



(51) International Patent Classification:

A61Q 5/06 (2006.01) A61K 8/85 (2006.01)
A61K 8/73 (2006.01)

(21) International Application Number:

PCT/EP2014/078227

(22) International Filing Date:

17 December 2014 (17.12.2014)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/919,066 20 December 2013 (20.12.2013) US
14155145.7 14 February 2014 (14.02.2014) EP

(71) Applicant: **AKZO NOBEL CHEMICALS INTERNATIONAL B.V.** [NL/NL]; Stationsstraat 77, NL-3811 MH Amersfoort (NL).

(72) Inventor: **BEVINAKATTI, Hanamanthsa**; 14 Gauguin Way, Somerset, New Jersey 08873 (US).

(74) Agent: **AKZO NOBEL IP DEPARTMENT**; Velperweg 76, NL-6824 BM Arnhem (NL).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM,

AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))



WO 2015/091650 A1

(54) Title: HAIR FIXATIVES INCLUDING STARCH ESTER BASED POLYGLUCOSE POLYMERS

(57) Abstract: A hair fixative composition includes at least one carboxylated starch ester based polyglucose polymer, an alcohol based solvent system, and a cosmetically acceptable additive, wherein the polyglucose polymer is soluble in the alcohol based solvent system. The polyglucose polymer is obtained by reacting at least one starch ester with at least one cyclic anhydride.

Hair Fixatives Including Starch Ester Based Polyglucose Polymers

Field of the Invention

The invention relates to personal care compositions comprising carboxylated starch ester polyglucose polymers. More specifically, the invention relates to hair fixative compositions comprising carboxylated starch ester polyglucose polymers that are soluble in alcohol based solvent systems.

Background of the Invention

Polymers used in personal care applications, such as hair styling and hair fixing, have conventionally been made using synthetic materials. In order for the polymers to be suitable in such personal care applications, they must be soluble in alcohol based systems, and in the case of aerosol based hair sprays, they must also be compatible with the propellant. Conventional synthetic polymers are generally inexpensive and provide acceptable performance; however, because they are not made from renewable resources, they are not sustainable. In addition, replicating the cost and performance of synthetic polymers is not easy.

Accordingly, there is a need for personal care polymers made from renewable sources that provide equal to or better performance at comparable costs than their synthetic alternatives and that are soluble in alcohol based systems, such as ethanol based systems and optionally, that are compatible with propellants, such as dimethyl ether.

Summary of the Invention

In an aspect, the present invention relates to a hair fixative composition comprising at least one carboxylated starch ester based polyglucose polymer; an alcohol

based solvent system; and a cosmetically acceptable additive. The polyglucose polymer is obtained by reacting at least one starch ester with an anhydride, such as a cyclic anhydride or an acyclic anhydride or mixtures thereof, and the polyglucose polymer is soluble in the alcohol based solvent system. The starch ester may be obtained by reacting starch with at least one acyclic anhydride, at least one cyclic anhydride or mixtures thereof.

In another aspect, the present invention relates to a method of preparing a hair fixative composition comprising reacting at least one starch ester with an anhydride, such as a cyclic anhydride or an acyclic anhydride or mixtures thereof, to form a starch ester based polyglucose polymer. In a further step, the method comprises dissolving or suspending the starch ester based polyglucose polymer in the alcohol based solvent system. The starch ester may be obtained by reacting starch with at least one acyclic anhydride, at least one cyclic anhydride or mixtures thereof.

In yet another aspect, the present invention relates to the use of the carboxylated starch ester based polyglucose polymer as defined herein as a hair fixative polymer in a hair fixative composition, as well as a method of styling hair, comprising applying the carboxylated starch ester based polyglucose polymer as defined herein to hair.

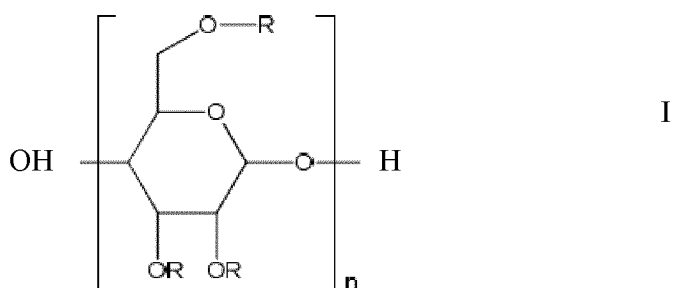
Detailed Description of the Invention

As used herein, the recitations of numerical ranges by endpoints include all numbers subsumed within that range (e.g., 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, 5, etc.). In addition, it is to be understood that for embodiments including ranges as described herein, the respective lower endpoints and respective upper endpoints described include combinations of the various lower and upper endpoints. For example, for ranges of 1 to 20 and 5 to 10, respectively, the ranges also include, without limitation, 1 to 10 and 5 to 20.

The hair fixative compositions of the present invention comprise carboxylated starch ester based polymers that combine the features of having a polysaccharide backbone having attached at least one ester group and at least one carboxyl functional group.

It has been found that the carboxylated starch ester based polyglucose polymers can provide hair fixative polymers that are not only made from renewable sources but that can also provide equal to or better hair styling performance, such as spray rate, viscosity, stiffness and high humidity curl retention, especially as hair spray polymers, at comparable costs than their synthetic alternatives. The inventive polymers are soluble in an alcohol based system and, optionally, they are also compatible with hair styling propellants.

The present invention generally relates to hair fixative compositions including at least one carboxylated starch ester based polyglucose polymer having the following structure (I):



wherein R = H, R_H or R_A or combinations thereof, wherein at least one R is R_A and wherein R_H is: -CO-R¹ wherein R¹ is C₁ - C₂₁ alkyl group, preferably a C₁ to C₁₀ alkyl group, and more preferably C₁ - C₃; and R_A is: (a) -CO-CH₂-CH(R²)-COOH wherein R² = H or C₁ - C₁₈ alkyl or alkenyl group, preferably a C₆ - C₁₈ alkenyl group, and more preferably a C₈, C₁₂ or C₁₈ alkenyl group; or b) -CO-CH=CH-COOH; or c) -CO-CH-C(=CH₂)-COOH; or d) -CO-C₆H₄-COOH or e) -CO-C₆H₈-COOH; and wherein n =

10 – 500 , more preferably 30 – 400, and still more preferably 30 – 150. The hair fixative compositions further include an alcohol based solvent system and a cosmetically acceptable additive wherein the polyglucose polymer is soluble in the alcohol based solvent system.

In the above formula (I), R_H represents hydrophobic groups and R_A represents groups having acid functionality and, optionally, hydrophobic functionality. In general, the carboxylated starch ester based polyglucose polymers are formed by reacting an ester of the polysaccharide, such as starch acetate, starch propionate, starch butyrate, starch acetate butyrate and starch acetate propionate with an anhydride, such as a cyclic anhydride or an acyclic anhydride. In an embodiment, the anhydride may be a substituted anhydride or an unsubstituted anhydride. In a further embodiment, the anhydride is more preferably a substituted anhydride. Suitable anhydrides include, but are not limited to such as a succinic anhydride, an alkenyl succinic anhydride, maleic anhydride, itaconic anhydride, phthalic anhydride or tetrahydrophthalic anhydride to give a succinate derivative, a maleate derivative, or an itaconate derivative, phthalate derivative or tetrahydrophthalate derivative or combinations thereof.

