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E. S. D.

TRÁMITE : 002 EVENTO : 001 ACTUACIÓN : 538

Referencia : Expediente No. **00-025.853**

Asunto : Solicitud de patente para: POLIMEROS ANFOTERICOS SOLUBLES EN AGUA QUE CONTIENEN NITRÓGENO CUATERNARIO Y SUS USOS EN FLUIDOS DE PERFORACION

Solicitante : **AKZO NOBEL N.V.**

Fecha de solicitud : 07 de abril de 2000

Publicada en : la Gaceta No. 523 del 27 de diciembre de 2002

1. Yo, Emilio FERRERO, identificado como aparece al pie de mi firma, actuando como apoderado en el asunto de la referencia, atentamente, solicito se efectúe el examen de patentabilidad de la solicitud en referencia según lo establecido en el artículo 44 de la Decisión 486 de la Comisión de la Comunidad Andina. Para tal efecto presento junto con este escrito el recibo No. 03-41,878 por valor de $335.000.00, que corresponde a la tasa fijada según lo dispuesto en la resolución No. 41687 del 24 de diciembre de 2002.

2. Ruego atentamente a la Señora Jefe se sirva ordenar que se anexe este recibo, para que se efectúe dicho examen y se continúe con el trámite de la solicitud.

Bogotá,
Señora Jefe,

EMILIO FERRERO
T.P.A. No. 31.929

COLO 11214-801-014-6
MRE/JFR/ID-000225/WPC11214 N I T. 860.041.367-3

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FECHA : JUNIO 16 DE 2003

***** C O N S I G N A C I O N *****

DEPOSITANTE	TIPO PAGO	BANCO	CUENTA	No. PAGO	FECHA PGO	Vr. PAGO
CAVELIER ABOGADOS	CONSIGNACION	BANCO POPULAR	050-00110-6	15534382	16/06/2003	17,765,000.00

***** C O N C E P T O *****

CANT.	RENTISTICO	CONCEPTO	TOTAL CONCEPTO
1	50005-01-01 SOLICITUDES	65 EXAMEN DE PATENTABILIDAD DE INVEN	335,000.00
		TOTAL : $	335,000.00

SON: TRESCIENTOS TREINTA Y CINCO MIL PESOS

RESPONSABLE : _____

RECIBO DE CAJA APLICADO AL EXPEDIENTE No._____

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US005663123A

United States Patent [19]

Goodhue, Jr. et al.

[11] Patent Number: 5,663,123

[45] Date of Patent: Sep. 2, 1997

[54] **POLYMERIC EARTH SUPPORT FLUID COMPOSITIONS AND METHOD FOR THEIR USE**

[75] Inventors: **K. Gifford Goodhue, Jr.**, Spring; **Max M. Holmes**, Dallas, both of Tex.

[73] Assignee: **KB Technologies Ltd.**, Spring, Tex.

[21] Appl. No.: **382,121**

[22] Filed: **Feb. 1, 1995**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 20,345, Feb. 19, 1993, Pat. No. 5,407,909, which is a continuation-in-part of Ser. No. 914,441, Jul. 15, 1992, abandoned.

[51] **Int. Cl.**[6] **E21B 33/14**; E21B 33/138; C09K 7/04

[52] **U.S. Cl.** **507/225**; 507/221; 507/220; 507/118; 507/122; 507/120; 507/121

[58] **Field of Search** 507/224, 225, 507/221, 220

[56] **References Cited**

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Primary Examiner—David B. Springer
Attorney, Agent, or Firm—Arnold, White & Durkee

[57] **ABSTRACT**

This invention relates to an earth stabilization fluid and to a method for using such an earth stabilization fluid. This invention uses a continuous phase that has been added to a borehole and a polymer material that forms gel masses having desired functional properties when added to the continuous phase.

61 Claims, 15 Drawing Sheets

POLYMERIC EARTH SUPPORT FLUID COMPOSITIONS AND METHOD FOR THEIR USE

CROSS-REFERENCE TO RELATED APPLICATIONS

The present application is a continuation-in-part of commonly-assigned, application Ser. No. 08/020,345 filed Feb. 19, 1993, now U.S. Pat. No. 5,407,969 which is is a continuation-in-part of commonly-assigned, application, Ser. No. 07/914,441, filed Jul. 15, 1992, now abandoned.

BACKGROUND OF THE INVENTION

1. Field of The Invention

This invention relates to polymer-based fluids for use in boring, excavating and trenching operations in the deep foundation construction industry, the subterranean construction industry, and in tunneling, in well drilling and in other applications of earth support fluids.

2. Description of Related Art

In creating foundations and shorings for buildings, bridges and other structures, and in excavating and subterranean boring for installation of utilities, barrier walls, transit ways and drainage systems, fluids have been used to support the surrounding earth during excavation operations. Whenever subterranean construction or excavation must be accomplished in granular, unstable, water-saturated or gas-charged earth formations, it has been customary to fill the boreholes, tunnel faces or excavations during the excavating or drilling process with water-based earth-support fluids, also known as slurries or muds. These fluids have consisted essentially of water, a thickening and/or filter-cake-building agent and earth solids from the excavation.

The conventional materials for making these fluids are clays such as bentonite and attapulgite. More recently, water-soluble polymers have been introduced and used in place of or in combination with such clays. (In this document "water-soluble", "soluble", "dissolved" and similar terms describing the "dissolution" of polymers refers to polymers that form either true solutions or colloidal dispersions. With regard to polymers, we use the concepts of water solubility and water dispersibility to colloidal dimensions interchangeably.) A widely used type of water-soluble polymer in these applications is a partially-hydrolyzed polyacrylamide (PHPA), in the form of a primarily linear, or non-crosslinked, long chain polymer with an anionic charge density of twenty to thirty mole weight. This type of polymer is available in liquid water-in-oil emulsion form and in dry form. Other polymers include guar gum, xanthan gum, cellulosic polymers, starch and blends of these. All of these polymers, including the PHPAs, have been prepared and applied in ways which are intended to accomplish complete dissolution or colloidal dispersion of the polymers when mixed with water to prepare earth support fluids.

With acrylic-polymer-based fluids containing no bentonite or other cake-building inorganic colloids, fluid loss control has been unattainable or poorly realized. The dissolved or colloidally dispersed water-soluble polymers, when selected and used according to past practice, could not plug the pores in the granular soil or create a filter cake as can bentonite and inorganic colloids. It has been impossible to adequately control fluid loss without adding mineral colloids or finely-divided materials such as native clays and silts incorporated into the slurry from the excavation.

In previous efforts to excavate when using acrylic-polymer-based systems, there has been little correlation or

matching of the viscosity or polymer concentration of the fluid to the characteristics or stabilization requirements of the soil or earth formation being excavated, or to the requirements for concrete-to-soil bonding for frictional load transfer. Essentially the same viscosity range and polymer concentration have been used regardless of the nature of the formation being excavated. This indicates a lack of understanding of the properties and performance achievable with the use of polymers.

In the polymer slurries there has been no counterpart of the bentonite filter cake. That is to say, there has been no effective means or medium—equivalent to the bentonite filter cake—of transferring hydrostatic pressure to the surrounding soil, or of controlling the loss of the slurry into permeable soil. The polymer slurries have been used with limited success, providing performance intermediate between simple water and a bentonite slurry. The lack of a pressure differential (or pressure drop) across a relatively thin medium at the excavation/soil interface prevents the efficient transmission of hydrostatic pressure to the walls of the excavation. Instead of this pressure being brought to bear at the wall of the excavation, which results in a supported wall, the pressure is diffused throughout the pore system of the soil near the excavation, resulting in lack of directional support of the soil. High rates of fluid loss result in large volumes of the slurry saturating the soil radially or laterally around the excavation. This saturation of the soil by fluid that is in near-perfect communication with the fluid in the excavation creates a zone around the excavation of essentially equalized pressure.

This equalization of pressure, and the attendant failure of the slurry to exert directional force against the soil, can result in collapse of the excavation. In dry or non-water-saturated granular or permeable soils, the lubricating effect of saturating the soil around the excavation with invaded slurry also contributes to the likelihood of collapse. These problems of excessive permeation by low-viscosity polymer fluid are especially severe when emulsion polymers are used in preparing the fluid, due to the oil and water-wetting surfactants in the emulsions. Deep permeation of a dry sand by polymer fluid containing emulsified oil and water-wetting surfactants can aggravate de-stabilization of the soil by fully wetting the grain-to-grain contact points and lubricating the grains of soil, such that any slight natural cohesion is destroyed and the soil collapses. Thus the absence of a means of transferring hydrostatic pressure, and the related lack of control of fluid loss into the soil, are serious detriments to the slurry excavation process and represent a major weakness in polymer slurry technology as previously practiced.

When using polymer-based systems, control of fluid loss has been achieved by adding bentonite, silts, and/or other available fines or colloids to the fluid or by boring native silts and clays in an attempt to form a mineral-enhanced filter cake on the face of the excavation. When a mineral-based or mineral supplemented slurry is used in fine-grain sands, the dispersed mineral colloids in the slurry can provide improved control of fluid loss because the pores in the soil are small. But mineral-based and mineral supplemented slurries, due to the thick filter cakes they create, reduce borehole or excavation gauge. This reduced gauge can reduce the diameter or thickness of formed or cast structures created in the excavations and boreholes. Similarly, mineral-based and mineral supplemented filter cakes can negatively affect the geometry of the formed or cast structures. Additionally, mineral-based or mineral supplemented filter cakes, as a sheath of continually reactive

and hydratable colloids at the interface between the concrete and surrounding earth, can reduce skin friction, or perimeter load shear, on which formed or poured structures rely for their load-bearing capacities. Reduced friction may promote instability, movement and stress on these structures, which can damage the subterranean structure and the superstructure that rests on them.

Historically, polymers were designed and intended to mix without forming masses or pearls of undissolved, incompletely dispersed or semi-hydrated polymer. It has been customary to prehydrate and maximize solubilization, homogenization and colloidal dispersion of these materials before introduction of the fluid into the excavation or borehole. This has been accomplished through the use of induction systems, recirculation, agitation, and processing of the polymer, and retaining the prepared fluid in a maturation tank for a period of time prior to introduction of the fluid into the excavation or borehole.

Clay slurries or muds are formulated with about five to ten percent bentonite in fresh water or about five to ten percent attapulgite in salty water. Whether the slurries are formulated with clays or polymers, the object is to create a viscous and/or dense (high specific weight) fluid that stabilizes and supports the walls of the excavation, excludes groundwater and gases from the excavation, and facilitates the progress of the construction project. A key to success in these efforts is to avoid loss or seepage of the excavating fluid into the surrounding earth during the excavating operation. If the fluid is lost into the earth formation and the excavation cannot be kept full of fluid, the excavation can collapse and groundwater or gases can enter the excavation. Excessive fluid loss can also disrupt naturally occurring cohesive forces between the formation solids.

The viscosity of the polymer-based earth support slurries has been maintained by design generally in a range of about 30 to about 45 seconds per quart as measured with a Marsh Funnel according to viscosity measurement procedures standardized by the American Petroleum Institute. This range of viscosities was felt, in light of "industry knowledge" of the prior art, to be the most effective and least damaging. Builders and engineers have expressed concerns that polymer slurries, especially high-viscosity polymer slurries, might interfere with the bonding of concrete to soil, thus degrading the frictional load-bearing capacity of structures such as bored piles. They have also expressed concerns that higher concentrations of polymer might interfere with concrete-to-rebar bonding and concrete compressive strength development.

These concerns, along with the perceived need to keep the cost of polymer fluids comparable on a unit volume basis with the cost of bentonite slurries, and the lack of appreciation of the fluid loss control and soil-stabilizing performance obtainable with high-viscosity polymer fluids, has caused polymer fluid viscosity and dosage recommendations to be held in low ranges.

The cohesion of granular earth solids exposed in-situ by slurry-excavation or loaded onto or into excavating tools is governed, aside from the inherent cohesion of the soil, by the earth binding capacity of the slurry and maintenance of pore water pressure and intergranular stresses. The earth binding capacity is the composition's affinity for earth solids, which causes the earth support fluid to chemically and physically bond or attach to exposed and excavated earth, both on the excavation tool and on and within the excavation walls. This property also preserves or improves the tendency of grains of earth to hold together in mass as opposed to separating into individual grains or smaller masses (improved cohesion). This improved cohesion aids in loading excavation tools and conveying of the earth solids up from the excavation. When an earth support fluid of high earth binding capacity permeates granular or permeable soil, it can preserve or improve the cohesion of the soil, which helps stabilize the excavation. The earth binding capacity is also manifested as the ability of the earth support fluid to film or encapsulate clay-bearing mineral solids and thereby reduce their tendency to adsorb, absorb or take up water.

When the conventional liquid emulsion PHPA is used as the primary slurry additive, it has occasionally been added directly into the borehole or excavation, and the drilling or excavating tools have been used to mix it with water and/or fluid in the borehole. However, this is not the industry-preferred method for emulsion PHPA addition, because it can produce agglomerates of undispersed, wasted polymer. These agglomerates have been documented to cause voids in concrete due to becoming intermingled with the concrete during placement and then slowly degrading, leaving holes or honeycomb structures within the concrete. Typically and preferably an reduction unit or in-line mixer, sometimes in conjunction with a hydration tank with recirculating pumps is utilized to assure complete solubilization or dispersion of the polymer prior to introduction to the excavation or borehole.

The ability to rapidly mix and yield polymer directly in the borehole or excavation is advantageous because it eliminates the need for costly, cumbersome mixing and processing equipment. It can significantly reduce time required to drill, excavate and construct piers, walls, pads, wells, etc.

