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WAVE SET COMPOSITIONS CONTAINING A POLYSACCHARIDE

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Int. Cl. A61k 7/10; A45d 7/06
U.S. Cl. 132—7 13 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to hair control compositions comprising a polysaccharide consisting essentially of a polymeric chain of glucopyranose units. The compositions are adapted to form a film about hair filaments without flakiness.

This application is a continuation-in-part of a prior application bearing the title "Polysaccharides and Methods for Production Thereof" having Ser. No. 449,581, filed Apr. 20, 1965, and now abandoned.

This invention relates to improved hair control compositions and to methods for their employment in hair application. More particularly, the invention relates to novel polysaccharide hair control compositions adapted to impart to the hair improved maintenance of the desired configuration.

Heretofore various natural gums such as gum karaya, acacia, tragacanth, and quince seed etc. have been employed in hair control compositions to provide a coating about hair filaments. However, due to the lack of standardization, the natural gums and their application in wave set compositions has been severely limited. Viscosities and other properties of natural gums will vary greatly from batch to batch depending on the source of material, climate, soil, method of extraction and other reasons which are difficult if not impossible to control.

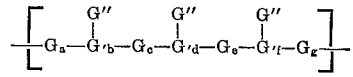
Various synthetic polymers have been offered for this purpose; however, such gums have a tendency to cause flakiness when the drying vehicle is evaporated. Moreover, many of the synthetic polymers have a disagreeable odor which often is impossible to mask. Among the synthetic polymers, polyvinylpyrrolidone has found extensive use in hair control compositions. However, when it is used in substantial quantities necessary to provide an adequate film an objectionable, sticky film as well as flakiness occurs. Another disadvantage of polyvinylpyrrolidone is that when it is applied or exposed to conditions wherein a relative humidity is greater than 50 percent, the resultant film becomes tacky and the hair thus loses its set.

It is an object of the present invention to provide a novel polysaccharide hair control composition capable of providing superior films on hair filaments.

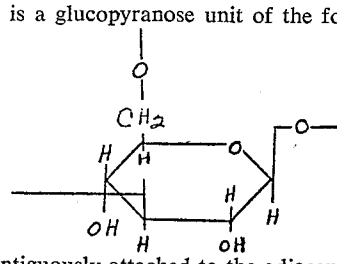
A further object is to provide a polysaccharide hair control composition adapted to form a film about the hair filaments without concomitant flakiness.

According to the present invention, there is provided a novel hair control composition adapted to form a film about an air filament which comprises water and a polysaccharide consisting essentially of a polymeric chain of glucopyranose units, the glucopyranose units being contiguously attached to another by a beta 1,3 linkage to form a polymeric chain, said polymeric chain having side chain glucopyranose units contiguously attached to the polymeric chain through a beta 1,6 linkage.

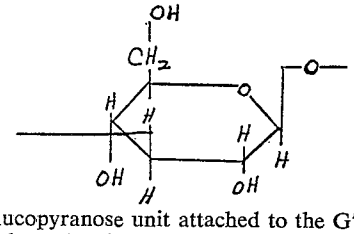
The polysaccharide employed hereein may be further represented by the structural formula:



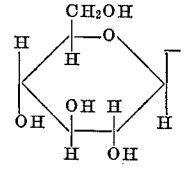
wherein G′ is a glucopyranose unit of the formula:



which is contiguously attached to the adjacent glucopyranose units through a beta 1,3 linkage in the polymeric chain and also appended to another glucopyranose unit through a beta 1,6 linkage to form a side chain. G is glucopyranose units of the formula:



G″ is a glucopyranose unit attached to the G′ glucopyranose unit through a beta 1,6 linkage of the formula:



N is an integer, and *a, b, c, d, e, f,* and *g* are integers from 0 to 1 such that the ratio of the sum of G units to G′ units (ie.,

gentiobiose) ranges from 3:1 to 4:3. Advantageously, *a, b, c, d, e, f,* and *g* are values that the ratio of the sum of G units to G′ units (gentiobiose) ranges from about 5:2 to about 3:2 with a ratio of between 2:1 to 3:2 providing superior properties when the polysaccharides are employed in an aqueous system.

