acid; 9,10-dihydroxy palmitic acid; 9,10-dihydroxy stearic acid; 2,3-dihydroxy stearic acid; 2-hydroxy stearic acid; 3-hydroxy stearic acid; 10-hydroxy stearic acid; 11-hydroxy stearic acid; 12-hydroxy stearic acid; and 9,10,12-trihydroxy stearic acid, and a second member selected from the group consisting of: shellolic acid, jalaric acid and laksholic acid.

23. A composition according to claim 1, in which the compound is shellac.

24. A composition according to the preceding claim, in
which the shellac is substantially 100% micronised.

25. A composition according to the preceding claim, in which the micronised shellac possesses an average particle size of below about 80 μm.

26. A composition according to claim 1, in which the starch is a native starch selected from potatoes, rice, tapioca, corn, pea, rye, oats, and wheat.

27. A composition according to claim 26, in which the starch comprises an amylose content, by weight, of between about 70% and about 95%.

28. A composition according to the preceding claim, in which the amylose content is between about 75% and about 85%.

29. A composition according to claim 26, in which the starch has an amylose content, by weight, of up to about 65%.

30. A composition according to claim 26, in which the starch has an amylose content, by weight, of up to about 45%.

31. A composition according to claim 26, in which the starch has an amylose content, by weight, of between about 30% and about 35%.

32. A composition according to claim 26, in which the starch has an amylose content, by weight, of between about 10 and about 15%.

33. A composition according to claim 1, in which the starch derivative is an ester or ether derivative of a: potato, rice, tapioca, corn, pea, rye, oat, or wheat starch.
34. A composition according to the preceding claim, in which the degree of substitution (DS) of the starch derivative is between 0.1 and 3.0.

35. A composition according to the preceding claim, in which the degree of substitution (DS) of the starch is from about 0.1 to about 2.1.

36. A composition according to the preceding claim, in which the degree of substitution (DS) of the starch is from about 0.5 to about 1.8.

37. A composition according to the preceding claim, in which the degree of substitution (DS) of the starch is from about 0.7 to about 1.8.

38. A composition according to the preceding claim, in which the degree of substitution (DS) of the starch is from about 0.9 to about 1.5.

39. A composition according to claim 33, in which the starch comprises an amylose content, by weight, of between about 70% and about 95%.

40. A composition according to the preceding claim, in which the amylose content is between about 75% and about 85%.

41. A composition according to claim 33, in which the starch has an amylose content, by weight, of up to about 65%.

42. A composition according to claim 33, in which the starch has an amylose content, by weight, of up to about 45%.

43. A composition according to claim 33, in which the starch has an amylose content, by weight, of between about 30% and about 35%.
44. A composition according to claim 33, in which the starch has an amylose content, by weight, of between about 10 and about 15%.

45. A composition according to claim 34, in which the starch is an ether derivative selected from the group consisting of alkyl ethers and hydroxyalkylethers.

46. A composition according to the preceding claim, wherein the ether derivative is selected from the group consisting of the methyl ether, propyl ether, butyl ether, hydroxyethyl ether and hydroxypropyl ether.

47. A composition according to claim 34, in which the starch is an ester derivative selected from the group consisting of: alkyl esters and hydroxyalkylesters.

48. A composition according to the preceding claim, wherein the ester derivative is selected from the group consisting of the methyl ester, propyl ester, and butyl ester.

49. A composition according to claim 33, in which the starch derivatives are acetates or propionates.

50. A composition according to claim 47, in which the starch ester has been obtained by reaction of starch with a mixed acid anhydride or with a mixture of different acid anhydrides.

51. A composition according to claim 50, in which the starch ester comprises at least two members selected from the group consisting of acetate, propionate, butyrate, pentanoate, hexanoate, heptanoate and octanoate.

52. A composition according to the preceding claim, in which the starch ester comprises both acetate and propionate groups bound to a common starch molecule.
53. A composition according to claim 51, in which the starch comprises both acetate and butyrate groups bound to a common starch molecule.

54. A composition according to claim 51, in which the starch comprises both propionate and butyrate groups bound to a common starch molecule.

55. A composition according to claim 51, in which the starch comprises both pentanoate and butyrate groups bound to a common starch molecule.