Whenever polymer has been used, a primary objective in mixing polymer into water or earth excavation fluid has been to create a homogeneous solution or mixture and to accomplish complete dispersion and dissolution of the polymer as readily as possible. Completely dissolving and homogenizing the polymer in the water or fluid has been considered a key to optimum performance. Incompletely homogenized polymer of any kind, whether in the form of agglomerates, polymer strings, "fisheyes," gels, microgels, pearls or masses has been seen as disadvantageous and wasteful. Avoiding the presence of incompletely hydrated polymer in the slurry has been a prime objective of fluid design and mixing practice.

At the relatively low polymer doses and/or viscosities previously used in acrylic polymer slurries, polymer depletion can occur when silty or clay-bearing soils are excavated. Earth solids disturbed by the excavating tool are mechanically dispersed into the slurry. The increased solids surface area thus exposed creates an increased demand for polymer as the reactive sites on the solid particles attract and bond to the oppositely charged sites on the polymer. This ionic bonding of polymer to dispersed solids depletes the concentration of dissolved or colloidal polymer in the system, such that the properties of the system become governed increasingly by earth solids content and less by the solution properties of the polymer. In a polymer-depleted, solids-laden system Marsh Funnel viscosity values can be maintained in reasonable ranges by the hydration and dispersion of native days, which in a high-concentration polymer system would not be allowed to hydrate and disperse. This solids-based viscosity can give a false sense of security because the viscosity of the system is in expected ranges but there is insufficient polymer available to stabilize the excavation.

The depletion of the polymer in the system allows further hydration of the walls of the excavation, with attendant

de-stabilization. At the low remaining concentration of polymer, the polymer acts as a flocculant instead of a viscosifier and stabilizer/protective coating agent. In the flocculated system the flocs of fine solids settle toward the bottom of the excavation and can form a soft mass of non-cohesive material which is difficult to remove with excavating tools. This soft material, if not removed, can create voids in formed concrete and can be detrimental to the integrity and bearing capacity of cast-in-place concrete structures formed in the excavations.

SUMMARY OF THE INVENTION

The invention is a fluid based on vinyl polymer(s), especially those based on acrylic chemistry, composed of water-soluble, water-swellable, hydratable and/or water-dispersible material(s) and a method for using certain water-soluble polymers, polyelectrolytes and buffers to prepare and maintain earth support fluids which are more functionally effective than those known previously. The use of natural polymers is also within the scope of the invention.

The earth support fluids are more functionally effective because they use a higher concentration of polymer, and/or increased ionic affinity, and/or higher viscosities, or because they contain a plurality of: partially-dissolved or hydrated or dispersible masses of synthetic, natural, or modified natural polymers; synthetic and natural resins and latexes; as well as all grafts and blends of the above materials with or without surfactants or hydration inhibitors. The earth support fluids are prepared and maintained without added commercial mineral colloids, and exhibit fluid loss control and preferably one or more of the following properties: borehole or excavation wall stabilization, earth solids encapsulation, improved management and separation of earth solids which have become dispersed into the fluids, improved cohesion of the excavated earth, and improved development of perimeter load transfer at concrete-to-earth interfaces in subterranean structures formed in excavations. It should be understood that for purposes of this application the terms "perimeter load transfer", "perimeter shear", and "skin friction" are used interchangeably.

The earth support fluids of certain embodiments of the invention are formulated and applied in ways which use viscous solutions of polymers in concentrations sufficient to provide a means of creating in granular or permeable soils a zone permeated with gelled or highly viscous, relatively immobile polymer fluid immediately adjacent to and surrounding an excavation. This permeated zone of reduced hydraulic conductivity at the soil/excavation interface—referred to herein as a pressure transfer zone—serves as a medium to efficiently transfer hydrostatic pressure from a column of fluid in the excavation to the walls of the excavation, thus supporting the walls during the excavating process. Limited permeation or invasion of the soil adjacent to the excavation by the viscous fluid creates the pressure transfer zone.

This polymer pressure transfer zone acts in effect as a pressure-reinforced structural support for granular or permeable softs which would tend to disintegrate and cave into the excavation in the absence of an effective soil-support medium. These effects of soil strengthening and the formation of an efficient pressure-transfer medium are achieved by preparing the earth support fluids with sufficient concentration of selected ionically-charged polymers to produce viscous fluids having high effective viscosity, or resistance to flow, at the low shear rates typically encountered at the excavation/soft pore system interface in geoconstruction or well-drilling operations conducted in soft. We have found that the Marsh Funnel viscosity measurement is a good indicator of viscosity requirements for pressure transfer zone formation and creation of an effective pressure transfer medium for providing directional support for the walls of the excavation. As is the case with a bentonite filter cake, the polymer pressure-transfer zone of the invention serves the important function of controlling fluid loss, i.e., loss of the earth support fluid from the excavation into the soft.

Improved cohesion of granular or permeable soils (e.g. sand) when permeated by a polymer-based slurry is primarily governed by a polymer's molecular structure, concentration, ionic character and charge density. The ability of charged sites on the polymer molecules to bond with or adhere to oppositely-charged sites on soil particles allows a polymer to increase bulk soil cohesion through an adhesive effect (bonding soil grains together). This effect is similar to the effect achieved by bonding a mass of sand grains together with a curable epoxy resin which hardens to form a cohesive and durable sand/resin complex, but in the case of the present invention the adhesive effect is temporary in practical application because the adhesive bonding agent is a viscous fluid or gel of polymer, which can be broken down by the alkalinity and calcium content of concrete or portland cement, instead of insoluble hardened epoxy resin.

Cationic polyelectrolytes can also be incorporated into the anionic-based polymer fluid to (a) promote coagulation or removal of suspended soil particles and/or (b) to promote structuring of the fluid. This structuring or interaction between the anionic polymer based fluid and the cationic material imparts a semi-viscoelastic character to the continuous viscous phase. This viscoelastieity makes the fluid more resistant to seepage into the soil. The resistance to fluid migration into the surrounding earth assists the efficient transfer of hydrostatic pressure as described above, supporting the soil.

A preferred embodiment of the present invention displays, due to the combination of molecular weight and anionic charge density and concentration of a polymer of the invention, and/or the viscosity of the prepared fluid, improved earth binding characteristics expressed by improved cohesion of exposed and excavated earth solids, especially sands and gravels. This improvement in earth binding and cohesion facilitates excavation operations, especially auger drilling, and results in greater productivity, improved excavation gauge, and improved preservation of the pre-excavation soil cohesion and pore water pressures in the surrounding earth.

The materials of the present invention which are used as precursors to the formation of hydrated or hydrating masses which form the discontinuous phase of the two-phase fluids, due to one or any combination of their properties (their ionic charge density, molecular weight, chemical composition, cross-linking, surfactant treatments, physical granulometry, particle shape, plasticity, hydration characteristics, solubility characteristics), can provide fluid loss control when used according to the methods defined in this patent.

This method provides for partially-hydrated, semi-solubilized, or functional, insoluble particles (hereinafter referred to as "pearls" or "masses") to be dispersed in the slurry at all times or at specific times of need during the excavation or drilling process. Effective fluid loss control in granular or permeable soils can also be achieved with a fluid of the invention when adequate concentration and/or viscosity of a functionally effective polymer(s), as described above, are employed to prevent or limit the permeation of

the soil by the fluid, or to permeate the soil surrounding the excavation with a zone of viscous, earth-binding, continuous or semi-continuous fluid or gel which resists flow or displacement. The polymer typically associates with the water molecules of the fluid, making the fluid mobile yet non-wetting.

The "gel masses" or "pearls" or "composition masses" of this invention are formed in one of three principal ways using the methods of the invention: (1) upon hydration of solid or emulsified particles or micelles of water-dispersible polymer (polymer/water); (2) by interaction of anionic, cationic and/or amphoteric organic polymeric materials such as vinyls, acrylics, polyacrylamides and polyamines (polymer/polymer); (3) by interaction of anionic, cationic and/or amphoteric organic polymeric materials with each other and with soil particles to form polymer/soil complexes or agglomerates (polymer/soil or polymer/polymer/soil). These masses are formed in a variety of sizes and shapes, including but not limited to planar configurations (such as a potato-chip configuration); spheroidal configurations, elongated finger-like or fibrous configurations, and deformable globules, rice hull shapes, straw-like shapes and ovoid shapes.

The dimensions of the hydrating or hydrated masses can range from about 10 microns to about 100 mm with presently available materials, and can be larger if composed of multiple individual masses which have fused together in the process of hydrating or by ionic interaction. Still larger hydrating or hydrated masses may be possible with modifications in the preparation of the dry compositions to produce larger dry particles which are the precursors of the hydrated masses. Relatively large masses can be produced through the addition of a cationic material to an existing anionic fluid, or the interaction among a cationic additive, the anionic polymer fluid, and soil particles. The smallest hydrated masses are produced by dissociation of larger hydrated masses or by direct hydration of finely-divided dry composition particles or by the ionic interaction created in an existing anionic fluid by misting or placing small droplets of a liquid cationic material into the slurry or placing a fine dry cationic material into the existing fluid.

The masses, when present in the fluid, can be partially or fully hydrated. The masses are preferably deformable. This deformability helps the masses conform to, lodge in and constrict or plug pore spaces in granular or permeable formations. This mechanism controls fluid loss, and is especially effective when used in conjunction with a high-dose, high-viscosity continuous or semi-continuous phase formed from dissolved functionally effective polymer(s).

The masses can have a finite life span in the fluid, corresponding to the time required for the masses to completely hydrate and dissolve in the case of compositions which are completely water-soluble. For compositions which are hydratable or water-swellable, the masses may go through phases of hydration followed by dissociation or adsorption to surrounding earth. During the hydrational phase the masses generally become larger; then at some point they can begin to dissociate and may produce many smaller hydrated particles in the fluid. Masses formed via in-situ reaction in an anionic based fluid with a cationic based additive may produce semi-hydrated to fully hydrated masses or globules which are indefinitely stable within the fluid system. These masses or globules are typically deformable and have a high affinity to bond or interact with soil.

The hydrated or partially-hydrated natural and synthetic polymers which form masses that plug the pores in granular or permeable soils, and thereby slow the seepage of the earth support slurry into the surrounding soil, are preferred. Polymers which exhibit earth binding capacity are also preferred. Polymers which allow high formation-to-concrete adhesion, which is expressed as "perimeter load transfer coefficient", or "perimeter load shear" are also preferred.

The ability of the polymeric and resinous materials to form both transient or degradable pearls or masses or form more persistent pearls or masses for controlling fluid loss, or for optimally plugging porosity in permeable formations is achieved in the manufacturing or processing of the material or during preparation of the fluid in the field by one or more of the following techniques: (a) partially crosslinking the material to retard hydration, reduce solubility, and increase branching; (b) highly crosslinking the material to retard hydration and reduce solubility; (c) surface treatment (including in-situ co-addition) of the materials, as with a surfactant, a coating, microencapsulation, or physical processing, to retard hydration; (d) blending the materials with co-additives (e.g. electrolytes, cations, etc.) which retard hydration; (e) granulation or flaking or agglomeration and sorting to optimize particle size of the dry materials, which impacts rate of hydration for hydratable materials and the size of semi-hydrated particles in the slurry; granulation and size sorting also impact pore-plugging performance of insoluble or plastic particulates; (f) copolymerizable surfactants being incorporated in the polymers backbone which impact hydrophilic tendencies; (g) polymerization to yield an amphoteric or ampholytic structure; (h) grafting materials together to form an optimized end material; (i) the incorporation of a hydrophobic or semi-hydrophobic, or non-water soluble material to retard water solubilization; (j) blending the materials in-situ with cationic co-additives (e.g. polyacrylamides, mannichs, polyDADMACs polyamines, polyMAPTACs, polyethylene imines, etc.) which interact with the anionic based slurry to form a variety of mass configurations; (i) blending the materials in-situ with cationic co-additives (e.g. polyacrylamides, mannichs, polyDADMACs, polyamines, polyMAPTACs, polyethylene imines etc.) which interact with the anionic based slurry to structure the fluid.

Within the scope of this invention are synthetic, natural and modified natural polymers, including blends and grafts, which are prepared and used in ways which create a fluid comprising a continuous liquid phase in which is present a plurality of hydrating or hydrated polymer masses. Examples of such materials are synthetic polymers and natural polymers such as polysaccharides, gums, biopolymers and combinations thereof. Also within the scope of this invention are fluids composed of water-soluble or water-dispersible synthetic polymers which exhibit one or more of the characteristics or performance attributes of the invention described herein, when a plurality of hydrating or hydrated polymer masses is not present. The polymer masses are helpful in obtaining the desired performance in granular or permeable soils, but adequate performance can often be obtained without the masses if the polymer selection, dosage, and fluid viscosity are in accord with the method of the invention as described herein.

In a preferred embodiment of this invention a vinyl copolymer forms both the continuous fluid phase and the discontinuous phase of hydrating or hydrated masses dispersed in the fluid. In an alternate embodiment, hydrating or hydrated masses of natural polymers or modified polysaccharides are suspended in a continuous fluid phase of solubilized anionic or amphoteric polymer. In an alternate embodiment, cationic materials are added to a continuous or

semi-continuous fluid phase coning solubilized anionic or amphoteric polymer to form masses or to increase the viscosity or structure of the excavation fluid. When cationic materials are introduced into an anionic or amphoteric based polymer system they can create an effect through bonding of cationic sites with anionic sites that increases the viscosity of the fluid and can increase the capacity of the fluid to hold particles in suspension. This increased structure can also decrease migration or permeation of the fluid into the surrounding earth.

The polymers of the present invention, when the creation of a plurality of hydrating or hydrated polymer masses is desired, are preferably added in a solid granular, flaked, or agglomerated state with the dry particles ranging in size from 0.01 mm to 50 mm (in certain flaked products), and currently in a range of 0.01 mm to 10.0 mm, and with the majority by weight of the particles being between 0.10 mm and 2.5 mm for most available products. All of these materials become larger when initial hydration occurs, although dissociation may eventually reduce the hydrated particle size.