The fermentate polysaccharides are further characterized by the following:

(a) Yielding only D-glucose when subjected to hydrolysis by 1 N sulfuric acid at approximately 100° C.;

(b) Yielding from about 20 to about 30 mole percent formic acid and a first residue when subjected to periodate oxidation as ascertained by the conventional analytical technique of carbohydrate chemistry which is more fully described by F. Smith and R. Montgomery, "The Chemistry of Plant Gums and Mucilages," Reinhold (New York, 1959), pp. 144–222;

(c) Said first residue yielding from about 20 to about 30 mole percent glycerol and an insoluble second residue when subjected to reduction by sodium borohydride followed by hydrolysis with dilute sulfuric acid (e.g. 0.1 N at 20° C. for six hours);

(d) Said second residue yielding only D-glucose when subjected to the enzymatic action of the beta 1,3 D-glucanase which is derived from the organism Basidimycete No. 806[1]; and

(e) Yielding a weight ratio of D-glucosee to gentio-

biose ranging from about 3:1 to about 4:3 and advantageously ranging from about 5:2 to about 3:2 and most preferably between 2:1 and 3:2 when the polysaccharide is subjected to the enzymatic action of the beta 1,3 D-glucanase which is derived from the organism Basidiomycete No. 806 (i.e. the ratio of

The polysaccharides have a terminal aldehyde and glucose units. Typical molecular weights of the polysaccharide are those that have an average molecular weight in excess of 19,000. Preferably employed are those polysaccharides having an average molecular weight of at least 50,000 with polysaccharides having an average molecular weight in excess of 100,000 being most preferred. Exemplary polysaccharides are those having a molecular weight ranging from about 20,000 to about 300,000.

The polymers employed in the instant hair control compositions are prepared by the reaction of certain organisms hereinafter disclosed in a medium containing a carbohydrate source material. Organisms which produce members of the polysaccharides herein disclosed include: *Sclerotium glucanicum,* Pillsbury Culture Code No. 13, n.s.p. (NRRL 3006); *Sclerotium delphinii* Jersveld/Welch, American Type Culture Collection No. 15198, (Source: Centraalbureau Voor Schimmelcultures Baarn, Netherlands); *Sclerotium delphinii* Welch/White, American Type Culture No. 15200; *Sclerotium rolfsii* Barnett, American Type Culture Collection No. 15203; *Sclerotium rolfsii* Barnett, American Type Culture Collection No. 15206; *Sclerotium rolfsii* Barnett, American Type Culture Collection No. 15201; *Sclerotium rolfsii* Barnett, American Type Culture Collection No. 15205; *Sclerotium rolfsii* Gilman, American Type Culture Collection No. 15195; *Sclerotium delphinii* Gilman, American Type Culture Collection No. 15197; *Sclerotium delphinii* Stevens I, American Type Culture Collection No. 15194; *Sclerotium delphinii* Welch/Mix, American Type Culture Collection No. 15199; *Sclerotium delphinii* Steven, American Type Culture Collection No. 15196. *Sclerotium coffeicolum* Stahel, American Type Culture Collection No. 15208; *Sclerotium rolfsii* QM, American Type Culture Collection No. 15202; *Sclerotium rolfsii* QM, American Type Culture Collection No. 15204; *Corticium rolfsii* Curzi/Balducci, American Type Culture Collection No. 15211; *Corticium rolfsii* (Sacc) Curzi, American Type Culture Collection No. 15212; *Corticium rolfsii* Curzi/Ficus, American Type Culture Collection No. 15209; *Sclerotinia gladoli* American Type Culture Collection No. 15207; *Stromatinia narcissi* Groves, American Type Culture Collection No. 15213.

Suitable carbohydrate source materials for preparing the polysaccharide via the above-mentioned organisms include sucrose, D-xylose, D-mannose, D-glucose (dextrose), L-arabinase, D-galactose, D-fructose, maltose, melezitose, raffinose, methylbeta-maltoside, aesculin, cellobiose, trehalose, L-rhamnose, cellulose and xylan or mixtures thereof.

In preparing the polysaccharides herein employed the carbohydrate source material is dissolved in an aqueous solution generally at a concentration ranging from about 3 to 15 percent by weight along with other culture medium nutrients such as a yeast extract and mineral salts (e.g. Czapek Dox Broth).

The organism is then added to the culture medium, the pH is adjusted between about 3–6 and the temperature is maintained between about 25–35° F. (e.g. for about 3–6 days) whereby the polysaccharide is formed. The polysaccharide is then isolated from the medium and washed with an alcohol (e.g. methanol).