In an embodiment of the present invention, the polysaccharide ester may be modified with a substituted anhydride in an amount from about 15 wt% to about 50 wt% based on weight percent of the polysaccharide ester. In another embodiment, the polysaccharide ester preferably may be modified with the substituted anhydride in an amount from about 20 wt% to about 45 wt%, and in yet another embodiment, more preferably from about 25 wt% to about 35 wt%.

Non-limiting examples of carboxylated starch ester based polyglucose polymers according to the invention include polymers of formula I wherein R_H is: $-\text{CO}-\text{R}^1$ wherein R^1 is a $\text{C}_1 - \text{C}_{21}$ alkyl group, preferably a C_1 to C_{10} alkyl group, and more preferably a $\text{C}_1 - \text{C}_3$ alkyl group and R_A is: (a) $-\text{CO}-\text{CH}_2-\text{CH}(\text{R}^2)-\text{COOH}$ wherein $\text{R}^2 =$

H or C₁ – C₁₈ alkyl or alkenyl group, preferably a C₆ – C₁₈ alkenyl group, and more preferably a C₈, C₁₂ or C₁₈ alkenyl group, and wherein n = 10 – 500, more preferably 30 – 400, and still more preferably 30-150; wherein R_H is: –CO–R¹ wherein R¹ is a C₁ – C₂₂ alkyl group, preferably a C₁ to C₁₀ alkyl group, and more preferably a C₁ – C₃ alkyl group and R_A is: b) –CO–CH=CH–COOH, wherein n = 10 – 500, more preferably 30 – 400, and still more preferably 30-150; R_H is –CO–R¹ wherein R¹ is a C₁ – C₂₂ alkyl group, preferably a C₁ to C₁₀ alkyl group, and more preferably a C₁ – C₃ alkyl group and R_A is: c) –CO–CH–C(=CH₂)–COOH, and wherein n = 10 – 500, more preferably 30 – 400, and still more preferably 30-150; wherein R_H is –CO–R¹ wherein R¹ is a C₁ – C₂₂ alkyl group, preferably a C₁ to C₁₀ alkyl group, and more preferably a C₁ – C₃ alkyl group and R_A is: d) –CO–C₆H₄–COOH, and wherein n = 10 – 500, more preferably 30 – 400, and still more preferably 30-150; where in R_H is –CO–R¹ wherein R¹ is a C₁ – C₂₁ alkyl group, preferably a C₁ to C₁₀ alkyl group, and more preferably a C₁ – C₃ alkyl group and R_A is: (e) –CO–C₆H₈–COOH, and wherein n = 10 – 500, more preferably 30 – 400, and still more preferably 30-150. In an embodiment, combinations of the above are also included. In an embodiment, the polyglucose polymers suitable for use in the present invention include, but are not limited to, starch acetate succinate octenyl succinate, starch acetate phthalate octenyl succinate or combinations thereof.

In an embodiment, the carboxylated starch ester based polyglucose polymers of the present invention may be present in the hair fixative composition in an amount from about 1 weight percent to about 10 weight percent, based on the weight of the hair fixative composition. In another embodiment, the polyglucose polymers are present in an amount from about 2 weight percent to about 8 weight percent. In yet another embodiment, the polyglucose polymers are present in an amount from about 3 weight percent to about 6 weight percent.

In a further aspect, the present invention provides a polyglucose polymer obtained by reacting a starch with an anhydride, which may be acyclic or cyclic, and then

further reacting the reaction mixture with another anhydride, which may also be acyclic or cyclic to obtain the polyglucose polymer. For example, in an embodiment the starch may be reacted with at least one acyclic anhydride to form a starch ester, which may be isolated or further reacted *in situ*, and then the reaction mixture or the isolated starch ester is further reacted with a cyclic anhydride to form the polyglucose polymer.

In one embodiment of the invention, the starch material that is first reacted with an anhydride, which anhydride may be acyclic or cyclic, is not a starch ether ester material.

In an embodiment, preferably the starch ester is obtained by reacting a starch with at least one acyclic anhydride, such as such as acetic, propionic or butyric anhydride or mixtures thereof, forming starch acetate, starch propionate or starch butyrate and/or mixtures thereof. In a further embodiment, the polyglucose polymer is obtained by reacting a starch ester with a cyclic anhydride, such as succinic anhydride, an alkenyl succinic anhydride, maleic anhydride, itaconic anhydride, phthalic anhydride or tetrahydrophthalic anhydride and/or mixtures thereof.

The polyglucose polymers of the present invention are based on starch or starch derivatives. The starch polymers can be prepared from any starch source, including, but not limited to corn, banana, barley, amaranth, arrowroot, canna, sorghum, wheat, rice, tapioca, potato, sago, pea or sweet potato. In an embodiment, the starch is from a corn, potato, wheat, rice or tapioca source. In another embodiment, the starch is from potato or corn source. Suitable starches and starch derivatives include, but are not limited to, saccharides or derivatives thereof. Suitable saccharides include, for example, oligosaccharides and polysaccharides (e.g., maltodextrins, corn syrups, pyrodextrins and starches) and their hydrogenated versions, such as hydrogenated starch or hydrogenated hydrolyzed starch. In an embodiment of the invention, the polyglucose polymers are obtained from maltodextrin, pyrodextrin or a low molecular weight starch or oxidized

starch. It has been found that polyglucose polymers based on starch do not work well when the polyglucose polymer is not soluble in the alcohol based solvent system. Accordingly, in embodiments of the invention, the weight average molecular weight of the starch is preferably less than about 500,000. Starches having such exemplary molecular weights are water soluble. In another embodiment, the weight average molecular weight (Mw) of the starch may be less than about 200,000. In yet another preferred embodiment, the weight average molecular weight of the starch may be less than about 100,000. In yet another preferred embodiment, the weight average molecular weight of the starch may be less than about 50,000. In an embodiment, the weight average molecular weight of the starch is about 1,000 or greater, in another embodiment preferably about 5,000 or greater and in yet another embodiment more preferably about 10,000 or greater.

In an even further embodiment, the polyglucose polymers may be obtained from maltodextrins, pyrodextrins and chemically modified versions of maltodextrins and pyrodextrins. In an embodiment, the polysaccharide is preferably maltodextrin having a dextrose equivalent (DE) of less than about 25, in another embodiment preferably about 20 or less and in yet another embodiment more preferably about 15 or less. In an embodiment, when the polysaccharide is maltodextrin, it may have a DE of about 1 or more, even more preferably about 5 or more and in yet another embodiment about 10 or more. The term dextrose equivalent, as used herein, is a measure of the amount of reducing sugars present in a sugar product, relative to glucose, and is a well known term of art.

In an embodiment, the starches used as the starting materials may also have a high amylose content. As used herein, the term "high amylose" is intended to include starch containing at least about 50%, in another embodiment preferably at least 70%, and in yet another embodiment more preferably at least 80% by weight amylose. The amylose portions of fractionated starches are also suitable.

In an embodiment, the starch ester based polyglucose polymer has a total degree of substitution (D.S.) in a range from about 1.0 to about 3.0. In another embodiment, the polyglucose polymer has a total D.S. in a range from about 1.5 to about 3.0, and in yet another embodiment from about 2.0 to about 2.9. The number of substituted hydroxyl groups per anhydroglucose unit is expressed as the degree of substitution (D.S.).