The fluids of the present invention, when the creation of a plurality of polymer masses is desired, can also be achieved through the addition of liquid polymers via methods designed to create discrete ionically reactive nuclei in the fluid. Liquid polymers in both solution and emulsion form of either cationic, anionic, or amphoteric charge character can be added via misting, controlled droplets, or specialized mixing equipment to produce the desired masses described hereinabove.

The fluids of the present invention have API Marsh Funnel viscosities as follows:

(a) Dual-phase fluids with masses formed by any means, for use in any type of soil or earth formation: about 28 seconds per quart or greater; more preferably about 32 seconds per quart or greater; and most preferably about 36 seconds per quart or greater.

(b) Single-phase anionic acrylic fluids for use in shale, clay, silt or other fine-grained soils or earth formations not classified as sand or coarser: greater than about 45 seconds per quart; more preferably greater than about 50 seconds per quart; and most preferably greater than about 55 seconds per quart.

(c) Single-phase anionic acrylic fluids for use in dry sand, gravel or other non-cohesive soils or earth formations: greater than about 60 seconds per quart; more preferably greater than about 70 seconds per quart; and most preferably greater than about 75 seconds per quart.

(d) Single-phase anionic acrylic fluids for use in wet sand, gravel or other non-cohesive soils or earth formations: greater than about 45 seconds per quart; more preferably greater than about 55 seconds per quart; and most preferably greater than about 60 seconds per quart.

(e) Single-phase fluids comprising a combination of any two or more materials of anionic, nonionic, amphoteric, associative and/or cationic nature, for use in any type soil or earth formation; greater than about 28 seconds per quart; more preferably greater than about 32 seconds per quart; and most preferably greater than about 36 seconds per quart. These fluids may be structured, possess an enhanced inter-associated or ionically bonded polymeric network, or they may be unstructured.

(f) Single-phase fluids comprising an associative polymer, for use in any type soil or earth formation; greater than about 28 seconds per quart; more preferably greater than about 32 seconds per quart; and most preferably greater than about 36 seconds per quart.

(g) Single-phase fluids comprising an amphoteric polymer, for use in any type soil or earth formation; greater than about 28 seconds per quart; more preferably greater than about 32 seconds per quart; and most preferably greater than about 36 seconds per quart.

(h) Single-phase fluids comprising a cationic polymer, for use in any type soil or earth formation; greater than about 28 seconds per quart; more preferably greater than about 32 seconds per quart; and most preferably greater than about 36 seconds per quart.

When the fluids are based on anionic polyacrylamides, and the viscosities are higher than about 40 seconds per quart, the dosage of the primary polymer (active basis) is preferably greater than about 0.7 grams per liter.

Increased viscosity is a key feature of certain embodiments of the present invention. Viscosity, polymer selection and polymer dosage are specified in relation to reactivity, hydrational potential, granularity, porosity, permeability and hydraulic conductivity of the earth formation. The resultant fluids should allow settling of disturbed earth solids larger than about 75 microns, or should suspend disturbed earth solids indefinitely until the fluid has been removed from the excavation or until solids-separation processes are effected. The fluids should also allow dispersion of additional fresh polymer or incorporation of other additives.

Polymeric earth support fluids based on anionic vinyls and other anionic polymer bases or carboxyl-containing polymers (e.g. polyacrylate, carboxymethylcellulose) are generally sensitive to contamination from divalent and polyvalent cationic contaminants such as earth metals (calcium, magnesium, iron, zinc, etc.), and to a lesser extent monovalent cations such as sodium and potassium. The sensitivity of such polymeric earth support fluids to such contaminants has certain benefits (e.g. allowing improved bonding between concrete and soil) and certain detriments (e.g. excessive concrete-induced degradation of fluid, causing increased consumption of polymer).

It has been known and practiced in the prior art to mitigate contamination from such sources by pre-treating the fluid with certain buffers such as sodium carbonate, sodium bicarbonate, and various phosphates. In clay-based drilling muds and slurries these buffers have also been used, usually in conjunction with organic thinners, as treatments to precipitate contaminants such as calcium to allow deflocculation of the clay-based systems and to restore their properties. The novelty in our use of buffers, sequestrants and hydroxides lies in the discovery that they can be used, alone or in combination, to offset the effects of cation contamination in polymer systems via novel processes of cation replacement and polymer hydrolysis.

In fluids of the invention comprising anionic polymers, soluble hydroxides present in high relative concentrations as hydroxyl ions can restore fluid viscosity and polymer functionality via a mechanism of "pulling" the contaminating cations off the passivated anionic sites on the polymer chain, which allows rehydration and uncoiling of the collapsed polymer. Excess hydroxyl ion, at pH levels above about 11.5, can also restore system viscosity and anionic functionality by hydrolyzing amide groups to carboxyl groups. This can be accomplished by treating the fluid first with a hydroxide (to initiate hydrolysis), followed by buffering with a weak acid, a phosphate, a phosphate ester, a phosphonate, or soluble bicarbonate to reduce pH and arrest hydrolysis after some amount of new carboxyl groups have been formed. Hydrolysis of amide to acrylate creates new

functional groups which restore viscosity and functionality to the system. In the prior art it was believed that the high-pH and high-soluble-calcium environment created by concrete or cement contamination caused irreversible precipitation of carboxyl-containing polymers.

In another novel and beneficial use of soluble hydroxides, the precipitates they form with such contaminating cations as magnesium are used alone or when complexed with polymers as sealing or plugging agents to control fluid loss in granular, permeable or fissured formations.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a graphic representation of the Marsh Funnel viscosity versus the CDP dosage. The term "CDP" shall be understood to refer to the trade name for a polymer based product within the scope of this invention marketed by KB Technologies Ltd.

FIG. **2** is a chart showing a comparison of viscosity development efficiency using a composition and method of this invention.

FIG. **3** is a graphic representation of the fluid loss control characteristics of the composition and method of this invention in comparison to prior art compositions and methods. FIG. **3** also shows the effects of hydration time on fluid loss control of a composition and method of this invention and on a prior art polymer composition and method, both compared to bentonite.

FIG. **4** is a chart showing filtration control performance versus time at equal hydration times (30 minutes) for a preferred embodiment of this invention and for a composition of the prior art.

FIG. **5** is a graphic representation of peak values of perimeter friction/cell pressure from extraction testing for fine sand specimens drilled under CDP slurries.

FIG. **6** is a graphic representation of a comparison of perimeter load transfer coefficients for various materials.

FIG. **7** is a graphic representation of viscosity development efficiency of CDP versus emulsion PHPA at high dosage ranges.

FIG. **8** is a graphic representation of a comparison of mean normalized perimeter shear for 24 hours contact time.

FIGS. **9***a* and **9***b* and **10***a* and **10***b* are graphic representations of borehole profiles for pile holes bored using the earth stabilization fluids of this invention.

FIG. **11** is a graphic representation of load test results measured as a function of depth versus unit shear resistance for concrete piles cast in holes bored using the earth stabilization fluids of this invention.

FIGS. **12**, **13**, and **14** are graphic representations of the "skin friction development" and filtration control effects for bored piles constructed using the earth stabilization fluids of this invention.

FIGS. **15**, **16**, **17**, and **18** are graphic representations of the "skin friction development" of model bored piles constructed using the earth stabilization fluids of this invention in comparison to the prior art use of bentonite and attapulgite.

FIG. **19** is a graphic representation of load test results in a bored pile constructed using the earth stabilization fluids of this invention compared to the conventional use of bentonite.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In a preferred embodiment an earth support fluid is formulated as an aqueous slurry having suspended therein a plurality of masses of partially-hydrated, or hydrating, water-soluble, water-swellable, hydratable and/or water-dispersible compositions (the "composition masses"). The earth support fluids contain suspended therein partially-dissolved and/or hydrated and/or dispersible synthetic or natural polymers, resins and/or latexes; and all grafts of the above compositions. The molecular weight of the composition(s) may vary over a wide range, e.g., 10,000–40,000,000 or higher. The invention, however, finds its greatest usefulness when anionic acrylic polymers having molecular weights of 100,000 or more, preferably one million or more, and most preferably in excess of 10,000,000 are applied to form the continuous phase as well as all or a portion of the discontinuous phase, which is the plurality of hydrating or hydrated polymer masses. Cationic polymers may also be added to the continuous anionic polymer phase to enhance the structuring characteristics of the fluid, or to produce or supplement a discontinuous phase.

In a second preferred embodiment, the fluid can be prepared or used without the composition masses, but with a sufficient concentration of a selected functionally effective polymer to provide adequate viscosity and/or earth binding capacity to provide one or more of the following functions: add cohesion to granular or permeable soils by acting as a permeating adhesive; limit or control loss of the fluid into granular or permeable soils and support the walls of the excavation via hydrostatic pressure transfer by impregnating the pore system of the soil with viscous polymer fluid which resists displacement, or by using a fluid so viscous that it cannot freely permeate the soil; improve, through cohesion enhancement and adhesive effects, the loading and conveyance of excavated soil spoils on and in tools such as augers and grabs; allow improved bonding of concrete to soil, and improved frictional load transfer as compared with existing slurry technologies.

The anionicity of the polymer may be obtained from the hydrolysis of acrylamide during the polymerization or from the copolymerization of acrylamide with the anionic monomers comprising acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid, vinyl or, styrene sulfonic acid, 2-acrylamido-2-methylpropane sulfonic acid (AMPS®) and the like, and water soluble salts thereof. The preferred anionic monomers are acrylic acid, methacrylic acid, maleic acid, vinyl or styrene sulfonates and AMPS® or their salts. Copolymers comprising acrylamide and/or other non-ionic monomer, with more than one anionic monomer foregoing is also within the scope of the invention.

The molar percentage of the comonomers in the polymer may vary within certain limits, provided that the total adds up to 100%. The anionic charge density will vary from about 5% to 90%, preferably 10% to 80%, and most preferably 35% to 65% in the polymer. The composition, anionicity, and molecular weight of the copolymer may be optimized for the particular earth formation and water conditions in order to achieve the desired drilling, boring, or excavation and earth supporting functions.

The anionic copolymer of the invention may be further modified by incorporating certain cationic monomers in the polymer forming ampholytic polymers. The cationic monomers are selected from the group consisting of: diallyldimethylammonium chloride, quaternized dimethylaminoethyl (meth)acrylates, and N,N-dimethylaminopropyl methacrylamide and combinations thereof. These cationic constituents may be reacted to form acid salts or quaternized using methyl chloride or dimethyl sulfate.

Non-ionic monomers for use in the practice of the present invention are selected from the group consisting:

acrylamide, methacrylamide, C_1 to C_{20} acrylates, N-vinyl pyrrolidone, vinyl acetate, styrene, N-vinyl formamide, N-vinyl acetamide or mixtures of the forgoing. Especially preferred is acrylamide.

A small amount of water insoluble/hydrophobic monomers such as C_5 to C_{20} long chain alkylates, hydroxyalkylates, and N-alkyl substituted acrylamides may also be incorporated in the copolymer of the invention. These hydrophobic groups tend to associate with one another in an aqueous solution to form an inter/intra molecular association. As a result, the solution viscosity is increased and the viscosity is relatively insensitive to salts as compared to polymers without the hydrophobic groups.

Polymerization of the monomers may be conducted in the presence of a crosslinking agent to form the crosslinked or branched composition. The crosslinking agent comprises molecules having either a double bond and a reactive group, two reactive groups or two double bonds. The agent may be selected from a group comprising N,N-methylenebisacrylamide, N,N-methylenebismethacrylamide, polyethyleneglycol di(meth) acrylate, glycidyl acrylate, acrolein, N-methylolacrylamide, alkylaldehydes C_1–C_{42}, glyoxal, diallylamine, triallylammoninm salts, ammonia, C_1 to C_{25} amines (including diamine or triamine), epichlorohydrin, diepoxy compounds or the like and mixtures of the foregoing. The crosslinking or branching is due to the inter or intra molecular reactions of the monomeric units in the polymer chain with the crosslinking agent. The agent is to be used in sufficient quantifies to assure a crosslinked or branched composition so long as the resulting polymer is still water soluble or hydratable. Preferably, 0.001% to 20%, and more preferably 0.01% to 10% based on the total monomer weight, is used for the purpose. The proportion of these materials in this application can range from 0.01 to 300 kilograms per cubic meter by dry weight of polymer on volume of water or slurry.

The rheological profile of the polymer fluid is significantly impacted by the anionicity and the degree and type of crosslinking, and the amount and type of cationic, associative or amphoteric material added. FIG. **2** is a chart showing a comparison of viscosity development efficiency using a composition and method of this invention.

The composition pearls or masses can exhibit a finite and controllable life span in the excavation fluid. This life span can range from several minutes to several weeks based on the composition chemistry, physical and chemical properties of the excavation fluid. The composition masses' life span can be controlled by any one or a combination of the following chemical mechanisms: (1) degree of crosslinking and/or branching; (2) method of crosslinking and/or branching; (3) solubility, and/or hydrophilic/hydrophobic nature of the compositions; and (4) inclusion of coadditives and/or surface treatments to the compositions.

The composition masses' life span may be influenced in-situ either positively or negatively by continued exposure to shear stress, exposure to cations or electrolytes, exposure to earth solids, or continued hydration over time. A composition pearl or mass can be defined as a discrete constituent, or element, existing independently within an excavation fluid, and possessing the characteristics given above in the Summary of Invention. These pearls or masses impart unique performance characteristics to the fluid allowing for the reduction of fluid loss to the excavated formation. The composition pearls' or masses' ability to decrease formation porosity at the formation interface is achieved through the pearls or masses being drawn into the formation voids and completely or partially plugging and sealing these voids.

As these composition pearls or masses build on one another they constrict or plug pore throats to reduce fluid loss. A filter cake or in-depth soil matrix seal of synthetic or natural polymer and/or resin is formed. This filter cake or seal may incorporate colloidal or dissolved water soluble polymer or resin to further improve filtration control and filter cake construction. When the fluid is formulated or used with the gel masses present, the optimization of these pearls or masses is a significant determinant of the performance and soil-sealing properties of the fluid and the filter cake or matrix seal. These composition pearls or masses of synthetic or natural polymer or resin or combinations thereof allow for the elimination of bentonite, silt, and/or other colloidal or finely divided material from the fluid design when used in one method of this invention.