The hair control compositions of the instant invention

[1] An organism in a collection maintained by the Microbiology Lab, Quartermaster Research & Engineering Center, Natick, Mass.

provide many advantages over those heretofore known. Included among such advantages is that when the hair control composition is applied to the hair, it produces a lustrous but natural looking film or sheath about each hair filament. Exposed to humid conditions the film about the hair filaments retains its identity and has an ability to absorb and retain moisture without concomitant development of tackiness or flakiness. The polysaccharide sheath is sufficiently sensitive to be removed from the hair by water washing (e.g. with a mild shampoo). Due to the polysaccharide film forming characteristic it is now possible to employ a lesser amount of polymer than heretofore used. An additional benefit provided over that of synthetic polymers conventionally employed is superior "lubricity." This lubricity is similar to that derived from natural materials; however the instant polysaccharide provides a gum standardization which was heretofore lacking from the natural gums. The hair conditioning composition provides excellent reset characteristics when hair previously treated and dried is subsequently combed with a wet comb.

Normally, the composition of this invention will contain from about 0.1 percent by weight to about 2.5 percent by weight of the polysaccharide based upon the total weight amount of water in the hair control composition. Advantageously, the amount of the polysaccharide in the hair control composition ranges from about .25 to about 1.5 weight percent with an amount ranging from about .3 weight percent to about 1.0 weight percent being preferred. Also contemplated with the present invention are concentrated hair control composition which may be subsequently diluted by the ultimate consumer.

Various hair control ingredients conventionally added to hair control compositions such as the natural and synthetic polymer, preservatives, coloring agents, perfumes and auxiliary drying agents, etc. and adaptable to the hair control compositions of the instant invention.

Typical natural polymers and derivatives thereof, although not necessarily included in the hair control composition herein provided, include gum karaya, acacia, tragacanth, quince seed, shellac, sodium alginate, bleached dewaxed shellac etc. Exemplary synthetically produced polymers include polyvinylpyrrolidone, maleic anhydride-ethylene oxide copolymers, copolymer of N-vinyl-ε-caprolactam, copolymers of vinyl pyrrolidone and vinyl ester of fatty acids such as vinyl acetate, vinyl stearate, methyl acrylate, copolymers of laurylmethacrylate and diethylaminoethyl methacrylate which has been reacted with an alkyl halide or sulfate such as methyl chloride or dimethyl sulfate to form a quaternary ammonium salt thereof, water soluble polyacrylic resins, etc.

To prevent microbial action a preservative is generally added to the wave control composition in an amount sufficient to prevent microbial degradation. Suitable preservatives are those conventionally used in the art to prevent microbial action and especially those previously employed in the hair control composition art. Typical preservatives are the alcohols (e.g. ethyl, butyl and propyl); organic acids such as benzoic acid, salicylic acid, sorbic acid and salts thereof (e.g. the sodium and calcium salts); p-chloro-m-xylenol; dichloro-m-xylenol; methyl chloro-thymol; 2,2′-methylenebis-(3,4,6-trichlorophenol), 3-acetyl-6-methyl-2H-pyran-2,4 (3H)-dione and sodium salt thereof; the esters of p-hydroxybenzoic acid such as methyl, ethyl, propyl and butyl, etc.

The aqueous polysaccharide solutions are odorless and will not mask various perfumes conventionally added to hair control compositions. In combination with perfumes the resulting composition produces an enhanced olefactory sense when compared to that of prior art hair control compositions containing perfumes. Perfumes adaptable herein include conventional perfumes such as one or more of the naturally occurring essential oils, one or more specific odorous synthetic organic compounds, or a blend of these essential oils and organic compounds. Citronella oil,

lemon oil, and bois de rose oil are representative of essential oil perfumes. Conventionally employed odorous organic material include citronella, vetiverol acetate, methyl phenyl carbinyl acetate, phenyl ethyl acetate, hydroxycitronella and phenyl ethyl alcohol.