56. A composition according to claim 51, in which the ratio of the members is about 1:1 with respect to the members.

57. A composition according to claim 51, in which the ratio of the members is about 1:2 with respect to the members.

58. A composition according to claim 51, in which the ratio of the members is about 1:3 with respect to the members.

59. A composition according to claim 51, in which the ratio of the members is about 1:20 with respect to the members.

60. A composition according to claim 1, further comprising at least one polymer selected from the group consisting of hydrophilic and/or hydrophobic polymers.

61. A composition according to claim 60, in which the composition comprises in an amount of up to 50%, by weight of the total composition, one or more hydrophilic polymers selected from the group consisting of: alkylcelluloses, hydroxyalkylcelluloses, hydroxyalkylalkylcelluloses, cellulose esters, hydroxyalkylcellulose esters, carboxyalkylcelluloses, carboxyalkyl-alkylcelluloses,
carboxyalkylcellulose esters and their alkali-metal salts; water-soluble or water-swellable synthetic polymers, poly(acrylic acids) and their salts, substantially water soluble poly(acrylic acid) esters, poly(methacrylic acids) and their salts and substantially water-soluble poly(methacrylic acid) esters, substantially water soluble poly(vinyl acetates), poly(vinyl alcohols), poly(vinyl acetate phthalates), poly(vinyl pyrrolidone), poly(crotonic acids); cationically modified acrylates and methacrylates possessing, for example, a tertiary or quaternary amino group, alkenol homopolymers and alkenol copolymers, and mixtures thereof.

62. A composition according to the preceding claim, in which the alkenol homopolymer is a polyvinyl alcohol which has a degree of hydrolysis of from about 80 mol% to about 100 mol%.

63. A composition according to the preceding claim, in which the number average molecular weight ranges are from about 15,000 to about 250,000.

64. A composition according to claim 61, in which the alkenol copolymer is a synthetic copolymer containing vinyl alcohol units and aliphatic units as is obtained by copolymerization of vinyl esters, with monomers selected from the group consisting of ethylene, propylene, isobutylene and/or styrene with subsequent hydrolysis of the vinyl ester group.

65. A composition according to claim 1, further comprising in an amount up to 60 % by weight of the composition, a synthetic hydrophobic polymer selected from the group consisting of polyolefines, vinylpolymers, polystyrenes; polyacrylonitriles; polyvinylcarbazoles; substantially water-insoluble poly(acrylic acid) esters or poly(methacrylic acid) esters; polyacetals (POM); polycondensates, thermoplastic polyesters, polycarbonates, polyurethanes, poly(alkylene terephthalates);
polyarylethers; thermoplastic polyimides; poly(hydroxybutyrate), poly(hydroxybutyrate-co-
hydroxyvalerate) and high molar-mass, substantially water-insoluble poly(alkylene oxides); ethylene/vinyl acetate copolymers (EVA); ethylene/vinyl alcohol copolymers 
(EVOH); ethylene/ethyl acrylate copolymers (EEA); ethylene-
acrylic acid copolymers (EAA); ethylene/methyl acrylate copolymers (EMA); ABS copolymers; styrene/acrylonitrile copolymers (SAN); and mixtures thereof.

A composition according to claim 65, in which the hydrophobic thermoplastic polymer has a set processing temperature within the range of about 95°C to about 210°C.

A composition according to claim 65, in which the polymer contains polar groups selected from hydroxyl, ether-, acid, ester and urethane groups.

A composition according to claim 1, which further comprises at least one member selected from the group consisting of extenders, fillers, lubricants, mold release agents, other plasticisers, flame retardants, stabilisers and colouring agents.

A composition according to the preceding claim, in which the other plasticisers are selected from the group consisting of low molecular weight poly(alkylene oxides); poly(ethylene-propylene glycols); pentaerythritol; propylene glycol; sorbitol; sodium diethylsulfoxuccinate; and phosphatides.

A composition according to claim 68, in which the flame retardants are present in the composition in an amount of from 0.5 to about 15%, by weight with respect to that of the total composition.