The carboxylated starch ester based polyglucose polymers can be used as obtained from their natural source or they can be chemically modified. Chemical modification includes hydrolysis by the action of acids, enzymes, oxidizers or heat, hydrogenation, esterification or etherification.

In another aspect, the hair fixative compositions comprise at least one polyglucose polymer and an alcohol based solvent system. As used herein, an alcohol based solvent system comprises at least one alcohol and may include further optional components, such as water, propellant or other non-alcohol, non aqueous solvents. The polyglucose polymer must be soluble in the alcohol based solvent system. In an embodiment, the amount of alcohol present in the solvent system may be about 1 weight percent or greater, in another embodiment preferably about 15 weight percent or greater, and in yet another embodiment, more preferably from about 25 weight percent or greater. In an embodiment, the amount of alcohol present in the solvent system may be about 99 weight percent or less, in another embodiment preferably about 50 weight percent or less and in yet another embodiment more preferably about 40 weight percent or less, based on total weight of the solvent system. In another embodiment, the alcohol solvent system may be anhydrous.

In an embodiment of the invention, the hair fixative composition will include no more than about 85% of volatile organic compounds (VOC), such as alcohol and/or propellant with the remainder of the solvent being water. In another embodiment, the

hair fixative compositions will comprise no more than about 55% volatile organic compounds.

For purposes of the present invention, the term “soluble” means that from about 1 to about 10 weight percent and in another embodiment preferably from about 3 to about 6 weight percent, of the polyglucose polymer is soluble, with or without neutralization, in the alcohol based solvent system. In an embodiment, alcohol based solvent systems suitable for use in the present invention comprise at least one C₁-C₆ straight or branched chain alcohol or mixtures thereof and, optionally, water, optionally one or more propellants and optionally one or more other non-alcohol, non-aqueous solvents. In an embodiment, the alcohol solvent in the alcohol based solvent system comprises at least one C₂ or C₃ alcohol or mixtures thereof. In an embodiment the solvent system is substantially free of non-alcohol organic solvents. In one embodiment the solvent system is substantially free of acetone. As used herein with respect to the solvent system, the term “substantially free” means that the solvent system contains less than 50%, alternatively less than 40%, alternatively less than 30%, alternatively less than 20%, alternatively less than 10%, alternatively less than 5%, of the non-alcohol organic solvent or acetone, respectively.

In an embodiment of the invention, the hair fixative compositions further include at least one neutralizing agent. In an embodiment of the invention, the polyglucose polymer is generally at least about 50% neutralized. In another embodiment, the polyglucose polymer is at least about 70% neutralized, and in an even further embodiment, the fixative polymer is 100% neutralized. Suitable basic neutralizing agents compatible with the composition can be employed, even inorganic materials such as sodium or potassium hydroxide. Generally organic amines or alkanolamines are readily used for neutralization. In an embodiment, the neutralizing agents include, but are not limited to ammonia; primary, secondary and tertiary amines; alkanolamines; and,

hydroxyamines such as 2-amino-2-methyl-propanol and 2-amino-2-methyl-1,3-propanediol, mono-, di- and tri- long chain fatty amines containing a C₄ to C₂₄ hydrocarbon chain, ethoxylates and propoxylates long chain (C₄ to C₂₄) fatty amines and mixtures thereof. In another embodiment, the neutralizing agents include aminomethylpropanol, and di- methyl stearamine, inorganic materials, such as sodium hydroxide and potassium hydroxide, and triethanolamine. In an embodiment of the invention, the neutralizing agent is an organic amine or alkanolamine. In an embodiment, combinations of neutralizing agents may also be used.

In an embodiment, the hair fixative compositions have spray rate in a range from about 0.3 to about 1.5 grams/sec. in an 80% VOC system at 3.5% solids and 40% DME, in another embodiment, preferably from about 0.5 grams/sec. to about 1.2 grams/sec., and in another embodiment, more preferably from 0.75 about to 0.9 grams/sec.

In addition to the above-described solvent systems, the present invention may further optionally include one or more propellants. In an embodiment of the invention where the hair fixative composition is a spray application, the polyglucose polymer is compatible with the propellant. By compatible, it is meant that the polyglucose polymer in the solvent system does not phase separate when the solution is mixed with the propellant. In an embodiment, the polyglucose polymer is preferably compatible with dimethyl ether as the propellant. For purposes of the present invention, the term "compatible" means that up to about 10 weight percent of the polyglucose polymer is soluble in the hair fixative composition that includes the propellant. In another embodiment, the polyglucose polymer is preferably soluble from about 1 to about 10 weight percent, and in yet another embodiment, from about 2 to about 8 weight percent and in still yet another embodiment from about 3 to about 6 weight percent in the hair fixative composition that includes the propellant.

Spray applications of the present invention require a mechanical device or pressurized aerosol container to generate the spray. The devices can be manual such as a pump or squeeze bottle or typical aerosol device such as bag-on-nozzle or pressurized can. If a pressurized can is used then the hair styling formulations of the present invention may further include a propellant. Such propellants include, without limitation, ethers, such as dimethyl ether; one or more lower boiling hydrocarbons such as C₃-C₆ straight and branched chain hydrocarbons, for example, propane, butane, and isobutane; halogenated hydrocarbons, such as, hydrofluorocarbons, for example, trichlorofluoromethane, dichlorodifluoromethane, 1,1-difluoroethane and 1,1,1,2-tetrafluoroethane, present as a liquefied gas; and the compressed gases, for example, nitrogen, air and carbon dioxide as well as mixtures of these propellants. In an embodiment of the invention, the propellant is present in an amount of about 25% to about 80% by weight of the hair fixative composition including the solvent system. In a further embodiment, the propellant is present in an amount of about 30% to about 60 % by weight. Alternatively, in certain spray applications, such as bag-on-nozzle spray applications or pump spray applications, such optional propellants are not required. The hair fixative compositions of the present invention include, but are not limited, to aerosol and non-aerosol hairsprays.

In general, in another aspect of the invention, the method for preparing the hair spray formulations of this invention includes dissolving, suspending or diluting the polyglucose polymer in the selected solvents, adding any modifying agents depending on the desired properties, and thereupon combining the resulting solution with the selected aerosol propellant.

With regard to amounts of the various components, in an embodiment the final hair fixative compositions may contain the starch ester based polyglucose polymer in a concentration ranging from about 1 to 10%, by weight; the alcohol based solvent in a concentration ranging from about 30 to 90%, by weight; and, if included, the optional propellant concentration in a range from 20 to 75%, by weight. In another embodiment

the final hair fixative compositions may contain the polyglucose polymer in a concentration ranging from about 2 to 8%, by weight; the solvent in a concentration ranging from about 25 to 55%, by weight; and, if included, the optional propellant concentration in a range from 25 to 55%, by weight.

In yet another aspect, the present invention relates to the use of the carboxylated starch ester based polyglucose polymer as defined herein as a hair fixative polymer in a hair fixative composition, as well as a method of styling hair, comprising applying the carboxylated starch ester based polyglucose polymer as defined herein to hair. In one embodiment the hair fixative composition is in the form of a spray, in one embodiment the spray is an aerosol spray, in one embodiment the spray is a non-aerosol spray. In one embodiment the hair fixative composition is in the form of a mousse. In one embodiment the hair fixative composition is in the form of a gel.

The application of the hair fixative compositions of the present invention may be prior to, during, or after the desired hair style has been achieved.