The interaction between the pearls or masses, the polymer, and the earth forms a filter cake on and within the excavation walls and, to a greater degree in coarse-grained soils, a polymer/soil viscous conglomerate or structure comprising the in-situ soil grains and the polymer/gel fluid which permeates the pore matrix of the soil under hydrostatic pressure. The polymer filter cake and the in-depth polymer/soft structure significantly assist in maintaining a stable side wall in the soil formation. Side wall stabilization is enhanced by reduction in fluid loss to the formation, maintenance of hydrostatic pressure differential transferred through the wall cake and in-depth matrix seal, and increased earth binding capacity of the fluid.

The polymer filter cake, or polymer/soft matrix, produced by this invention significantly reduces the fluid loss to the surrounding formation. Excessive fluid loss to the soil formation, especially when the lost fluid is water or low-dosage polymer/water fluid, hydrates the formation and disrupts the natural cohesive forces between formation solids. This loss of cohesive forces causes side wall sloughing and cave-ins. The polymer/soil matrix maintains a significantly more stable excavation than that known in the prior art by reducing or inhibiting the hydration of the formation and/or changes in soil pore pressure and maintaining a hydrostatic pressure differential through or across the polymer/soil matrix.

FIG. **3** shows the fluid loss control versus polymer hydration time of a preferred embodiment of this invention and two other commercially available construction drilling slurry products. Hydration times shown in FIG. **3** are time elapsed between introduction of polymer into mix water and initiation of filtration test. Hydration time is a principal determinant of the presence, abundance and quality of the partially-hydrated or hydrating gel masses in the fluid. Generally, as hydration time is increased, the number of discrete gel masses is reduced and the gel masses which are present become larger and more elastic. Thus the pore-plugging effect of the gel masses is reduced and the fluid must rely on continuous-phase viscosity and polymer-to-soil-grain bonding (adhesion) to control fluid loss, increase soil cohesion and effect the other functions of the invention. In developing data for FIG. **3**, commercially available products were mixed at low shear with a single corrugated disk impeller at approximately 3,000 RPM. The products were stirred for 5 to 10 minutes and were unstirred during the remainder of the hydration time. Bentonite was mixed at a high shear to assure good dispersion. The test was conducted at a 5 psi pressure differential against a manufactured, artificial sand stone disk, ¼" thick having a permeability of 20 darcies and a pore diameter of 60 microns nominal.

US005387675A

United States Patent [19]

Yeh

[11] Patent Number: 5,387,675

[45] Date of Patent: Feb. 7, 1995

[54] **MODIFIED HYDROPHOBIC CATIONIC THICKENING COMPOSITIONS**

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[52] **U.S. Cl.** **536/18.7**; 536/22.1; 536/50; 536/52; 536/114; 536/120

[58] **Field of Search** 536/18.7, 22.1, 50, 536/52, 120, 114

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,467,647	9/1969	Benninga	260/209
3,760,881	9/1973	Kiel	166/308
3,833,527	9/1974	Puikkinen et al.	260/9
4,031,307	6/1977	DeMartino et al.	536/114
4,264,322	4/1981	Lewis et al.	8/479
4,276,414	6/1981	Tessler	536/114
4,403,360	9/1983	Finney et al.	8/151
4,454,617	6/1984	Moates et al.	8/151
4,568,481	2/1986	Harris, Jr.	252/8.55 R
4,758,282	7/1988	Stober et al.	127/34
4,918,181	4/1990	Karcher et al.	536/114
4,959,464	9/1990	Yeh	536/114
5,186,928	2/1993	Birtwistle	424/70
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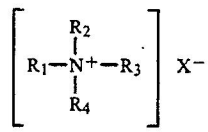
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Primary Examiner—Ronald W. Griffin
Attorney, Agent, or Firm—Andrew M. Solomon

[57] **ABSTRACT**

Water soluble quaternary ammonium ethers of polysaccharides or polyols wherein the quaternary ammonium ether substituents correspond to the formula



(I)

wherein R_1 is a monohydroxylated or polyhydroxylated alkyl group containing between about one and about six carbon atoms; R_2 and R_3 are independently, alkyl groups containing between about one and about six carbon atoms; R_4 is an alkyl group containing between about six and about 24 carbon atoms; and X is a halide, wherein the degree of substitution of said ethers ranges from about 0.001 to about 0.5. is provided. The composition have multiple uses as thickeners and are particularly suited for use in personal care products.

12 Claims, No Drawings

MODIFIED HYDROPHOBIC CATIONIC THICKENING COMPOSITIONS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a cationic thickening composition. More specifically, the composition is a polysaccharide or polyol which is reacted with a hydroxylated quaternary ammonium halide wherein the quaternary ammonium halide contains a long chain aliphatic group containing at least 6 carbon atoms. The resulting compositions function to increase the viscosity of an aqueous solution and have widespread uses, for example, in cosmetics and in oil recovery.

2. Technology Description

Natural and synthetic polymers containing hydroxy groups have been used as thickeners for foods, coatings, paints, explosive slurries, oil well fluids, cosmetics and other personal care products, and many other functional applications.

One class of polymers that have been widely used as suspending and viscosity agents are polygalactomannans. Polygalactomannans are polysaccharides composed principally of galactose and mannose units and are usually found in the endosperm of leguminous seeds such as guar, locust bean, honey locust, flame tree, and the like. The polygalactomannans may be used in either their natural form or may be substituted with one or more functional groups (e.g., carboxymethyl group). In practice, to thicken a fluid the polygalactomannans may either be added by themselves, or with other viscosity modifiers such as other polygalactomannans, xanthan gum and the like.

Other polymers proposed for use as thickening agents include unmodified and modified starches, methyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose, polyols such as polyvinyl alcohol, glycols, glycerols, polyacrylamide, polyvinylpyrrolidone, xanthan gum and the like.

U.S. Pat. No. 3,467,647 discloses polysaccharides containing both cationic and anionic substituents. Amongst the starting polysaccharides which are then modified according to this patent include starches, locust bean gum (carob gum) and guar gum. Suggested cationic substituents include primary, secondary or tertiary amino groups, quaternary ammonium, sulphonium or phospinium groups. The reference suggests that cationic groups may be introduced into the polysaccharide molecule by reacting the polysaccharide with any of the following reagents: ethylene imine, N-(2-hydroxyethyl) ethylene imine, cyanamide, beta morpholinoethylchloride, beta diethyl aminoethylchloride, 3-diethyl amino 1,2-epoxypropane dimethyl aminoethyl methacrylate, N-(2,3-epoxypropyl) trimethyl ammonium chloride, (4-chlorobutene-2)-trimethyl ammonium chloride, 2-chloroethyl methyl ethyl sulphonium iodide and 2-chloroethyl tributylphosphonium chloride.

U.S. Pat. No. 3,760,881 discloses well treating fluids which are prepared with complexes formed by the reaction of aliphatic quaternary ammonium compounds with water-soluble compounds such as monosaccharides, disaccharides, trisaccharides, polysaccharides, and long chain synthetic hydroxylated polymers, such as polygalactomannans. Preferred quaternary substituents include trimethyl alkyl ammonium chlorides, wherein alkyl represents a long chain alkyl group having between about 6 and about 18 carbon atoms. The reference does not disclose nor suggest that the quaternary ammonium halide be hydroxylated. A preferred polygalactomannan mentioned is guar gum.

U.S. Pat. No. 3,833,527 discloses a water soluble hemicellulose material made soluble by the reaction of a hemicellulose with an adduct comprising 3-chloro-2-hydroxypropyltrimethylammonium chloride or glycidyltrimethylammonium chloride. The hemicellulose is made water soluble to effect its disposal from waste effluent streams of pulp mills.

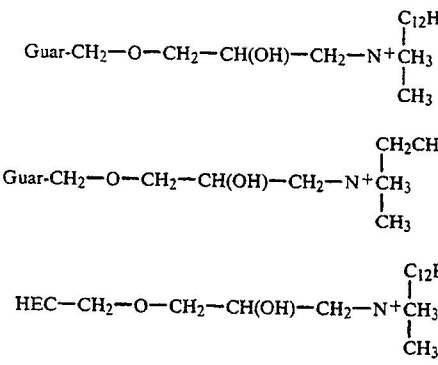
U.S. Pat. No. 4,031,307 discloses cationic polygalactomannan compositions. The compositions are prepared by reacting a polygalactomannan with a quaternary ammonium halide compound. The reactant quaternary ammonium halide compound contains three alkyl groups containing between one and six carbon atoms and one alkenyl group containing between one and six carbon atoms. An example of one such reactant is 4-chloro-2-butenyl trimethylammonium chloride. The degree of substitution on the polygalactomannan compound ranges between 0.05 and 2.5.

U.S. Pat. Nos. 4,264,322; 4,403,360 and 4,454,617 disclose dye compositions for textile fibers. The compositions comprise an admixture of immiscible gel phases, wherein one gel phase is thickened with a cationic gelling agent and wherein a second gel phase, which is dispersed in the first gel phase, is thickened with an anionic gelling agent. Suggested cationic gelling agents for the first phase include cationic polygalactomannans containing quaternary ammonium groups. Specific examples of such cationic reactants include 2,3-epoxypropyltrimethylammonium chloride, hydroxypropyltrimethylammonium chloride, tetramethylammonium chloride and bromide, benzyltrimethylammonium chloride and bromide, tetraethylammonium chloride and bromide, tetrabutylammonium chloride and bromide, methylpyridinium chloride and bromide, benzylpyridinium chloride and bromide, trimethyl-p-chlorobenzylammonium chloride and bromide, and triethanolmethylammonium chloride and bromide.

U.S. Pat. No. 4,758,282 discloses a dry process for the production of cationic galactomannans by reaction of the galactomannan starting material with an alkylidene epoxide in the presence of water and in the presence of finely divided hydrophilic silicic acid. The preferred alkylidene epoxide is 2,3-epoxypropyltrimethylammonium chloride. The reference further discloses that the reaction between the galactomannan and the epoxide be carried out in the presence of 0.5 to 5% of 2,3-epoxypropyldodecyldimethylammonium acetate.

U.S. Pat. No. 4,959,464 discloses derivatized polygalactomannan compounds. The compounds are prepared by reacting a polygalactomannan with a derivatizing agent, followed by the addition of an aluminum salt to crosslink the surface of the resulting compound. One class of derivatizing agents disclosed is quaternary ammonium alkylating agents. Specific examples of such agents are 2,3-epoxypropyl trimethylammonium chloride and 3-chloro-2-hydroxypropyl trimethyl ammonium chloride.

EP 0 405 664 discloses personal care compositions, and specifically liquid and solid soap compositions containing a cationic polymer which has a non-labile bulky amine moiety. Specific examples of preferred bulky amine polymers include the following:



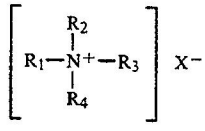
These polymers have a degree of substitution reported to be ranging from about 0.5 to about 4, preferably between 1 and 2.5 and are used to replace comparable quaternary polymers which do not contain the bulky amine moiety and are alleged to be malodorous. As these levels of substitution it is nearly impossible to manufacture the molecules, and where possible, the molecules are extremely expensive to manufacture.

Despite the above, there still is a need for compositions which demonstrate enhanced viscosity behavior.

BRIEF SUMMARY OF THE INVENTION

In accordance with the present invention, novel water soluble cationic viscosity increasing compositions are provided. The compositions provide enhanced viscosities when added in solution and provides both cationic and hydrophobic properties. They also can provide a synergistic increase in viscosity when combined with one or more anionic viscosity increasing compositions and can also interact with surfactants and salts to enhance viscosity and in some cases form a cross-linked gel. The novel composition comprises a polysaccharide or polyol which is reacted with a hydroxylated quaternary ammonium halide wherein the quaternary ammonium halide contains a long chain aliphatic group containing at least 6 carbon atoms.

In accordance with a preferred embodiment, the present invention comprises water soluble quaternary ammonium ethers of polysaccharides or polyols wherein the quaternary ammonium ether substituents correspond to the formula



(I)

wherein R_1 is a monohydroxylated or polyhydroxylated alkyl group containing between about one and about six carbon atoms; R_2 and R_3 are independently, alkyl groups containing between about one and about six carbon atoms; R_4 is an alkyl group containing between about six and about 24 carbon atoms; and X is a halide. In particularly preferred embodiments, the polymers comprise polygalactomannans derived from guar gum or locust bean gum, and preferably guar gum. Further, the preferred degree of substitution of the quaternary ammonium groups onto the polymer is between about 0.001 and about 0.5. In addition, R_1 preferably comprises a 2-hydroxypropyl group and R_4 comprises an alkyl group having between 10 and 21 carbon atoms.

The compositions are particularly effective as thickening agents. They may be used for a number of functional applications such as in textiles, paper products, explosives, oil field chemicals, agricultural applications, personal care products, cosmetics and the like.

It has been difficult in the past to provide water soluble materials containing long chain alkyl groups. The presence of the cationic groups allows the present materials to be both hydrophobic and water soluble. As a result these materials may be used in a number of applications which are water based, such as personal care products, which are ultimately less expensive to make as water is the primary solvent utilized.

Another embodiment of the present invention comprises a process for producing a viscous liquid or a gel. The process comprises the step of adding to a solvent, preferably water, 0.5 parts to about 2.0 parts per 100 parts viscous liquid or gel of the above defined cationic polymer. A further embodiment comprises provided a highly cross-linked gel by adding known cross-linking agents to the solvent.

A third embodiment of the present invention comprises a textile, paper product, explosive, oil field chemical, agricultural chemical, personal care product or cosmetic including an amount of the above-defined cationic polymer.