A composition according to claim 70, in which the flame retardants are selected from the group consisting of
diethyl-N,N-bis(2-hydroxyethyl) aminomethyl phosphonate; dimethyl methylphosphonate; phosphonic acid, methyl-, dimethylester, polymer with oxirane and phosphorus oxide; aliphatic phosphate/phosphonate oligomers; tributyl phosphate; triphenyl phosphate; tricresyl phosphate; 2-ethylhexyl diphenyl phosphate; tributoxyethyl phosphate; guanidinium phosphate; (hydroxypropyl) sec.butyl phosphine oxide; polypropoxylated dibutyl pyrophosphoric acid; a mixture of phosphonic acid, methyl-,(5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl)methyl ethyl ester, P-oxide and phosphonic acid, methyl-, bis [[5-ethyl-2-methyl-1,3,2-dioxaphosphorinan-5-yl]methyl] ester, P,P'-dioxide; ammonium polyphosphate; ethylenediamine polyphosphate; melamine phosphate; dimelamine phosphate; and microencapsulated red phosphorous.

72. A composition according to claim 70, in which the flame retardants are selected from the group consisting of guanidinium sulfate; ammonium sulfate; ammonium sulfamate; and tetrakis (hydroxymethyl) phosphonium sulfate.

73. A composition according to claim 70, in which the flame retardant is selected from the group consisting of ammonium polyphosphate and/or ethylenediamine polyphosphate, guanidinium phosphate, ammonium sulphate and/or guanidinium sulfate.

74. A composition according to claim 68, in which the stabilisers are selected from thiobisphenols, alkyldienbisphenols, secondary aromatic amines; uv absorbers and quenchers; hydroperoxide decomposers; free radical scavengers; and anti-microbial agents.

75. A composition according to claim 68, in which the colouring agents are selected from azo dyes, organic or inorganic pigments, or colouring agents of natural origin.

76. A composition according to claim 68, further
including, in an amount of up to 5% by weight of the composition, animal or vegetable fats, having a melting point of at least 50°C and being selected from triglycerides of C12-, C14-, C16- and C18- fatty acids.

77. A composition according to any preceding claim, when in the form of a melt.

78. A composition according to claim 77, when in the form of a solid shaped articles, including a granulate or pellet.

79. The composition of claim 77, when shaped into articles by a process selected from the group consisting of: injection molding, compression molding, filming, blow molding, vacuum forming, thermoforming, extrusion, co-extrusion, foaming, and combinations thereof.

80. A finished article made from the melt according to claim 77, the article being selected from the group consisting of bottles, sheets, films, packaging materials, pipes, cups, rods, laminated films, sacks, bags, pharmaceutical capsules, granules and powders.

81. The use of a compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group as a processing aid in the manufacture of a composition comprising (a) a starch and/or a derivative of a starch, and optionally (c) one or more compounds selected from the group consisting of hydrophilic and/or hydrophobic polymers.

82. A method of preparation of a composition according to any one of claims 1 - 71, comprising:

(i) forming a melt from a composition comprising (a) a starch and/or a derivative of a starch, and optionally (c) one or more compounds selected from the group consisting of
hydrophilic and/or hydrophobic polymers;

(ii) admixing thereto before, during or after melt formation, at least one compound which comprises at least one component having a molecular weight of less than 2,000 and which has at least one carboxyl group and at least one hydroxyl group;

(iii) plasticising the mixture until a uniform melt is obtained and optionally drying the mixture during melt formation and/or plastification to a moisture content of less than 15% by weight of the total composition.
# INTERNATIONAL SEARCH REPORT

**Classification of Subject Matter**

According to International Patent Classification (IPC) or to both National Classification and IPC

| Int.Cl. 5 | C08L3/00; C08L93:02 |

**Fields Searched**

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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

**Documents Considered to be Relevant**

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<td>US, A, 3 261 705 (JOHN GALLAGHER) 19 July 1966 see column 1, line 65 - line 69</td>
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<td>X</td>
<td>DATABASE WPI Week 66, Derwent Publications Ltd., London, GB; AN 22582F &amp; JP,B,41 013 998 (SHIONOGI &amp; CO) 4 June 1966 see abstract</td>
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<td>A</td>
<td>EP, A, 0 344 118 (WARNER-LAMBERT COMPANY) 29 November 1989</td>
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<td>A</td>
<td>WO, A, 9 112 186 (FRANZ HAAS WAFFELMASCHINEN INDUSTRIEGESELLSChaft) 22 August 1991</td>
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**Certification**

Date of the Actual Completion of the International Search

19 JULY 1993

Date of Mailing of this International Search Report

09.8.93

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Officer

LESEN H.W.M.
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<td>P,X</td>
<td>WO.A,9 214 782 (NOVAMONT S.P.A.) 3 September 1992 see page 17; examples 4-9</td>
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 19/07/93

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