Optionally, cosmetically acceptable additives may be incorporated into the hair fixative compositions of this invention in order to modify certain properties thereof. One such optional additive may, in addition to the polyglucose polymer, a second polymer, such as a hair fixative polymer. Non-limiting examples of these additional hair fixative polymers include: from Akzo Nobel Surface Chemistry LLC, AMPHOMER® 4961, AMPHOMER®, and AMPHOMER® LV-71 polymers (octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer), AMPHOMER® HC polymer (acrylates/octylacrylamide copolymer) and BALANCE® CR polymers (acrylates copolymer), BALANCE® 47 polymer (octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer), RESYN® 28-2930 polymer (VA/crotonates/vinyl neodecanoate copolymer), RESYN® 28-1310 polymer (VA/Crotonates copolymer), FLEXAN® polymers (sodium polystyrene sulfonate),

DynamX polymer (polyurethane-14 (and) AMP-Acrylates copolymer), RESYN® XP polymer (acrylates/octylacrylamide copolymer), STRUCTURE® 2001 (acrylates/stearth-20 itaconate copolymer) and STRUCTURE® 3001 (acrylates/ceteth-20 itaconate copolymer); from Ashland Inc., OMNIREZ-2000® (PVM/MA half ethyl ester copolymer), GANEX P-904® (butylated PVP), GANEX V-216® (PVP/hexadecene copolymer) GANEX® V-220 (PVP/eicosene copolymer), GANEX® WP-660 (tricontanyl PVP), GANTREZ® A425 (butyl ester of PVM/MA copolymer), GANTREZ® AN-119 PVM/MA copolymer, GANTREZ® ES 225 (ethyl ester of PVM/MA copolymer), GANTREZ® ES425 (butyl ester of PVM/MA copolymer), GAFFIX® VC-713 (vinyl caprolactam/PVP/dimethylaminoethyl methacrylate copolymer), GAFQUAT® 755 (polyquaternium-11), GAFQUAT® HS-100 (polyquaternium-28) AQUAFLEX® XL-30 (Polyimide-1), AQUAFLEX® SF-40 (PVP/Vinylcaprolactam/DMAPA Acrylates Copolymer), AQUAFLEX® FX-64 (Isobutylene/Ethylmaleimide/Hydroxyethylmaleimide Copolymer), ALLIANZ® LT-120 (Acrylates/C1-2 Succinates/Hydroxyacrylates Copolymer), STYLEZE® CC-10 (PVP/DMAPA Acrylates Copolymer), STYLEZE® 2000 (VP/Acrylates/Lauryl Methacrylate Copolymer), STYLEZE® W-20 (Polyquaternium-55), Copolymer Series (PVP/Dimethylaminoethylmethacrylate Copolymer), ADVANTAGE® S and ADVANTAGE® LCA (VinylcaprolactamNP/Dimethylaminoethyl Methacrylate Copolymer), ADVANTAGE® PLUS (VA/Butyl Maleate/Isobornyl Acrylate Copolymer); from BASF, The Chemical Company, ULTRAHOLD STRONG (acrylic acid/ethyl acrylate/t-butyl acrylamide), LUVIMER® 100P (t-butyl acrylate/ethyl acrylate/methacrylic acid), LUVIMER® 36D (ethyl acrylate/t-butyl acrylate/methacrylic acid), LUVIQUAT® HM-552 (polyquaternium-16), LUVIQUAT® HOLD (polyquaternium-16), LUVISKOL® K30 (PVP) LUVISKOL® K90 (PVP), LUVISKOL® VA 64 (PVP/VA copolymer) LUVISKOL® VA73W (PVP/VA copolymer), LUVISKOL® VA, LUVISET® PUR (Polyurethane-1), LUVISET® Clear (VP/MethacrylamideNinyl Imidazole Copolymer), LUVIFLEX® SOFT (Acrylates Copolymer), ULTRAHOLD® 8 (Acrylates/Acrylamide Copolymer), LUVISKOL® Plus

(Polyvinylcaprolactam), LUVIFLEX® Silk (PEG/PPG-25/25 Dimethicone/Acrylates Copolymer); from The Dow Chemical Company, ACUDYNE® 180, ACUDYNE® 1000, and ACUDYNE® DHR (Acrylates/Hydroxyesters Acrylates Copolymer), ACUDYNE® SCP (Ethylencarboxamide/AMPSA/Methacrylates Copolymer), and the ACULYN® rheological modifiers; from Mitsubishi and distributed by Clariant Corporation, DIAFORMER® Z-301, DIAFORMER® Z-SM, and DIAFORMER® Z-400 (methacryloyl ethyl betaine/acrylates copolymer), from Nalco Company, FIXOMER® A-30 and FIXOMER® N-28 (INCI names: methacrylic acid/sodium acrylamidomethyl propane sulfonate copolymer); from The Lubrizol Corporation, FIXATE® G-100 (AMP-Acrylates/Allyl Methacrylate Copolymer), FIXATE PLUS® (Polyacrylates-14), FIXATE® SUPERHOLD (Polyacrylate-2 Crosspolymer), and FIXATE® FREESTYLE (Acrylates Crosspolymer-3) CARBOPOL® Ultrez 10 (Carbomer), CARBOPOL® Ultrez 20 (Acrylates/C10-30 Alkyl Acrylates Copolymer), AVALURE® AC series (Acrylates Copolymer), AVALURE® UR series (Polyurethane-2, Polyurethane-4, PPG-17/IPDI/DMPA Copolymer); polyethylene glycol; water-soluble acrylics; water-soluble polyesters; polyacrylamides; polyamines; polyquaternary amines; styrene maleic anhydride (SMA) resin; polyethylene amine; and other conventional polymer that is polar solvent soluble or that can be made soluble through neutralization with the appropriate base. A combination of one or more of the above hair fixative polymers is also contemplated as within the scope of the present invention. In an embodiment of the invention, the hair fixative polymer is preferably chosen from octylacrylamide/acrylates/butylaminoethyl methacrylate copolymers, acrylates/octylacrylamide copolymers, acrylates copolymer, octylacrylamide/acrylates/butylaminoethyl methacrylate copolymers, VA/crotonates/vinyl neodecanoate copolymers, VA/Crotonates copolymers, sodium polystyrene sulfonates, polyurethane-14 (and) AMP-Acrylates copolymers, acrylates/octylacrylamide copolymers, acrylates/stearth-20 itaconate copolymers, acrylates/ceteth-20 itaconate copolymers and combinations thereof.

In an embodiment of the invention, the optional hair fixative polymer may be present in the hair fixative composition in an amount of about 0.1 to 10% by weight based on total weight of the composition. In a further embodiment, the fixative polymer is present in an amount of about 1 to 10% by weight and in a further embodiment in an amount of about 1 to 7% by weight.

Further optional cosmetically acceptable additives may also include: plasticizers, such as glycols, phthalate esters and glycerine; silicones; emollients, lubricants and penetrants such as lanolin compounds, protein hydrolyzates and other protein derivatives, ethylene oxide adducts, and polyoxyethylene cholesterol; UV absorbers; dyes and other colorants; and, perfumes. Mixtures of these optional additives may also be included. As previously noted, the polymeric binders of this invention show little or no tendency to adversely chemically interact with such additives.