Accordingly, it is an object of the present invention to provide a novel composition which can increase the viscosity of a liquid and, when combined with other viscosity modifiers, demonstrates a superior viscosity profile as compared to the materials individually.

It is another object of the present invention to provide a process for producing a viscous liquid or gel using a novel composition.

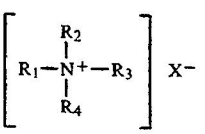
A further object of the present invention to provide a paper product, explosive, oil field chemical, agricultural chemical, textile, personal care product or cosmetic which includes a novel thickener composition.

These, and other objects, will readily be apparent to those skilled in the art as reference is made to the detailed description of the preferred embodiment.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

In describing the preferred embodiment, certain terminology will be utilized for the sake of clarity. Such terminology is intended to encompass the recited embodiment, as well as all technical equivalents which operate in a similar manner for a similar purpose to achieve a similar result.

The present invention comprises water soluble quaternary ammonium ethers of polysaccharides or polyols wherein the quaternary ammonium ether substituents correspond to the formula



(I)

wherein R_1 is a monohydroxylated or polyhydroxylated alkyl group containing between about one and about six carbon atoms; R_2 and R_3 are independently, alkyl groups containing between about one and about

six carbon atoms; R_4 is an alkyl group containing between about six and about 24 carbon atoms; and X is a halide, the degree of substitution of said polysaccharide or polyol ranging from about 0.001 to 0.5.

A number of materials can be used as the starting polysaccharide or polyol. Particularly preferred are polygalactomannans. Polygalactomannans are polysaccharides composed principally of galactose and mannose units and are usually found in the endosperm of leguminous seeds, such as guar, locust bean, honey locust, flame tree, and the like. Guar flour, for example, is composed mostly of a galactomannan which is essentially a straight chain mannan with single membered galactose branches. The mannose units are linked in a 1-4-β-glycosidic linkage and the galactose branching takes place by means of a 1–6 linkage on alternate mannose units. The ratio of galactose to mannose in the guar polymer is, therefore, one to two. Guar gum has a molecular weight of about 1.5 million daltons.

Locust bean gum is also a polygalactomannan gum of similar molecular structure in which the ratio of galactose to mannose is one to four. Guar and locust bean gum are the preferred sources of the polygalactomannans, principally because of the commercial availability thereof.

In use the polygalactomannan may be either in its natural state (i.e., pure guar gum or locust bean gum) or may be derivatized. Derivatized polygalactomannans include one or more non-ionic groups. Examples of such polygalactomannans include hydroxypropyl guar, hydroxyethyl guar, and the like. Such derivatized polygalactomannans are sold by Rhône-Poulenc Inc. under the trade names Jaguar 8012, Jaguar 8060, Jaguar 8000, Jaguar HP-20 and Jaguar HP-23.

Alternative materials which may be selected as the starting material include starches, celluloses, xanthan gum, alginates and polyols. Examples of starches include both natural and modified starches, such as dextrinated, hydrolyzed, oxidized, cross-linked, alkylated, hydroxyalkylated, acetylated, or fractionated (e.g., amylose and amylopectin). The starch may be of any origin, for example, corn starch, wheat starch, potato starch, tapioca starch, sago starch, rice starch, waxy corn starch or high-amylose corn starch.

Examples of celluloses include hydroxyethyl cellulose, hydroxypropyl cellulose, and alkyl celluloses.

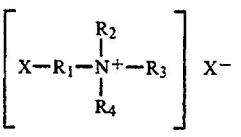
Examples of alginates include starch alginate.

Examples of polyols include polyvinyl alcohol, polyethylene glycol and glycerol.

When the starting material selected is a polygalactomannan, it is preferred that the degree of substitution ranges from about 0.001 to about 0.5. By the term "degree of substitution" as employed herein is meant the average substitution of cationic or anionic groups per anhydro sugar unit in the polysaccharides, and particularly, polygalactomannan gums. In guar gum, the basic unit of the polymer consists of two mannose units with a glycosidic linkage and a galactose unit attached to the 6-hydroxyl group of one of the mannose units. On the average, each of the anhydro sugar units contains three available hydroxyl sites. A degree of substitution of three would mean that all of the available hydroxyl sites have been esterified with formate ester groups.

Particularly preferred embodiments of the present invention comprise cationic polygalactomannans having a degree of substitution of about 0.01 to about 0.50 more preferred embodiments have a degree of substitution of about 0.01 to about 0.40, and most preferred embodiments comprise cationic polygalactomannans having a degree of substitution of about 0.02 to about 0.20.

The cationic nature is obtained by utilizing a substituent of formula (II)



(II)

wherein R_1, R_2, R_3, R_4, and X are as defined above. Particularly preferred monomers include those wherein R_1 preferably comprises a 2-hydroxypropyl group, R_2 and R_3 comprise methyl groups, R_4 comprises an alkyl group having between 10 and 21 carbon atoms and X comprises chloride. Examples of such monomers include 3-chloro-2-hydroxypropyl N,N,N-dodecyldimethylammoniumchloride, 3-chloro-2-hydroxypropyl N,N,N-cocoalkyldimethylammonium chloride, and 3-chloro-2-hydroxypropyl N,N,N-octadecyldimethylammonium chloride. Such chemicals are commercially available from The Degussa Chemical Company under the trade names QUAB-342, QUAB-360 and QUAB-426.

The cationic derivatives of the polymers, and particularly guar gum or locust bean gum are prepared by contacting solid guar gum or locust bean gum with the above-defined haloalkyl-substituted quaternary ammonium compound and a stoichiometric excess of alkali metal hydroxide or ammonium hydroxide in a reaction medium comprising an aqueous solution of water-miscible solvent, at a temperature between about 10° C. and about 100° C. for a reaction period sufficient to achieve a desired degree of substitution.

The solid guar gum or other polygalactomannan which is etherified can be in the form of endosperm splits or in the form of finely divided powder which is derived from the endosperm splits. It is important that the polygalactomannan gum being etherified with quaternary ammonium groups remains as a solid phase in the reaction medium during the reaction period.

Further details on the synthesis of cationic quaternary ammonium type polymers are provided in U.S. Pat. No. 4,031,307. To the extent necessary, this patent is incorporated by reference.

In use, the inventive compositions can effectively function as thickeners when added to a solvent, typically water. This typically comprises adding between about 0.5 and about 2.0 parts of the cationic polymer per 100 parts of viscous liquid or gel. While the viscosity profile obtained by using the cationic polymers alone is adequate, results can be synergistically enhanced when using the cationic polymers in solution in combination with anionic polymers in solution to produce an amphoteric blend composition. While less preferred, the anionic and cationic polymers can be first mixed together in solid form and then added as a blend composition in a solvent.

Such amphoteric polygalactomannan blend compositions are typically produced by combining solutions of both cationic and anionic polymers in respective amounts so that the positive and negative charges are equally balanced. The respective amounts of anionic and cationic solutions are added together based primarily upon the degree of substitution of each. For exam-

ple, larger amounts of a low degree of substitution cationic polymer solution may be added to smaller amounts of a high degree of substitution anionic solution.

While in the preffered embodiment, the amounts of anionic and cationic solutions are added to produce a charge neutral solution, the amounts of each may be varied to yield solutions which have an overall positive or negative charge. Although not as enhanced as when producing a charge neutral solution, some synergistic effect is achieved by unbalanced charged additions.

For easy handling and ready dispersibility, the gums should have a particle size of less then about 100 mesh. Other components, e.g., fillers, wetting agents, dispersants, bactericides, fungicides and the like can be mixed with the powdered blends of the invention if so desired.

It is believed that the viscosity and/or firmness of the gel increases with increasing amounts of blend composition added. At lower levels the gels are pumpable viscous liquids. Increasing the amount of blend composition can yield a firm, cohesive gel.

The novel cationic polymers have a wide number of possible uses. Amongst them are as suspending agents for various solids, such as in oil field chemicals, for use in textiles, for use in paper products, for use in cosmetics and other personal care products, for use with agricultural products, for use is explosives, and the like. Other uses will readily be appreciated by those skilled in the art.

A feature of the inventive cationic polymers is their affinity towards water. In general, long chain aliphatic hydrocarbon compounds do not have an affinity to water, making the reaction with polymers such as polygalactomannans difficult to achieve. The inventors have discovered that if reagents of formula (II) are used, the reaction conditions are improved. In this class of reagents the long chain alkyl group is linked on the nitrogen atom to form an ammonium salt and is water soluble. As a result, it is believed that the inventive materials are ideally suited for use in aqueous based personal care products such as cosmetics, lotions, and the like.

The invention is described in greater detail by the following non-limiting examples.

EXAMPLE 1

2000 parts of oxidized guar gum are slurried in 80% isopropanol. 50 parts of 50% NaOH are added and the mixture is stirred for 30 minutes. 380 parts of QUAB-342, 3-chloro-2-hydroxypropyl N,N,N-dodecyldimethylammonium chloride, are added and the etherification reaction is conducted at 70°–80° C. over a period of about one to six hours. The reaction mixture is neutralized to a pH of about 7 with acetic acid, washed with isopropanol, recovered and air dried. The degree of substitution for this material is about 0.01.

A 2% aqueous solution of this compound in water is prepared by adding 2 parts of this composition to 98 parts of water. The viscosity determined by a Brookfield RTV Viscometer at 20 rpm is above 4000 cps.

EXAMPLE 2

100 parts of a 40% solution of QUAB-342, 40 parts water and 3 drops of concentrated HCl are mixed together and added to 267 parts of Jaguar 8012, a guar gum manufactured by Rhône-Poulenc Inc. The mixture is mixed at room temperature for about 20 to 30 minutes. 19 parts of a 50% NaOH solution is sprayed onto the solution, the mixture is mixed at room temperature for about 20 to 30 minutes and the mixture is then heated in a closed container at about 70°–80° C. for about two to three hours. The mass is cooled to room temperature and is sprayed with a solution of 7.2 grams acetic acid and 11 ml of water. The mixture is washed twice with acetone and dried in an oven. The viscosity of a 1% aqueous solution of this material is 150 cps. The viscosity of a 2% aqueous solution of this material is 2600 cps. The viscosity of a 1% solution of this material in methanol is 300 cps. The viscosity of a 2% solution of this material in methanol is 3150 cps.

To demonstrate the enhanced viscosity effects when combining this material with an anionic material, one gram of this material is added to 179 ml of water. The viscosity profile of this solution is shown below under Sample A. 15 grams of an ammonium lauryl sulfate solution and 3 grams of NH_4Cl are added to the solution. The viscosity profile of this solution is shown below under Sample B. 20 grams of an ammonium lauryl sulfate solution and 3 grams of NH_4Cl are added to the initial solution. The viscosity profile of this solution is shown below under Sample C. 20 grams of an ammonium lauryl sulfate solution and 4 grams of NH_4Cl are added to the initial solution. The viscosity profile of this solution is shown below under Sample D.

Viscosity Profile of Example 2 Material (cps)

LVT RPM	Sample A	Sample B	Sample C	Sample D
.3	—	—	500	1800
.6	—	—	300	1300
1.5	80	—	216	1040
3.0	90	100	160	940
6.0	85	95	140	900
12	80	92.5	130	975
30	72	96	126	935
60	65	—	—	890

Qualitatively, Sample B is slightly thicker than Sample A but still watery. Sample C becomes a viscous, associated solution, and Sample D becomes a cross-linked gel which is very soft and elastic. It is further attempted to replicate the experiment by first adding the ammonium lauryl sulfate solution to the water and then adding the material of Example 2. Using this addition sequence, the solution does not thicken.

EXAMPLE 3

The synthesis procedure of Example 2 is repeated except that the acetone washing step is omitted. The viscosity of a 1% aqueous solution of this material is 60 cps. The viscosity of a 2% aqueous solution of this material is 360 cps. The viscosity of a 1% solution of this material in methanol is 150 cps. The viscosity of a 2% solution of this material in methanol is 1700 cps.

To demonstrate the enhanced viscosity effects when combining this material with an anionic material, one gram of this material is added to 179 ml of water. The viscosity profile of this solution is shown below under Sample A. 15 grams of an ammonium lauryl sulfate solution and 2 grams of NH_4Cl are added to the solution. The viscosity profile of this solution is shown below under Sample B. 15 grams of an ammonium lauryl sulfate solution and 3 grams of NH_4Cl are added to the initial solution. The viscosity profile of this solution is shown below under Sample C. 20 grams of an ammonium lauryl sulfate solution and 3 grams of NH_4Cl are added to the initial solution. The viscosity profile of this

solution is shown below under Sample D. 20 grams of an ammonium lauryl sulfate solution and 4 grams of NH_4Cl are added to the initial solution. The viscosity profile of this solution is shown below under Sample E.

Viscosity Profile of Example 3 Material (cps)

LVT RPM	Sample A	Sample B	Sample C	Sample D	Sample E
.6	50	200	1250	2100	—
1.5	64	152	1100	1920	8000
3.0	60	138	920	1720	8000
6.0	52	125	875	1700	7600
12	52	122.5	850	1500	6300
30	50	127	890	1440	5100
60	48.5	120	890	1290	4500

COMPARATIVE EXAMPLE 4

The testing of Examples 3 and 4 is repeated except that the cationic polymer is replaced by Quatrisoft Polymer LM-200, a commercially available cationic polymer manufactured by Amechol Corp. The polymer will initially associate with small amounts (0.25%) of the ammonium lauryl sulfate solution to provide enhanced viscosities, but once the amounts of the ammonium lauryl sulfate solution are increased (0.50% or above), the viscosity decreases. Further, once any amount of salt such as NH_4Cl is added, the LM-200 "salts out" such that the polymer floats to the top of the solution.

COMPARATIVE EXAMPLE 5

The testing of Examples 3 and 4 is repeated except that the cationic polymer is replaced by Jaguar 8012, a commercially available non-ionic polymer that does not have a long chain alkyl group. For all additions of ammonium lauryl sulfate and NH_4Cl added, the viscosities are lower than those obtained when producing solutions of the Jaguar 8012 alone.