The hair control compositions may be applied to the hair by any suitable fashion such as by an atomizer, hand application or by an aerosol system. A typical aerosol system consists of a pressure package having a valve-controlled outlet containing a gaseous or volatile liquid propellant and the wave control composition of the present invention, illustrative of the usual gaseous or liquified gas propellants are nitrogen; carbon dioxide; nitrousoxide; the lower alkanes (e.g. propane, isobutane, etc.) and preferably the saturated, halogenated aliphatic, hydrocarbons known by the trade name "Freon" and which include, for example, 1,1-difluoroethane; 1,2-dichloro-1,1,2,2-tetrafiuoroethane; trichlorotrifluoroethane; dichlorodifluoro methane; monochlorodifluoro methane; monochlorotrifluoro methan; 1-monochloro-1,1-difluoroethane, or mixtures thereof. The amounts of volatile liquid propellants employed may vary over a wide range depending upon whether and to what extent the film forming material is soluble therein, larger quantities being employed when it dissolves the polysaccharide. Generally, the entire amount of volatile liquid propellant will be from 100 percent to 300 percent, preferably not over 230 percent by weight of the hair control compositions. In an aerosol system the amount of polysaccharide based upon the total water content generally ranges from about 0.1 to about 1 weight percent with an amount ranging from about 0.2 to about .75 being preferred.

The following examples are illustrative of the invention:

EXAMPLE I

(A) Preparation of the polysaccharide

Into a sterile culture medium consisting of:

300 parts distilled water
9 parts sucrose
0.9 part $NaNO_3$
0.3 part K_2HPO_4
0.15 part KCl
0.3 part autolyzed yeast
0.003 part $FeSO_4$

was inoculated with a loopful of *Sclerotium rolfsii* Barnett, American Type Culture Collection No. 15206 and incubated for 3 days at approximately 28° C. on a rotary shaker. The resultant culture was placed in a sterile blender, homogenized and set aside for use as an inoculum.

An aqueous carbohydrate source was prepared by dissolving the following ingredients in 500 gallons of water.

Ingredients:	Pounds
Glucose	86
Magnesium sulfate	6.45
Potassium dihydroorthophosphate	4.3
Sodium nitrate	8.6
BBL yeast extract	4.3

The pH of the resulting medium was adjusted to 4.5 with hydrochloric acid and then heated for one hour at 15 p.s.i. and pressure at 250° F.

After the cultured medium had cooled, 15 pounds of the previously prepared homogenized inoculum was added to a fermenter vessel equipped with variable speed agitation, a sterile air supply and temperature control means. The medium was incubated for 5 days at a temperature of 28° F. and at an agitation rate of 96 r.p.m. and an aeration rate of 0.1 vol./vol. of medium per minute. The fermentate was then removed into a smaller vessel to which 129,000 pounds of water were added. After thorough mixing the diluted fermentate was heated to approximately 90 to 95° C., cooled, and then filtered via a diatamaceous earth filter for removal of mold cells.

To the filtrate an equal volume of methanol was added. Within a few minutes, the product rose to the surface as a fibrous mass and was removed therefrom by skimming. The polysaccharide was washed twice with a methanol and then dried in an oven at 50° C. The resultant fibrous mat of polysaccharide was then comminuted to a fine powder.

Polysaccharide chemical and physical results

Specific rotation $[\alpha]_D$ +4.4° (in NaOH)
Products from polymer acid hydrolysis: Glucose
Mole percent formic acid derived from periodate oxidation: 25.5
Hydrolysis product of periodate oxidized gum: Glycerol
Average degree of polymerization: 750 glucopyranose units
Enzymatic hydrolysis products by β1-3 glucanase: 2:1 moles glucose gentiobiose

Viscosity of aqueous solutions.—After 24 hours (Brookfield viscometer—23° C.—30 r.p.m.—No. 3 spindle):

	Cps.
1.0%	2200
1.25%	3280
1.5%	About 4400

Additional information relating to the preparation of other polysaccharides and polysaccharides thereof is disclosed in my copending application S.N. 449,581.

Preparation and use of the hair conditioning composition

A 0.35 aqueous solution of the polysaccharide prepared in accordance with Example I was applied to extremely fine and dry hair by hand application until the hair was thoroughly wetted. The hair was then curled into the desired hair style and allowed to dry. The hair thus treated had a more lustrous but natural appearance. The hair set was soft and silky in appearance with more than sufficient rigidity to maintain the set. Each hair filament was provided with a separate coating or sheath of polysaccharide film without concomitant matting between the hair filaments. Changes in relative humidity failed to effect the set with no development of flakiness or tackiness resulting therefrom. By employing a wetted comb it was possible to change the hair style by resetting the hair.

The hair set was readily removed from the hair by washing with water.