Further optional ingredients can include, but are not limited to, preservatives, colorants, fragrances, viscosity modifiers, vitamins, herbal extracts such as sterols, triterpenes, flavonoids, coumarins, non-glycosidic diterpenes (sterebins) spathulenol, decanoic acid, 8,11,14-ecosatrienoic acid, 2-methyloctadecane, pentacosane, octacosane, stigmasterol, bsitosterol, a- and b-amyrine, lupeol, b-amyrin acetate, and pentacyclic triterpene, include sunscreen actives such as such as a p-methoxycinnamate or an aminobenzoate (UVB absorber) or benzene or an anthranilate (UVA absorber) medicaments, moisturizers, anti-itch or anti-dandruff ingredients and the like.

The resulting hair fixative formulations exhibit the characteristics required of such a product. They possess good antistatic properties, adhere well to hair, are easily removed by soapy water or shampoos, allow the hair to be readily combed, do not yellow on aging, do not become tacky when exposed to high humidities, and have excellent curl retention under high humidity conditions.

The method for preparing the hair fixative compositions of the present invention can be performed in a number of different ways, and depends on the polyglucose polymer used. However, in a further aspect of the invention, the invention provides a nonlimiting method for preparing the hair fixative composition. The method comprises suspending or dissolving the polyglucose polymer in an alcohol based solvent systems, for example comprising one or more C₁-C₆ alcohols. In an embodiment, the method further includes neutralizing the solution with a neutralizing agent, such as aminomethylpropanol. In an embodiment, the one or more alcohols may comprise ethanol in combination with isopropanol or n-propanol, optionally in a weight ratio of about 80:20 to about 20:80 ethanol to isopropanol. In yet another embodiment, optionally, the method further includes the step of adding propellant to the composition. In a further optional step, the method may also include adding water to the composition either before, during or after suspending the polyglucose polymer in the alcohol or after the neutralizing step.

In an embodiment, the polyglucose polymers of the present invention are suitable for use in hair fixative compositions, such as hair sprays, mousses or gels.

The following examples are intended to exemplify the present invention but are not intended to limit the scope of the invention in any way. The breadth and scope of the invention are to be limited solely by the claims appended hereto.

Examples

GENERAL SYNTHESIS METHOD FOR POLYGLUCOSE POLYMERS

Starch acetate (or propionate) succinate octenyl succinate polymers

A reaction vessel equipped with an agitator and condenser kept under nitrogen atmosphere and immersed in an oil bath for heating was charged with specified amount of (see Table 2) starch, acetic acid, sodium acetate (or sodium hydroxide) and acetic anhydride (or propionic anhydride). The amount of acetic (or propionic) anhydride

was adjusted to take care of the moisture level generally present in the starch. The mixture was heated to 125-130°C under stirring until the reaction showed completion as monitored by IR for the disappearance of the anhydride peak. Once all the acetic (or propionic) anhydride was reacted, the reaction mixture was cooled to about 100-110°C, OSA was added and the stirring continued at 110-115°C until the reaction showed completion as monitored by IR for the disappearance of the anhydride peak due to OSA. Succinic acid was then added to the reaction mixture and the stirring was continued at 110-115°C until all the succinic anhydride reacted as monitored by IR. The reaction mixture was then cooled to 70°C and then poured to a vigorously stirred water (about 5 times the weight of the reaction mixture) at ambient temperature. After stirring for 30 min., the solid separated was filtered, washed with water until all the residual acetic acid was washed off and dried in oven at 45°C overnight to give solid product.

Several other starch acetate (or propionate) succinate octenyl succinate using different starch source were prepared using essentially the same procedure mentioned above but using different quantities of raw-materials as detailed in Table 2 (Examples 1-13 and 16-26)

Starch acetate octenyl succinate phthalate polymers

These were made using essentially the same procedure as described above, except that after all the acetic anhydride was reacted, specified amount of phthalic anhydride was added followed by OSA after 2 hours of addition of phthalic anhydride. Details of the raw-materials to make these products are detailed in Table 2, Examples 14, 15 and 27.

Table 1 summarizes the various Examples of polyglucose polymers synthesized in accordance with the present invention.

Table 1: Examples of Polyglucose Polymers^a

Example #	Starch used ^b	DS values (Theoretical) ^c					Acid value meq/g	Compatibility in		Spray Rate g/sec
		Acetic anhydride	Propionic anhydride	Succinic anhydride	OSA	Phthalic anhydride		80% VOC ethanol system ^d	40% DME system ^e	
<u>1</u>	A	1.62	0	0	0.52	0	1.76	Insoluble	-	-
<u>2</u>	A	1.6	0	1.58	0	0	3.79	Soluble	Insoluble	-
<u>3</u>	A	0	1.7	1.07	0	0	2.56	Soluble	Insoluble	-
<u>4</u>	A	2.19	0	1.05	0	0	2.70	Soluble	Insoluble	-
<u>5</u>	A	2.19	0	0.63	0	0	1.92	Soluble	Insoluble	-
<u>6</u>	A	2.19	0	0.42	0.21	0	2.20	Soluble	Soluble	0.80
<u>7</u>	A	2.19	0	0.21	0.42	0	2.28	Soluble	Soluble	0.83
<u>8</u>	A	2.19	0	0	0.63	0	2.04	Soluble	Soluble	0.76
<u>9</u>	A	2.19	0	0.32	0.32	0	1.98	Soluble	Soluble	0.89
<u>10</u>	A	2.19	0	0.32	0.52	0	2.52	Soluble	Soluble	0.86
<u>11^f</u>	A	2.19	0	0.21	0.42	0	2.02	Soluble	Soluble	0.84
<u>12^f</u>	A	2.19	0	0.21	0.52	0	2.34	Soluble	Soluble	0.79
<u>13^f</u>	A	2.19	0	0.32	0.32	0	1.94	Soluble	Soluble	0.78
<u>14</u>	A	2.1	0	0	0	0.6	1.55	Soluble	Insoluble	-
<u>15</u>	A	2.1	0	0	0.3	0.4	2.80	Soluble	Soluble	0.71
<u>16</u>	A	2.1	0	0	0.2	0.5	2.67	Soluble	Soluble	0.79
<u>17</u>	B	1.8	0	1.54	0	0	3.72	Soluble	Insoluble	-
<u>18</u>	B	0	1.8	1.54	0	0	2.66	Insoluble	-	-
<u>19</u>	B	0	1.84	1.05	0	0	2.36	Soluble	Insoluble	-
<u>20</u>	B	2.32	0	0.41	0.2	0	2.24	Soluble	Soluble	0.79
<u>21</u>	B	2.32	0	0.2	0.41	0	2.24	Soluble	Soluble	0.80
<u>22^f</u>	C	1.6	0	0	0.6	0	1.97	Insoluble	-	-
<u>23^f</u>	C	2.18	0	0.21	0.42	0	2.08	Insoluble	-	-
<u>24^f</u>	C	2.18	0	0.21	0.52	0	2.03	Soluble	Soluble	0.69
<u>25^f</u>	C	1.89	0	0.21	0.52	0	2.14	Soluble	Soluble	0.62
<u>26^f</u>	C	1.89	0	0.32	0.52	0	2.38	Soluble	Soluble	0.74
<u>27</u>	C	2.1	0	0	0	0.6	1.99	Soluble	Insoluble	-

a) Unless otherwise mentioned, all reactions were carried out using sodium acetate as catalyst.

b) A = Glucidex 1, a potato based maltodextrin from Roquette with DE 5 max;

B= Glucidex-2, a waxy maize based maltodextrin from Roquette with DE 5 max;

C = Star Dri-1, a waxy maize based maltodextrin from Tate & Lyle with DE 1.

c) Amount of anhydride used to give the theoretically calculated Degree of Substitution (DS) values on starch. The actual DS values obtained were not measured.

d) Compatibility of 3.5 wt% polymer in 80:20 wt% ethanol:water with 90% neutralization level using AMP at ambient temp.

e) Compatibility of 3.5 wt% polymer in 80% VOC ethanol system with 40% DME at ambient temp.

f) Using NaOH instead of NaOAc as catalyst.