EXAMPLE 6

1000 parts of oxidized guar gum are slurried in 1000 parts of isopropanol. 120 parts of NaOH are added and the mixture is stirred for about 20–30 minutes. 1050 parts of QUAB-342, 3-chloro-2-hydroxypropyl dimethyl dodecyl ammonium chloride, are added and the etherification reaction is conducted at 65° C. over a period of 1.5 to 6 hours. After cooling, the reaction product is washed with acetone to remove the excess reagent and cationic byproducts. The degree of substitution for this material is about 0.055. A 2% aqueous solution of this compound in water is prepared by adding 2 parts of this composition to 98 parts of water. The viscosity determined by a Brookfield RTV Viscometer at 20 rpm is 1550 cps.

EXAMPLE 7

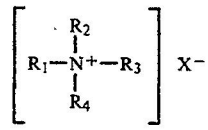
1000 parts of oxidized guar gum are slurried in 1000 parts of isopropanol. 120 parts of NaOH are added and the mixture is stirred for about 20–30 minutes. 1250 parts of QUAB-360, 3-chloro-2-hydroxypropyl N,N,N-cocoalkyldimethylammonium chloride, are added and the etherification reaction is conducted at 65° C. over a period of 1.5 to 6 hours. After cooling, the reaction product is washed with acetone to remove the excess reagent and cationic byproducts. The degree of substitution for this material is about 0.031.

A 2% aqueous solution of this compound in water is prepared by adding 2 parts of this composition to 98 parts of water. The viscosity determined by a Brookfield RTV Viscometer at 20 rpm is 1875 cps.

Having described the invention in detail and by reference to the preferred embodiments thereof, it will be apparent that modifications and variations are possible without departing from the scope of the appended claims.

What is claimed is:

1. Water soluble quaternary ammonium ethers of polysaccharides or polyols wherein the quaternary ammonium ether substituents correspond to the formula



(I)

wherein R_1 is a monohydroxylated or polyhydroxylated alkyl group containing between one and about six carbon atoms; R_2 and R_3 are independently, alkyl groups containing between one and about six carbon atoms; R_4 is an alkyl group containing between about six and about 24 carbon atoms; and X is a halide, wherein the degree of substitution of said ethers ranges from about 0.001 to about 0.5.

2. The composition according to claim **1** wherein said polysaccharide or polyol is selected from the group consisting of polygalactomannans, starches, celluloses, xanthan gum and alginates.

3. The composition according to claim **2** wherein said polysaccharide or polyol comprises a polygalactomannan.

4. The composition according to claim **3** wherein said polygalactomannan comprises a derivatized or underivatized guar gum or locust bean gum.

5. The composition according to claim **4** wherein the degree of substitution of said quaternary ammonium groups is between about 0.01 and about 0.50.

6. The composition according to claim **5** wherein R_1 comprises a 2-hydroxypropyl group.

7. The composition according to claim **6** wherein R_2 and R_3 comprise methyl groups.

8. The composition according to claim **7** wherein R_4 comprises an alkyl group having between about 10 and about 21 carbon atoms.

9. The composition according to claim **8** wherein R_4 is selected from the group consisting of dodecyl, cocoalkyl and octadecyl groups.

10. The composition according to claim **9** wherein the degree of substitution of said quaternary ammonium groups is between about 0.02 and about 0.50.

11. The composition according to claim **1** wherein X comprises chloride.

12. The composition according to claim **5** which is cross-linked.

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(54) Method and composition for thickening or stabilizing aqueous media with polyamphoteric polysaccharides.

(57) A method for thickening, stabilizing, controlling mobility or enhancing water retention in electrolyte-containing or non-electrolyte-containing aqueous media employs neutrally-charged polyamphoteric graft copolymers of polysaccharides with zwitterionic monomers or cationic/anionic monomer pairs. These polyampholytes are characterized by their unique resistance to loss of intrinsic viscosity in the presence of electrolytes. These polyampholytes may be prepared by an inverse emulsion method of graft copolymerization. Once such electrolyte-tolerant polyampholyte is a novel composition prepared by graft copolymerization of guar gum.

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graft copolymers also offer the advantage over those disclosed in the references of economy, ease of preparation and ease of handling in the form disclosed herein.

The preparation of an electrolyte-tolerant polyampholyte from starch or hydroxyethyl cellulose by graft copolymerization with a water soluble cationic/anionic monomer pair and a neutrally-charged water soluble monomer has been reported. Salamone, J.C., et al., "Aqueous Salt Absorption by Ampholytic Polysaccharides," Polymer, 26: 1234-1238 (1985). These polysaccharide polyampholytes exhibited increasing viscosity with the addition of increasing amounts of sodium chloride in solution. They also exhibited increasing water absorbancy, particularly in the presence of electrolytes, when the percent incorporation of the ionic monomers onto the polyampholyte was increased.

It was noted by Salamone, et al., that use of cobalt-60 radiation to initiate graft copolymerization leads to tough, rubber-like copolymers, presumably caused by excessive cross-linking. Copolymers prepared by cobalt-60 initiation were not water soluble. Successful results were only reported using cerium (IV) initiation. (See also, Kao-Ching Lin, Hydrophilic, Ampholytic Graft Copolymers, M.S. Thesis, University of Lowell, September, 1983.) However, cerium (IV) initiation has the disadvantage that highly toxic material must be handled. Thus, there is a need for a method of graft polymerization of polysaccharides which may be carried out using another type of initiation.

Other disadvantages of known methods for preparing polysaccharide polyions, such as difficulty concentrating the product, isolating the polyampholyte from the reaction medium for various applications, or handling unstable reagents, have been addressed in the literature. For example, U.S. Pat. No. 4,017,460, issued April 21, 1977, to Tessler discloses a method for preparing amphoteric starch derivatives where the zwitterionic reagent is synthesized in situ from a secondary amine and an acid or ester of an acid. This method ameliorates problems associated with preparation and handling of unstable reagents. However, this reference concerns starch derivatives and does not address the problems associated with known methods for graft copolymerization of the polyampholytes of this invention.

Thus, there is a need for economical, commercially feasible, high molecular weight polyampholytes for thickening and stabilizing electrolyte-containing aqueous media.

SUMMARY OF THE INVENTION

This invention provides a method for thickening or stabilizing aqueous media and electrolyte-containing aqueous media comprising the use of water-dispersible, neutrally-charged, polyamphoteric graft copolymers of polysaccharides with zwitterionic monomers or cationic/anionic monomer pairs which are resistant to loss of intrinsic viscosity in the presence of electrolytes. This method finds use in papermaking, oil drilling, oil recovery and other processes where high molecular weight polyionic compounds are used to thicken, control mobility, retain water, or stabilize electrolyte-containing aqueous media.

This invention also provides a method of preparing polysaccharide derived polyampholytes, which method is a modification of the inverse emulsion method taught in U.S. Pat. No. 4,690,996, issued September 1, 1987, to Shih, et al. The inverse emulsion method for providing water soluble graft copolymers comprises (a) providing an inverse emulsion of an aqueous discontinuous phase comprising the polysaccharide and a zwitterionic monomer or a cationic/anionic monomer pair and, optionally, comonomers, with a hydrophobic continuous phase containing a solvent and a surfactant or surfactants; and (b) grafting the monomer or monomers onto the polysaccharide by free radical polymerization in the presence of an initiator. Suitable ionic monomers include zwitterionic monomers, cationic/anionic monomer pairs or any polymerizable water soluble ionic monomer or monomers capable of yielding the equimolar ratio of anionic to cationic moieties which is essential to the electrolyte tolerant properties useful herein.

Additionally, this invention provides neutrally-charged, water-dispersible polyampholytes prepared by graft copolymerization of guar gum with ionic monomer(s) which comprise zwitterionic monomer(s) or cationic/anionic monomer pairs, wherein the polyampholytes are characterized by resistance to loss of intrinsic viscosity in the presence of electrolytes.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method herein for thickening and stabilizing aqueous media and electrolyte-containing aqueous media comprises the addition to the media of polyampholytes which are graft copolymers of a polysaccha-

ride with a zwitterionic monomer or a cationic/anionic monomer pair. The amount of polyampholyte used may be readily adjusted by the practitioner to suit a particular application. In a preferred embodiment for an oil drilling mud application, 2-3 pounds per barrel (ppb) of the polyampholyte are used to thicken the drilling mud.

The polyampholyte herein may be prepared by any method known in the art for graft copolymerization of polysaccharides. For example, free radical initiation with chemicals, high energy radiation or heat may be employed in solution, suspension, emulsion or other medium useful for graft copolymerization. In a preferred embodiment, the polyampholyte is prepared in an emulsion by free radical synthesis with thermal initiation. Together with the zwitterion or cationic/anionic monomer pair, a neutrally-charged reactive comonomer is graft copolymerized onto the polysaccharide to improve the reaction efficiency. The polyampholyte thickening and stabilizing agents herein must possess a substantially equal number of positive and negative charges following copolymerization.

Polysaccharides are defined herein to include polysaccharide-containing polymers obtained from plant, animal and microbial sources, including those which are presently known and those which may become known in the future. Examples of polysaccharides are starch, cellulose, gums and derivatives of each.

Starches, including those derived from corn, potato, wheat, rice, sago, tapioca, waxy maize, or sorghum and amylose, as well as the conversion products and derivatives thereof, are the preferred substrates due to their cost and availability. For certain end uses, derivatized starches, such as esters and ethers, have been found effective. In particular, starches derivatized with allyl glycidyl ether have shown optimum properties in the graft copolymerization method disclosed herein.

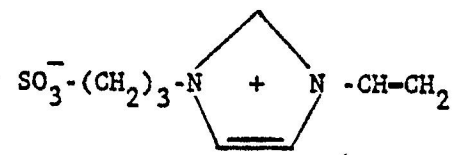
The polysaccharide may be used in any form so long as that form renders the polymer molecules available for graft copolymerization. For example, in a preferred embodiment an acid-converted starch derivative is gelatinized by cooking in water to yield an aqueous starch dispersion. In such a dispersion, the starch molecules are more readily accessible for graft copolymerization than are the starch molecules of an aqueous starch granule slurry.

The amount of polysaccharide may vary from 5 to 95%, preferably from 20 to 50% by weight of the final graft copolymer.

Suitable monomers for preparing the thickening and stabilizing agents herein include any water-soluble, unsaturated compounds that are capable of free radical polymerization, which are selected to yield an equal number of positive and negative charges on the graft copolymer, as evidenced by its neutral charge.

Water soluble is defined herein to mean monomers which have a minimum solubility of 5% by weight in water at 25° C. Such monomers include acrylic and methacrylic acid; acrylamide, methacrylamide, acrylonitrile; N,N-dialkylaminoalkyl acrylates and methacrylates (wherein the alkyl group contains 1 to 4 carbon atoms); ethylenically unsaturated quaternary ammonium salts such as N,N,N-trimethylaminoethyl methacrylate methylsulfate or halide, 2-hydroxy-3-methacryloxypropyltrimethyl-ammonium methyl sulfate or halide, vinylbenzyltrialkylammonium methylsulfate or halide; sodium or ammonium styrenesulfonate; vinyl pyrrolidone; hydroxyl alkyl acrylates and methacrylates; sodium 2-acrylamide-2-methylpropane sulfonate, etc. Various other water-soluble monomers suitable for graft polymerization with polysaccharides are known to those skilled in the art.

In a preferred embodiment, a zwitterionic monomer, such as 1-vinyl-3-(3-sulphopropyl)imidazolium inner salt, or 4-vinyl-(1-sulphopropyl) pyridinium inner salt is used. The formula of 1-vinyl-3(3-sulphopropyl) imidazolium inner salt, which is also known as 1-vinyl-imidazolium sulfobetaine (VISB), is:

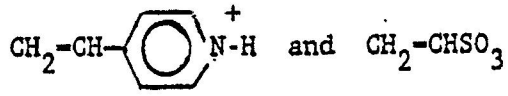


(VISB)

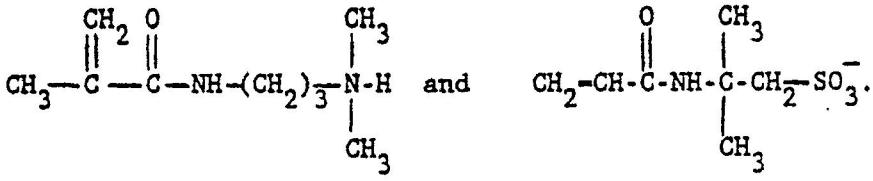
If a cationic/anionic monomer pair is used, the cationic monomer may be selected from a group including: methacrylamidopropyltrimethylammonium chloride, dimethyldiallylammonium chloride, diethyldiallylammonium chloride, 2-methacryloxyethyltrimethylammonium chloride, trimethylmethacryloxyethylammonium methosulfate, 2-acrylamido-2-methylpropyltrimethylammonium chloride, vinylbenzyltrimethylammonium chloride, and the like.

The anionic monomer may be selected from a group including: 2-acrylamido-2-methylpropanesulfonic acid, sodium styrenesulfonate, (meth)acrylic acid, methacryloxyethylsulfonic acid, and the like.

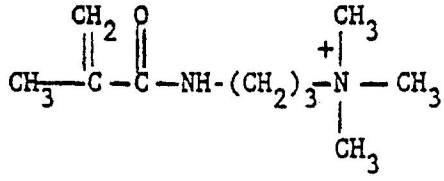
Suitable cationic/anionic monomer pairs include 4-vinylpyridinium ion/vinyl sulfonate ion, characterized by the structures:

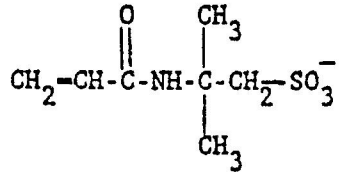


and 3-methacrylamidopropyldimethylammonium ion/2-acrylamido-2-methylpropanesulfonate ion, characterized by the structures:



In a preferred embodiment, the cationic/anionic monomer pair consists of 3-methacrylamidopropyltrimethylammonium ion/2-acrylamido-2-methylpropanesulfonate ion (TMAPMA-AMPS). The formula of the TMAPMA-AMPS pair is:





If a reactive nonionic comonomer is to be used, suitable comonomers include any nonionic water-soluble monomer, such as: (N,N-dimethyl) acrylamide, hydroxyethyl (meth)acrylate, alkyl substituted acrylamides, (meth)acrylates, N-vinyllactones (e.g., N-vinyl-2-pyrrolidone), and the like. In a preferred embodiment, acrylamide is used as the nonionic reactive monomer.