What is claimed is:

1. A hair control composition adapted to provide a shaped mass of hair by coating the hair filaments with a polysaccharide, said composition comprising an aqueous solution of a polysaccharide consisting essentially of a polymeric chain of glucopyranose units, said glucopyranose units being contiguously attached to one another by a beta 1,3 linkage to form a polymeric chain, said polymeric chain having beta 1,6 glucopyranose units contiguously attached to the polymeric chain through a beta 1,6 linkage.

2. The hair control composition according to claim 1 wherein the amount of polysaccharide based upon the amount of water ranges from about .2 percent by weight to about 2 percent by weight and the polysaccharide is further characterized by yielding a weight ratio of D-glucose to gentiobiose from about 2:1 to about 3:2 when the polysaccharide is subjected to the enzymatic action of a beta 1,3 D-glucanase which is derived from the organism Basidiomycete QM No. 806.

3. The hair control composition according to claim 2 wherein the amount of polysaccharide ranges from about .5 to about 1.0 weight percent based upon the total amount of the molecular weight of the polysaccharide is at least 50,000.

4. The hair control composition according to claim 3 wherein the polysaccharide is characterized by yielding a weight ratio of D-glucose to gentiobiose of about 2:1 when the polysaccharide is subjected to the enzymatic

action of a beta 1.3 D-glucanase which is derived from the organism Basidiomycete QM No. 806.

5. The hair control composition according to claim **4** wherein the polysaccharide is characterized by yielding a weight ratio of D-glucose to gentiobiose of about 3:2 when the polysaccharide is subjected to the enzymatic action of a beta 1,3 D-glucanase which is derived from the organism Basidiomycete QM No. 806.

6. A package comprising a pressure-tight container having a valve-cotnrolled outlet and containing

(a) an improved hair control composition comprising an aqueous solution of a polysaccharide wherein the polysaccharide consists essentially of a polymeric chain of glucopyranose units, said glucopyranose units being contiguously attached to one another by a beta 1,3 linkage to form a polymeric chain, said chain having beta 1,6 glucopyranose units contiguously attached to the polymeric chain through a beta 1,6 linkage and

(b) a propellant in an amount sufficient to force said hair control composition out of the container.

7. The package according to claim **6** wherein the polysaccharide has a molecular weight in excess of 19,000 and is further characterized by yielding a weight ratio of D-glucose to gentiobiose from about 2:1 to about 3:2 when the polysaccharide is subjected to enzymatic action of a beta 1,3 D-glucanase which is derived from the organism Basidiomycete QM No. 806.

8. The package according to claim **7** containing a polysaccharide which is characterized by a weight ratio of D-glucose to gentiobiose of about 2:1 when subjected to the enzymatic action.

9. The packaging according to claim **8** containing a polysaccharide which is characterized by a weight ratio of D-glucose to gentiobiose of about 3:2 when subjected to the enzymatic action.

10. A process of shaping human hair and hair filaments comprising the steps:

(a) applying to the hair an aqueous solution of a polysaccharide, the polysaccharide consisting essentially of a polymeric chain of glucopyranose units, said glucopyranose units being contiguously attached to one another through a beta 1,3 linkage to form a polymeric chain, said polymeric chain having beta 1,6 glucopyranose units contiguously attached to the polymeric chain through a beta 1,6 linkage, said solution forming a pliable mass of hair filaments,

(b) working and shaping the pliable mass into a desired form, and

(c) drying the shaped mass thus forming a coating about the hair filaments capable of retaining the hair in the desired form.

11. The process according to claim **10** wherein the polysaccharide has an average molecular weight in excess of 19,000, said polysaccharide being further characterized by yielding a weight ratio of D-glucose to gentiobiose from 2:1 to about 3:2 when the polysaccharide is subjected to enzymatic action of a beta 1,3 D-glucanase which is derived from the organism Basidiomycete QM No. 806.

12. The process according to claim **11** wherein the polysaccharide has an average molecular weight of at least 50,000 and the weight ratio of D-glucose to gentiobiose is about 2:1 when said polysaccharide is subjected to enzymatic action of a beta 1,3 D-glucanase which is derived from the organism Basidiomycete QM No. 806.

13. The process according to claim **11** wherein the polysaccharide has an average molecular weight of at least 50,000 and the weight ratio of D-glucose to gentiobiose is about 3:2 when said polysaccharide is subjected to enzymatic action of a beta 1,3 D-glucanase which is derived from the organism Basidiomycete QM No. 806.

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