Table 2 - Details of the raw-materials used to make the Polyglucose polymers^a

a)Weights shown are in grams.

Example No.	Starch	Acetic Acid	Sodium Acetate ^b	Acetic anhydride	Propionic anhydride	Succinic Anhydride	OSA	Phthalic anhydride
1	30	45	12.1	37.7	0	0	19.4	0
2	29.5	41	11.2	37.1	0	27.3	0	0
3	19.1	19	7.2	0	30.6	11.8	0	0
4	32.4	32	12.3	51	0	20	0	0
5	32.4	32	12.3	51	0	12	0	0
6	32.2	32	12.3	51	0	8	8.4	0
7	32.4	32	12.3	51	0	4	16.8	0
8	32.4	32	12.3	51	0	0	26.2	0
9	64.8	64	24.6	102	0	12	25.2	0
10	64.8	64	24.6	102	0	12	42	0
11	64.8	30	6 ^c	117.3	0	8	33.6	0
12	64.8	30	6 ^c	117.3	0	8	42	0
13	64.8	30	6 ^c	117.3	0	12	25.2	0
14	50.7	30	7.4	76.3	0	0	0	26.6
15	50.7	30	7.4	76.3	0	0	18.9	17.8
16	50.7	30	7.4	76.3	0	0	12.6	22.2
17	32.4	45	12.3	40.8	0	30	0	0
18	32.4	32	12.3	0	52	30	0	0
19	19.1	19	7.2	0	31.2	11.8	0	0
20	32.4	32	12.3	51	0	8	8.4	0
21	32.4	32	12.3	51	0	4	16.8	0
22	64.8	36	6 ^c	94.5	0	0	48.1	0
23	64.8	30	6 ^c	117.3	0	8	33.6	0
24	64.8	30	6 ^c	117.3	0	8	42	0
25	64.8	20	6 ^c	106.1	0	8	42	0
26	64.8	20	6 ^c	106.1	0	12	42	0
27	51.6	80	7.4	81.5	0	0	0	26.6

b) Unless otherwise mentioned, sodium acetate was used as a catalyst.

c) Sodium hydroxide was used as a catalyst instead of sodium acetate.

A. SUBJECTIVE TEST PROCEDURES

Subjective evaluations as provided in the Examples comparing AMPHOMER® polymer, each using 3.5 wt% of the polymers using 80 wt% VOC ethanol-water and 40 wt% DME or as otherwise identified using statistical design method at 95% confidence level were conducted. The results of the Subjective Evaluations conducted are reported in the Tables that follow as indicated.

The following procedures were used to conduct the evaluations of the subjective performance of the polyglucose polymers of the present invention.

Gloss:

Gently handle the swatches so as not to break the films. Visually inspect the swatches to determine which has **more** shine/gloss.

Stiffness:

Gently handle swatches and feel for differences in stiffness. Using two fingers, hold the middle of the swatch in a horizontal position - does one bend more than the other? Choose the one that is **more** rigid.

Spring:

While holding the swatch in one hand, gently pull on an edge with the other hand three times only. Look for spring back, and bounce. The **more** elastic the better the Spring.

Webbing:

While holding the swatch in both hands, gently pull outward on the edges approx. 4". (Do this three times only to avoid damage to the bonds. If the bonds are destroyed then the dry combing may appear to be easier to comb). The **more** net like the better the Webbing.

Dry Comb:

Comb through each swatch (5) times and evaluate ease of combing. Choose the one that combs **more** easily.

Flake:

Visually inspect both swatches after combing. Check the teeth of the comb for flake accumulation. Holding the swatch at the bound end run your fingernail down the length of the tress then inspect. Choose the one with **more** flakes.

Anti-Stat:

Holding swatch at bound end comb through vigorously 10 times then evaluate for extent of fly aways generated. Choose the one with **more** fly aways.

Feel:

Handle swatches and determine preference. Choose the one that feels **more** silky / cleaner.

Table 3 - Subjective evaluation^a of the Polyglucose Polymers of Examples 6-16, 20, 21 and 24-26 compared to AMPHOMER® polymer using 3.5 wt% polymer using 80% VOC ethanol-water and 40% DME at 95% confidence level

Example No.	Gloss	Stiffness	Spring	Webbing	Dry comb	Flake	Antistat	Feel
Glucidex-1 based polymers								
6	-	=	=	=	=	=	+	-
7	=	=	-	-	=	=	=	=
8	-	-	=	=	=	-	=	=
9	-	=	=	=	+	+	+	=
10	=	=	=	=	=	=	=	=
11	-	=	-	-	=	=	=	=
12	-	-	-	=	+	+	=	+
13	-	=	=	=	=	=	+	+
15 ^b	-	-	-	-	=	=	=	=
15 ^c	=	-	-	=	+	=	+	=
16 ^b	=	-	-	=	+	-	=	=
16 ^c	-	=	-	=	=	-	+	=
Glucidex-2 based polymers								
20	=	=	-	=	+	=	=	+
21	=	-	-	=	+	=	=	=
Star Dri-1 based polymers								
24	-	-	-	=	=	+	=	+
25	-	=	-	=	=	=	+	=
26	-	=	=	=	=	=	+	=

a) Unless otherwise mentioned, all polymers were neutralized to 90% level using AMP.

b) 100% neutralized.

c) 70% neutralized.

= not statistically different; + superior; - inferior

Based on the results shown in Table 3, all samples were considered to provide adequate subjective performance to warrant further testing of objective performance.

Table 9 - Shampoo removability of representative starch polymers as compared to AMPHOMER® polymer

Sample	Stiffness after shampooing	Flake after shampooing	Dry feel after shampooing
Example 17	+	+	+
Example 20	+	=	=

= not statistically different; + superior; - inferior

Based on the subjective test results shown in Table 9, all samples were considered to provide overall stastically superior shampoo removability compared to AMPHOMER® polymer.

A. DETERMINATION OF SPRAY RATE

MATERIALS/EQUIPMENT:

Vented fume hood
 Safety glasses
 Top loading balance (0.01 gram accuracy)
 Seconds' timer

PROCEDURE: Run In Duplicate

AEROSOL HAIR SPRAY

- 1 Weigh can of hair spray and record weight.
- 2 Place can in fume hood. Using constant pressure, depress actuator for ten seconds.
- 3 Re-weigh can and record weight.

Calculation: Initial Weight – Weight After Spraying = grams/second

Note: if duplicates do not agree to within 0.03 g/sec, repeat procedure

NON-AEROSOL HAIR SPRAY

- 1 Weigh pump bottle of hair spray and record weight

- 2 Place bottle in fume hood. Consistently and completely, depress the actuator ten times (“bursts”).
- 3 Re-weigh pump bottle and record weight.