The monomers listed herein may be used in any form desired for a particular application. Thus, where a monomer is listed herein in its acid form, the salt form is meant to be included, and vice versa.

The amount of ionic monomer may vary from 95 to 5%, preferably from 80 to 50%, by weight of the final graft copolymer. The amount of the reactive nonionic comonomer may vary from 0-50% by weight of the total monomer in the final graft copolymer. Amounts used depend upon the particular monomers selected and intended end-use of the graft copolymer.

In a preferred embodiment, VISB and acrylamide are grafted onto an allyl glycidyl ether derivative of a waxy maize starch that has been acid-converted to 85 water fluidity (WF) and gelatinized prior to polymerization with VISB. In a second preferred embodiment, a cationic/anionic monomer pair, TMAPMA-AMPS, and acrylamide are grafted onto the same starch derivative following conversion and gelatinization. The composition, by weight, of the final graft copolymer is approximately 55 to 60% starch and 45 to 40% monomer, of which the ionic to nonionic monomer ratio, by weight, is 2 to 1.

These polyampholytes which are prepared from polysaccharides that have been graft copolymerized with suitable ionic and non-ionic monomers may be used as a low cost alternative in any industrial application wherein synthetic polyampholyte stabilizers, thickeners or water loss control agents, such as those discussed herein, are advantageously employed. For example, the polysaccharide-derived thickeners and stabilizers herein may find use in paper making, oil drilling or oil flood recovery.

The preferred method of graft copolymerization of these polysaccharides is by the inverse emulsion method disclosed herein. The inverse emulsion method of this invention comprises two steps wherein a

water dispersible polyampholyte that is characterized by resistance to loss of viscosity in the presence of electrolytes is prepared from a polysaccharide, a zwitterionic monomer or monomer pair, and, optionally, a neutral reactive monomer. In the first step, the method provides for emulsification of the polysaccharide and a zwitterionic monomer or a cationic/anionic monomer pair, and, optionally, a neutral comonomer, with an inert hydrophobic solvent and an oil soluble surfactant, or surfactants. In the second step, the method provides for graft polymerization of the monomer or monomers onto the natural polymer by free radical polymerization in the presence of a thermal initiator and heat.

In a preferred embodiment, the aqueous discontinuous phase contains amounts of polysaccharide ranging from 5 to 95%, preferably from 20 to 50%, by weight of the final graft copolymer. The aqueous phase also contains amounts of monomer ranging from 95 to 5%, preferably from 80 to 50%, by weight of the final graft copolymer. The aqueous phase also contains amounts of nonionic comonomer ranging from 0-50% by weight of the total monomer present.

The continuous phase of the emulsion contains a hydrophobic solvent and an oil-soluble surfactant, or surfactants.

Solvents suitable for the practice of this invention are selected from a large group of organic liquids which include liquid hydrocarbons and substituted liquid hydrocarbons. The preferred group of organic liquids are hydrocarbon liquids, most preferably aliphatic hydrocarbon liquids, which include blends of aromatic and aliphatic hydrocarbon compounds which contain from 4 to 8 carbon atoms. Thus, such organic hydrocarbon liquids as benzene, xylene, toluene, mineral oils, kerosenes, naphthas, and in certain instances, petroleum oils may be used.

Any conventional water-in-oil surfactant can be used in forming the emulsion. The surfactant may be cationic, anionic or nonionic in nature, so long as it does not react with the polymer to form a nonequimolar charge ratio on the graft copolymer. Particularly suitable surfactants are the oil soluble polyhydroxyethylated nonionic surfactants, for example, hydroxyethylated nonyl phenols, hydroxyethylated long-chain mono-carboxylic acids and fatty acids, fatty acid esters of sorbitol and hydroxyethylated fatty acid esters of sorbitol. The surfactant is present in an amount of 1 to 30% by weight, preferably 2 to 15% by weight of the total emulsion.

Free radical yielding initiators useful herein in polymerization of ethylenically unsaturated monomers, include but are not limited to initiators such as benzoyl peroxide, lauroyl peroxide, potassium persulfate; and redox couples such as tertiary butyl hydroperoxide and sodium metabisulfite; and the like, advantageously in amounts ranging between 0.002 and 0.2% by weight of the oil or monomer phase, depending upon the solubility of the initiator. Other free radial initiators may also be used herein.

Elevated reaction temperatures, advantageously between 40° and 70° C., are used with free radical yielding initiators. Within such a temperature range, conversion is substantially complete in from one-half to several days, depending upon monomer and reaction variables.

The reaction is generally carried out at atmospheric or substantially atmospheric pressure. However, super-atmospheric pressure is advantageously used when volatile ingredients are involved.

In practice, the water-in-oil emulsifying agent is dissolved in the oil phase, while the free radical initiator is dissolved in the oil or monomer phase, depending upon whether an oil or water-soluble initiator is used. The natural polymer and monomer or comoners, or an aqueous dispersion prepared by slurring the natural polymer in water with the water soluble monomer or comonomers is then added to the oil phase with agitation until the water phase is emulsified in the oil phase, and the reaction is carried out as indicated above. The order of addition of reaction media ingredients is not important. The reaction is continued with agitation until conversion is substantially complete. A polymeric latex emulsion is thereby obtained. The polymer is separated from the reaction medium advantageously by adding an organic solvent and filtering, and is then washed and dried. Alternatively, the latex reaction product can be used as such.

The resulting polyampholyte can be used as an additive, particularly in paper making, oil flood recovery and oil drilling, where the viscosity or water retention capacity of an electrolyte-containing brine must be enhanced. Polyampholytes prepared from natural polymers by the method of this invention can be used as a low cost alternative in any industrial process wherein a synthetic polyampholyte can be used as a stabilizer, water loss control agent or thickener.

A further advantage to the polyampholytes produced herein is the ability of these emulsions to be inverted in the presence of water so that the polymer rapidly goes into solution. As such, these polymer containing emulsions release the polymer in the water in a very short period of time when compared to the amount of time required to dissolve a comparable solid graft copolymer. This rapid inversion renders the emulsions especially suited for water retention and thickening applications.

This advantageous rapid inversion method of introducing chemical compositions into aqueous solutions or dispersions was taught in U.S. Pat. No. Re. 28,576, issued October 21, 1975, to Anderson, et al.

The guar gum graft copolymer herein may be prepared by any method known in the art for grafting monomers onto natural polymers, such as free radical synthesis with chemical initiators, high energy radiation initiation or thermal initiation. The copolymerization may occur in solution, suspension, emulsion or in any medium which is known in the art, or which may become known in the art for graft copolymerization. The guar gum and the monomer or comonomers may be used in any proportion suitable for synthesis of a graft copolymer which is characterized by resistance to loss of intrinsic viscosity in the presence of electrolytes and dispersibility in water.

In a preferred embodiment, wherein the inverse emulsion method of this invention is used for the graft copolymerization of guar gum, the amount of guar gum may range from 5 to 95%, preferably from 20-50%, by weight of the final graft copolymer. Accordingly, the amount of the monomer or comonomer may range from 95 to 5%, preferably from 80 to 50%, by weight of the final graft copolymer.

The amount of nonionic reactive comonomer may range from 0 to 50% by weight of the total monomer in the final graft copolymer. Amounts used depend upon the particular monomers used and intended end-use of the graft copolymer.

Guar gum, or any neutrally-charged, water-dispersible derivative of guar gum, such as a hydroxypropyl ether of guar gum, may be used as the starting polymer for grafting.

In a preferred embodiment, a hydroxypropyl ether of hydrolyzed guar gum is used. This derivative is much less viscous and therefore, more readily emulsified than guar gum. If underivatized guar gum is preferred for a particular end-use, the quantity of surfactant and organic solvent is increased to assist in the formation of an emulsion.

Suitable monomers are described in the discussion of the thickening and stabilizing agents of this invention, supra.

It will, of course, be recognized by those skilled in the art that the specific end use application will dictate the optimal composition of the graft copolymer. Thus, for example, while some compositions may provide superior thickening properties, other compositions, such as are readily determined by the practitioner, should be used in formulating graft copolymers to be used as retention aids.

In the following examples, which are merely illustrative of the various embodiments of the present invention, all parts are by weight and all temperatures in degrees Celsius unless otherwise indicated.

Example 1

This example describes the solution preparation of a starch graft copolymer with VISB which is characterized by salt insensitivity similar to that of a VISB homopolymer or a VISB and acrylamide copolymer.

The VISB monomer was prepared according to the procedure disclosed by J.C. Salamone, et al, in Polymer 18; 1058 (1977). A VISB homopolymer and a VISB and acrylamide copolymer were prepared as controls for comparison with the polysaccharide graft copolymers of this invention.

The homopolymerization reaction of the VISB monomer was carried out under nitrogen at 60° C for 24 hours. The behavior of this homopolymer in salt solutions was consistent with results reported by J.C. Salamone, et al., in A.C.S. Symp. Ser, 187:337 (1980) and in Polymer, 19:1157 (1978).

The copolymerization reaction of the VISB with acrylamide was carried out in solution. Acrylamide (5g) and VISB (10g) were dissolved in degassed water (40g) in a 250 ml four-neck round-bottom flask, equipped with a mechanical stirrer, condenser, addition funnel and nitrogen gas inlet. The temperature of the mixture was raised to 65° C. An initiator, 4,4'-azo-bis(4-cyanovaleric acid), (60 mg in 3 ml water) was added in three portions, each one hour apart. The polymerization then continued for 3 hours. The polymerization was quenched with 5 drops of monomethyl ether hydroquinone solution (1% ethanol solution).

A starch graft copolymer with VISB was prepared using a derivatized starch. An acid-hydrolyzed waxy maize starch was treated with 1% allyl glycidyl ether to form the ether derivative. A total of 100 parts of acid-hydrolyzed waxy starch (85 WF) was slurried in an aqueous solution of 1.5 parts of sodium hydroxide and 25 parts sodium sulfate in 150 parts water, then 1.0 part allyl glycidyl ether was added to the starch slurry. The mixture was agitated at 40° C for 16 hours and the pH was lowered to 5.5 by adding 9.3% aqueous hydrochloric acid. The starch derivative was recovered by filtration, washed three times with water and air dried.

A starch dispersion was prepared by cooking 18.75 g of this derivatized starch in 50 g water for 20 minutes. VISB (7.5 g) and 60 mg of 4,4'-azo-bis(4-cyanovaleric acid), a thermal initiator, were added to the cooked starch dispersion. The reaction was heated to 65° C, stirred for 24 hours and terminated by the

was recorded. The drainage of a blank which contained no drainage aid was also determined. The results are shown in Table VIII.

A 28 percent improvement (calculated as percentage reduction in drain times) in drainage was obtained from the starch graft copolymer compared to the blank sample. The commercially used amphoteric starch derivative showed almost no improvement in drainage from the high conductivity stock compared to the blank sample.

Thus, the polysaccharide graft copolymers of this invention are useful as thickeners and stabilizers in industrial applications requiring performance in the presence of electrolytes.

Table VIII

High Conductivity Paper Pulp Stock Drainage	
Sample	Time in seconds
Blank	52
Polycationic Starch Derivative (0.26% Nitrogen; 0.1% Phosphorus)	50
Starch Graft Copolymer*	37

* Allyl glycidyl ether (1% treatment) derivative of 85 WF waxy maize starch copolymerized with VISB and acrylamide.

Claims

1. A method for thickening, stabilizing, controlling mobility or enhancing water retention in electrolyte-containing or non-electrolyte-containing aqueous media, comprising the addition to the aqueous media of a water-dispersible neutrally-charged polyamphoteric graft copolymer of a polysaccharide with a zwitterionic monomer or a cationic/anionic monomer pair, wherein the polyamphoteric graft copolymer is characterized by resistance to loss of intrinsic viscosity in the presence of electrolytes.

2. The method of Claim 1, wherein the zwitterionic monomer is 1-vinyl-3-(3-sulphopropyl)imidazolium inner salt, or wherein the cationic/anionic monomer pair is 3-methacrylamidopropyltrimethylammonium ion/2-acrylamido-2-methyl-propanesulfonate ion.

3. The method of Claim 1, wherein the polysaccharide is selected from the group comprising starches, celluloses, gums and their derivatives.

4. The method of Claim 1, wherein the electrolyte-containing aqueous media comprises a stock used in the manufacture of paper.

5. The method of Claim 1, wherein the electrolyte-containing aqueous media comprises a drilling mud used in the recovery of oil.

6. A method for preparing water-dispersible polyamphoteric graft copolymers which are resistant to loss of intrinsic viscosity in the presence of electrolytes, comprising the steps of:

(a) providing an inverse emulsion of an aqueous discontinuous phase, comprising a polysaccharide and a zwitterionic monomer or a cationic/anionic monomer pair, with a hydrophobic continuous phase containing a solvent and a surfactant or surfactants; and

(b) grafting the monomer or monomers onto the polysaccharide by free radical polymerization in the presence of an initiator.

7. The method of Claim 6, wherein the polyamphoteric graft copolymers contain an equimolar ratio of cationic and anionic substituents, and wherein a mixture of the zwitterionic monomer or the cationic/anionic monomer pair and at least one reactive non-ionic comonomer(s) is grafted onto the polysaccharide to yield a neutrally-charged polyamphoteric graft copolymer which contains non-ionic comonomer(s), comprising up to 50% by weight of the total monomer in the final graft copolymer.