Calculation: Initial Weight – Weight After Spraying = grams/”burst”

Note: if duplicates do not agree to within 0.03 g/”burst”, repeat procedure

Valve Specification (procured from a company called Aptar)

Product VX-81

Body: VX Barbed .013 NOV T ARIAN

Stem: VX80 .343 FC 1 x .013 ORIFICE

GASKET: VX .045 BUTYL CODE 501

SPRING: VS STAINLESS STEEL .018 OPEN C

CUP: HIPRO BNA PGFR GSK AL EP T/B D

TUBE: .122 ID

TUBE LENGTH: 09 00/16”

Actuator Specification (from Aptar)

REF NO: XL002838

PRODUCT: XL200 SHIP OUT

LABNUM: XL200 VX MISTY TAP .023 MISTY

BUTTON: VX XL 200 MISTY TAP WHITE

INSERT: .023 MISTY BLACK

C. PROCEDURE FOR DETERMINING HIGH HUMIDITY CURL RETENTION (HHCR)

The following procedures were used to conduct the evaluations of the objective performance of the polyglucose polymers of the present invention as determined by high humidity curl retention. The high humidity curl retention properties of hair styling compositions including polyglucose polymers of the present invention were measured. The tests were each conducted at 72°F (22°C) and 90% Relative Humidity over a period of 24 hours. The tests were performed on 10" long x 2-gram swatches of European virgin brown hair (9 replicate swatches per sample). Curl retention testing is run in a humidity chamber set at 70°F/90% Relative Humidity for a total of 24 hours. Readings for % Curl Retention are read and recorded at time intervals of 15, 30,

60, 90 min, 2, 3, 4, 5, and 24 hrs. The hair styling compositions were tested according to the following procedures:

1. Wet hair swatch, comb through to remove tangles and squeeze out excess water (run swatch between thumb and index finger).
2. Apply sample to swatch, gently "work into" swatch and comb through.
3. Roll swatch on 1/2" diameter Teflon mandrel. Carefully remove rolled swatch from mandrel and secure with two hair clips.
4. Place curls on tray and dry in oven overnight.
5. Remove dried curls from oven and let cool to room temperature.
6. Suspend curls, from bound end of swatch, on graduated clear, transparent curl retention boards.
7. Remove clips from curls and gently unwind with glass rod making sure to "break" the curl.
8. Take initial curl length readings before placing boards and curls into environmental chamber (70°F, 90% relative humidity).
9. Record curl lengths at the 15, 30, 60, 90, 2, 3, 4, 5, and hour time intervals.
10. At conclusion of test, remove boards and curls from chamber.
11. Clean used hair swatches.
12. Calculate % Curl Retention and comparison of samples.

The Samples were prepared as follows:

HHCR was run in a constant temperature and humidity chamber. Curls were rolled on a mandrel and allowed to dry overnight. The curls were then sprayed with the polymer solutions (3.5 wt% polymer using 80% VOC ethanol-water and 40% DME) and allowed to dry. Then the curls were hung on a board placed in the oven and the percent of curl loss was tracked over 24 hrs.

The high humidity curl retention properties of hair styling compositions including polyglucose polymers of the present invention according to the Examples as shown in the following Tables as indicated were measured and compared to the use of AMPHOMER® polymer in the same hair styling composition.

Table 4 - HHCR results of Glucidex-1 based starch acetate succinate octenyl succinates of Examples 6-10 made using NaOAc as catalyst (using 3.5 wt% polymer) at 90% neutralization level compared to AMPHOMER® polymer using 3.5% polymer using 80% VOC ethanol-water and 40% DME at 95% confidence level

Example No.	5hrs	24hrs
Example 6	82 (=)	82 (=)
Example 7	82 (=)	80 (=)
Example 8	83 (=)	81 (=)
Example 9	81 (=)	78 (=)
Example 10	73 (=)	71 (=)
Amphomer	76	74

= not statistically different; + superior; - inferior

As shown in Table 4, all Examples provided statistically equal HHCR performance compared to AMPHOMER® polymer.

Table 5 - HHCR results of Glucidex-1 based starch acetate succinate octenyl succinates of Examples 11-13 made using NaOH as catalyst (using 3.5 wt% polymer) at 90% neutralization level compared to AMPHOMER® polymer using 3.5% polymer using 80% VOC ethanol-water and 40% DME at 95% confidence level

Example No.	5hrs	24hrs
Example 11	71 (=)	67 (=)
Example 12	79 (=)	72 (=)
Example 13	72 (=)	70 (=)
Amphomer	72	66

= not statistically different; + superior; - inferior

As shown in Table 5, all Examples provided statistically equal HHCR performance compared to AMPHOMER® polymer.

TABLE 6 - HHCR results of Glucidex-1 based starch acetate phthalate octenyl succinates of Examples 15 and 16 made using NaOAc as catalyst (using 4 wt% polymer) compared to AMPHOMER® polymer using 4.0% polymer using 80% VOC ethanol-water and 40% DME at 95% confidence level

Example No.	5hrs	24hrs
15 ^a	31 (-)	22 (-)
15 ^b	84 (=)	83 (=)
16 ^a	31 (-)	25 (-)
16 ^b	83 (=)	81 (=)
Amphomer	90	89

a) Polymer was neutralized to 100% level using AMP;

b) 70% neutralized.

= not statistically different; + superior; - inferior

As shown in Table 6, the Examples having 70% neutralization provided statistically equal HHCR performance compared to AMPHOMER® polymer. On the other hand, the Examples having 100% neutralization had poor HHCR performance.

Table 7 - HHCR results of Glucidex-2 based starch acetate succinate octenyl succinates of Examples 20 and 21 (using 3.5 wt% polymer) at 90% neutralization level at 90% neutralization level compared to AMPHOMER® using 3.5% polymer using 80% VOC ethanol-water and 40% DME at 95% confidence level

Example No.	5hrs	24hrs
Example 20	30 (-)	19 (-)
Example 21	64 (=)	56 (-)
Amphomer	76	74

= not statistically different; + superior; - inferior

As shown in Table 7, Example 20 had poor HHCR performance compared to AMPHOMER® polymer at 5 hrs, while Examples 20 and 21 each had poor HHCR performance compared to AMPHOMER® polymer at 24 hrs.

TABLE 8 - HHCR results of Star Dri-1 based starch acetate succinate octenyl succinates of Examples 24-26 (using 3.5 wt% polymer) at 90% neutralization level compared to AMPHOMER® polymer using 3.5% polymer using 80% VOC ethanol-water and 40% DME at 95% confidence level

Example No.	5hrs	24hrs
Example 24	52 (-)	45 (-)
Example 25	52 (-)	48 (-)
Example 26	66 (=)	63 (=)
Amphomer	71	69

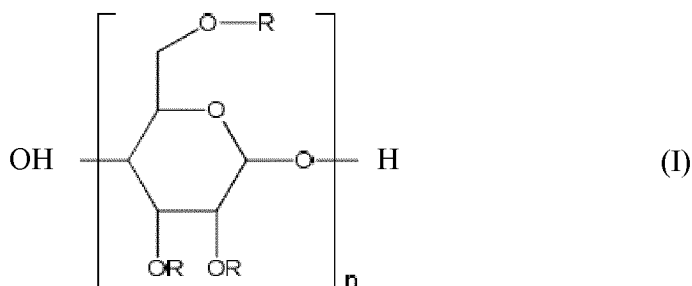
As shown in Table 8, Examples 24 and 25 provided poor HHCR performance compared to AMPHOMER® polymer, while Example 26 provided performance statistically equal to AMPHOMER® polymer.

All documents cited in the Detailed Description of the Invention are, in relevant part, incorporated herein by reference; the citation of any document is not to be construed as an admission that it is prior art with respect to the present invention.

While particular embodiments of the present invention have been illustrated and described herein, the invention is not intended to be limited to the details shown. Rather, various modifications may be made in the details within the range and scope of equivalents of the claims and without departing from the spirit and scope of the invention.

We claim:

1. A hair fixative composition comprising:
 - at least one carboxylated starch ester based polyglucose polymer obtained by reacting at least one starch ester with a first at least one cyclic anhydride;
 - an alcohol based solvent system, wherein the alcohol based solvent system comprises at least one C₁-C₆ straight or branched chain alcohol or mixtures thereof; and
 - at least one cosmetically acceptable additive;
 - wherein the at least one carboxylated starch ester based polyglucose polymer is soluble in the alcohol based solvent system.
2. The hair fixative composition of claim 1 wherein at least one starch ester is obtained by reacting a starch with a second at least one anhydride.
3. The hair fixative composition of claims 1 or 2 wherein the first at least one cyclic anhydride is selected from the group consisting of a succinic anhydride, an alkenyl succinic anhydride, maleic anhydride, itaconic anhydride, phthalic anhydride, tetrahydrophthalic anhydride and combinations thereof.
4. The hair fixative composition of claims 2 or 3 wherein the second at least one anhydride is acyclic or cyclic or mixtures thereof, preferably acetic, propionic or butyric anhydride or mixtures thereof.
5. The hair fixative composition of any one of claims 1-4 wherein the at least one carboxylated starch ester based polyglucose polymer has the following structure (I):



wherein $R = H, R_H$ or R_A or combinations thereof, wherein at least one R is R_A and wherein R_H is: $-\text{CO}-R^1$ wherein R^1 is a $C_1 - C_{21}$ alkyl group; and R_A is: (a) $-\text{CO}-\text{CH}_2-\text{CH}(R^2)-\text{COOH}$ wherein $R^2 = H$ or a $C_6 - C_{18}$ alkenyl group, or b) $-\text{CO}-\text{CH}=\text{CH}-\text{COOH}$, or c) $-\text{CO}-\text{CH}-\text{C}(=\text{CH}_2)-\text{COOH}$, or d) $-\text{CO}-\text{C}_6\text{H}_4-\text{COOH}$, or e) $-\text{CO}-\text{C}_6\text{H}_8-\text{COOH}$; and wherein $n = 10 - 500$.

6. The hair fixative composition of any one of claims 1-5 wherein the at least one starch ester is selected from the group consisting of starch acetate, starch propionate, starch butyrate, starch acetate butyrate, starch acetate propionate and combinations thereof.
7. The hair fixative composition of any one of claims 1-6 wherein the alcohol based solvent system further comprises water, one or more propellants or one or more non-alcohol, non-aqueous solvents or mixtures thereof.
8. The hair fixative composition of any one of claims 1-7 wherein the at least one carboxylated starch ester based polyglucose polymer is present in the hair fixative composition in an amount from 1 weight percent to 10 weight percent, based on the weight of the hair fixative composition.
9. The hair fixative composition of any one of claims 1-8 wherein the at least one starch ester is obtained from starch that is an oligosaccharide, a polysaccharide or

a hydrogenated oligosaccharide or a hydrogenated oligosaccharide, preferably maltodextrin, corn syrup or pyrodextrin.

10. The hair fixative composition of claim 9 wherein the starch is maltodextrin having a dextrose equivalent from 1 to 25.
11. The hair fixative composition of any one of claims 1-10 wherein the at least one carboxylated starch ester based polyglucose polymer is at least 50% neutralized.
12. The hair fixative composition of any one of claims 1-11 wherein the hair fixative composition is an aerosol hairspray or a non-aerosol hairspray.
13. The hair fixative composition of any one of claims 1-12 wherein the at least one cosmetically acceptable additive is selected from the group consisting of one or more second hair fixative polymers, plasticizers, UV absorbers, dyes, perfumes, preservatives, viscosity modifiers, vitamins, sunscreen actives, moisturizers, anti-itch or anti-dandruff ingredients and mixtures thereof.
14. A method of preparing a hair fixative composition of any one of claims 1-13 comprising:
 - reacting at least one starch ester with a first at least one anhydride to form the at least one carboxylated starch ester based polyglucose polymer; and
 - dissolving or suspending the resulting at least one carboxylated starch ester based polyglucose polymer in the alcohol based solvent system;
 - optionally neutralizing the at least one carboxylated starch ester polyglucose polymer; and
 - optionally reacting a starch with a second at least one anhydride to form the at least one starch ester; and
 - adding at least one cosmetically acceptable additive.

15. The use of a carboxylated starch ester based polyglucose polymer as defined in any one of the claims 1 to 11, as a hair fixative polymer in a hair fixative composition.

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2014/078227

A. CLASSIFICATION OF SUBJECT MATTER
 INV. A61Q5/06 A61K8/73 A61K8/85
 ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 A61Q A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 344 183 B2 (PAUL CHARLES W [US] ET AL) 5 February 2002 (2002-02-05)	15
Y	examples 4e, 5-7 column 7, lines 12-24	1-14
Y	----- US 2012/258052 A1 (MUELLER BURKHARD [DE] ET AL) 11 October 2012 (2012-10-11) example E3	1-15
Y	----- US 3 790 664 A (KROCHOCK D ET AL) 5 February 1974 (1974-02-05) examples 1-3 column 2, lines 45-51	1-15
X	----- GB 810 306 A (UPJOHN CO) 11 March 1959 (1959-03-11) examples III, IV, V, VII, X, XI page 15, lines 39-52	1-10,13, 14
	----- -/--	

<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C.	<input checked="" type="checkbox"/> See patent family annex.
--	--

<p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>
--	---

Date of the actual completion of the international search <p style="text-align: center; font-size: 1.2em;">27 April 2015</p>	Date of mailing of the international search report <p style="text-align: center; font-size: 1.2em;">20/05/2015</p>
---	---

Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <p style="text-align: center; font-size: 1.2em;">Grenouillat, N</p>
--	---

INTERNATIONAL SEARCH REPORT

International application No PCT/EP2014/078227

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p> DATABASE GNPD [Online] MINTEL; 1 November 2010 (2010-11-01), "Nourishing Conditioner", XP002723845, Database accession no. 1431176 Product information: Ingredients ----- </p>	1-13,15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2014/078227

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
US 6344183	B2	05-02-2002	AR 014830 A1	28-03-2001
			AU 2367899 A	21-10-1999
			BR 9915626 A	24-07-2001
			US 2001007655 A1	12-07-2001
			ZA 9902593 A	09-10-2000
US 2012258052	A1	11-10-2012	DE 102009054978 A1	22-06-2011
			EP 2521595 A2	14-11-2012
			US 2012258052 A1	11-10-2012
			WO 2011080005 A2	07-07-2011
US 3790664	A	05-02-1974	CA 958645 A1	03-12-1974
			DE 2150619 A1	20-04-1972
			FR 2111663 A1	09-06-1972
			GB 1360657 A	17-07-1974
			IT 988053 B	10-04-1975
			US 3790664 A	05-02-1974
			ZA 7106819 A	28-06-1972
GB 810306	A	11-03-1959	NONE	