8. Neutrally charged, water-dispersible polyampholytes prepared by graft copolymerization of guar gum with ionic monomer(s) which comprise a zwitterionic monomer or a cationic/anionic monomer pair, wherein the polyampholytes are characterized by resistance to loss of intrinsic viscosity in the presence of electrolytes.

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(54) Anionic sulfonated thickening compositions.

(57) A novel composition suitable for use as a thickener comprising an anionic hydroxy containing polymer which is partially or completely substituted by one or more sulfonate groups derived from an ethylenically unsaturated monomer is provided. The composition is capable of producing enhanced viscosities either when used alone, or when combined with a cationic polymer and distributed in a solvent. The composition is suitable for use in foods, explosives, oil field chemicals, textile fibers, paper produces, personal care products, agricultural chemicals and cosmetics.

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mers, pp. 446-465, 1991, discusses the use of certain polymer combinations which provide enhanced viscosities as compared to the viscosities of the individual polymers. Combinations mentioned include poly(styrene sulfonate) and either xanthan gum or hydroxyethyl cellulose, poly(vinyl sulfonate) and xanthan gum, a quaternary-ammonium-salt modified guar and either hydroxypropyl guar or hydroxyethyl cellulose, and a sulfonated guar (D.S. of 0.10; chemical name not mentioned) and either hydroxyethyl cellulose or carboxymethylhydroxyethyl cellulose. These combinations are suggested for use in oil recovery.

Despite the above, there still is a need for compositions which demonstrate enhanced viscosity behavior.

Brief Summary of the Invention

In accordance with the present invention, a novel anionic viscosity increasing composition is provided. The composition provides a synergistic increase in viscosity when combined with one or more cationic viscosity increasing compositions. The novel composition comprises a hydroxy containing polymer which is partially or completely substituted by one or more sulfonate groups derived from an ethylenically unsaturated monomer containing one or more sulfonate groups.

In particularly preferred embodiments, the polymers comprise anionic polygalactomannans derived from guar gum or locust bean gum, and preferably guar gum. Further, the preferred degree of substitution of the sulfonate groups onto the polymer is between about 0.01 and about 1.0. In addition the sulfonate groups are preferably derived from monomers of 2-acrylamido-2-methylpropane sulfonic acid and 1-allyloxy-2-hydroxypropyl sulfonic acid and salts thereof.

The compositions are particularly effective as thickening agents.

They may be used for a number of functional applications such as in foods, explosives, oil field chemicals, agricultural applications, cosmetics and the like.

Another embodiment of the present invention comprises a process for producing a viscous liquid or a gel. The process comprises the step of adding to a solvent, preferably water, 0.1 parts to about 2.0 parts per 100 parts viscous liquid or gel of a hydroxy containing polymer which is partially or completely substituted with one or more sulfonate groups derived from an ethylenically unsaturated monomer containing one or more sulfonate groups.

A third embodiment of the present invention comprises a food, explosive, oil field chemical, agricultural chemical, textile fiber or cosmetic including an amount of a hydroxy containing polymer which is partially or completely substituted with one or more sulfonate groups derived from an ethylenically unsaturated monomer containing one or more sulfonate groups.

Accordingly, it is an object of the present invention to provide a novel composition which can increase the viscosity of a liquid and, when combined with other viscosity modifiers, demonstrates a superior viscosity profile as compared to the materials individually.

It is another object of the present invention to provide a process for producing a viscous liquid or gel using a novel composition.

A further object of the present invention to provide a food, explosive, oil field chemical, agricultural chemical, textile fiber or cosmetic which includes a novel thickener composition.

These, and other objects, will readily be apparent to those skilled in the art as reference is made to the detailed description of the preferred embodiment.

Detailed Description of the Preferred Embodiment

In describing the preferred embodiment, certain terminology will be utilized for the sake of clarity. Such terminology is intended to encompass the recited embodiment, as well as all technical equivalents which operate in a similar manner for a similar purpose to achieve a similar result.

The present invention comprises an anionic polymer containing hydroxy groups, preferably polygalactomannans having a degree of substitution of about 0.01 to about 3.00, wherein said anionic polymer contains one or more sulfonate groups derived from an ethylenically unsaturated monomer containing sulfonate groups.

A number of materials can be used as the starting polymer. Particularly preferred are polygalactomannans. Polygalactomannans are polysaccharides composed principally of galactose and mannose units and are usually found in the endosperm of leguminous seeds, such as guar, locust bean, honey locust, flame tree, and the like. Guar flour, for example, is composed mostly of a galactomannan which is essentially a straight chain mannan with single membered galactose branches. The mannose units are linked in a 1-4-β-glycosidic linkage and the galactose branching takes place by means of a 1-6 linkage on alternate mannose units. The ratio of galactose to mannose in the guar polymer is, therefore, one to two. Guar gum has a molecular weight of about 1.5 million daltons.

Locust bean gum is also a polygalactomannan gum of similar molecular structure in which the ratio of galactose to mannose is one to four. Guar and locust bean gum are the preferred sources of the polygalactomannans, principally because of the commercial availability thereof.

In use the polygalactomannan may be either in its natural state (i.e., pure guar gum or locust bean gum) or may be derivatized.

Derivatized polygalactomannans include one or more non-ionic groups. Examples of such polygalactomannans include hydroxypropyl guar, hydroxyethyl guar, and the like. Such derivatized polygalactomannans are sold by Rhône-Poulenc Inc. under the trade names Jaguar 8012, Jaguar 8060, Jaguar 8000, Jaguar HP-20 and Jaguar HP-23.

Alternative materials which may be selected as the starting material include starches, celluloses, xanthan gum and polyols. Examples of starches include both natural and modified starches, such as dextrinated, hydrolyzed, oxidized, cross-linked, alkylated, hydroxyalkylated, acetylated, or fractionated (e.g., amylose and amylopectin). The starch may be of any origin, for example, corn starch, wheat starch, potato starch, tapioca starch, sago starch, rice starch, waxy corn starch or high-amylose corn starch.

Examples of celluloses include hydroxyethyl cellulose, hydroxypropyl cellulose, and alkyl celluloses.

Examples of polyols include polyvinyl alcohol, polyethylene glycol and glycerol.

By the term "degree of substitution" as employed herein is meant the average substitution of cationic or anionic groups per anhydro sugar unit in the polysaccharides, and particularly, polygalactomannan gums. In guar gum, the basic unit of the polymer consists of two mannose units with a glycosidic linkage and a galactose unit attached to a hydroxyl group of one of the mannose units. On the average, each of the anhydro sugar units contains three available hydroxyl sites. A degree of substitution of three would mean that all of the available hydroxyl sites have been esterified with formate ester groups.

Particularly preferred embodiments of the present invention comprise anionic sulfated polygalactomannans having a degree of substitution of about 0.01 to about 1.0.

The anionic nature is obtained by utilizing a substituent having one or more sulfonate groups derived from ethlyenically unsaturated monomers containing one or more sulfonate groups. Examples of such monomers include the sodium salt of 2-acrylamido-2-methylpropane sulfonic acid and the sodium salt of 1-allyloxy-2-hydroxypropylsulfonic acid. The former monomer is derived from 2-acrylamido-2-methylpropane sulfonic acid, which is commercially available from Lubrizol and sold under the trade name LZ 2401 and the later monomer is commercially available from Rhône-Poulenc Inc. and sold under the trade name Sipomer Cops I.

The formation of ether linkages between the sulfonated substituent and the polymer occurs by directly adding the substituent to the polygalactomannan, preferably in the presence of a water-miscible solvent such as toluene. The reaction temperature generally is between about 10°C and about 100°C. Reactivity of the polymer with the substituent may be aided by utilizing a small amount of an initiator. Examples of suitable initiators include ammonium persulfate. pH buffers, such as disodium phosphate, may also be optimally added.

Once dissolved in solution, and in particular, water, the sulfonated polymer may be crosslinked to provide a strong, thixotropic aqueous solution. Crosslinking of the solution is accomplished by adding aluminum acetate to the solution and adjusting the pH until the solution dramatically increases in viscosity. When using the ethylenically unsaturated monomers containing sulfonate groups in accordance with the present invention, the pH is adjusted to above 8. This is in contrast to other anionic polygalactomannans such as carboxymethyl guar and carboxymethylhydroxypropyl guar, which tend to crosslink under acidic conditions (pH of 5 to 6).

In use, the inventive compositions can effectively function as thickeners when added to a solvent, typically water. This typically comprises adding between about 0.1 and about 2.0 parts of the sulfonated anionic polymer per 100 parts of viscous liquid or gel. While the viscosity profile obtained by using the anionic sulfonated polymers alone is adequate, results are synergistically enhanced when using the anionic sulfonated polymers in combination with 0.1 to about 2.0 parts cationic polymers, particularly cationic polygalactomannans, to produce an amphoteric blend composition.

Such amphoteric polygalactomannan blend compositions are typically produced by combining solutions of both cationic and anionic polymers in respective amounts so that the positive and negative charges are equally balanced. The respective amounts of anionic and cationic solutions are added together based primarily upon the degree of substitution of each. For example, larger amounts of a low degree of substitution cationic polymer solution may be added to smaller amounts of a high degree of substitution anionic solution.

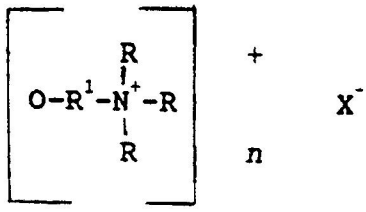
While in the preferred embodiment, the amounts of anionic and cationic solutions are added to produce a charge neutral solution, the amounts of each may be varied to yield solutions which have an overall positive or negative charge. Although not as enhanced as when producing a charge neutral solution, some synergistic effect is achieved by unbalanced charged additions.

The cationic polygalactomannan used to form the amphoteric composition has a degree of substitution of between about 0.01 and about 3.0. Particularly preferred are cationic polygalactomannans having a degree

of substitution of between about 0.01 and about 1.0.

Illustrative cationic groups suitable for the practice of the present invention include quaternary ammonium groups. Typical of quaternary ammonium groups are tetramethylammonium chloride and bromide, benzyltrimethylammonium chloride and bromide, tetraethylammonium chloride and bromide, tetrabutylammonium chloride and bromide, methylpyridinium chloride and bromide, benzylpyridinium chloride and bromide, trimethyl-p-chlorobenzylammonium chloride and bromide, and the like, wherein each of the said groups is derivatized in the form of a radical which is substituted in a hydrocolloid gelling agent by means of an alkylene or oxyalkylene linkage.

The polymeric structure of suitable polygalactomannans including cationic groups include vinyl polymers and copolymers, ion exchange resins, polysaccharides, and the like. Illustrative of this class of hydrocolloids are polygalactomannan gums containing quaternary ammonium ether substituents as described in U.S. Patent No. 4,031,307:



wherein R is an alkyl group containing between one and about six carbons atoms, R^1 is an alkylene group containing between one and about six carbon atoms, X is chlorine or bromine, and *n* is an integer which correlates with the degree of substitution of the quaternary ammonium ether substituents in a polygalactomannan gum cationic gelling agent. The said alkyl and alkylene group can contain other atoms such as oxygen, sulfur and halogen.

The cationic derivatives of guar gum or locust bean gum are prepared by contacting solid guar gum or locust bean gum with a haloalkyl-substituted quaternary ammonium compound and a stoichiometric excess of alkali metal hydroxide or ammonium hydroxide in a reaction medium comprising an aqueous solution of water-miscible solvent, at a temperature between about 10°C and about 100°C for a reaction period sufficient to achieve a degree of substitution by quaternary ammonium ether groups between about 0.01 and about 3.00.

The solid guar gum or other polygalactomannan which is etherified can be in the form of endosperm splits or in the form of finely divided powder which is derived from the endosperm splits. It is important that the polygalactomannan gum being etherified with quaternary ammonium groups remains as a solid phase in the reaction medium during the reaction period.

Further details on the synthesis of these polymers are provided in U.S. Patent No. 4,031,307. To the extent necessary, this patent is incorporated by reference.

Examples of commercially available polygalactomannans having one or more substituted cationic quaternary ammonium groups include Jaguar C-13, Jaguar C-13S, Jaguar C-14, Jaguar C-17 and Jaguar C-14S, all sold by Rhône-Poulenc Inc.

Other cationic polygalactomannans having a degree of substitution between about 0.01 and 3.00 include those which contain other cationic groups such as acid salts of primary, secondary, and tertiary amines, sulfonium groups or phosphonium groups.

Other cationic polymers that are not polygalactomannans and which may be combined with the inventive anionic polymers include cationic acrylic amides.

In preparing gels containing both the inventive anionic polymers and cationic polymers, the cationic polymer can be mixed with the inventive anionic polymer in the desired ratio in solid form and then added to water. The blend will disperse and hydrate in cold water with no need for heat or high shear agitation. Alternatively, and more preferably, separate aqueous solutions containing anionic polymers and cationic polymers can be mixed together. For easy handling and ready dispersibility, the anionic and cationic polymers should have a particle size of less then about 100 mesh. Other components, e.g., fillers, wetting agents, dispersants, bactericides, fungicides and the like can be mixed with the powdered blends of the invention if so desired.

The fact that interaction between different polymers can provide enhanced viscosities is known. See, for example, Borchardt, "Viscosity Behavior and Oil Recovery Properties", Chapter 29, Water Soluble Polymers, American Chemical Society, 1991. What is surprising about this invention is that by utilizing cationic polymers, preferably polygalactomannans in combination with the specific inventive sulfonated anionic polymers a dual advantage is achieved. The first advantage is the enhanced viscosity caused by the molecular interaction of the cationic polygalactomannan with the anionic polymer as compared to the viscosity obtained with a charge

neutral polygalactomannan. The second advantage is the ionic interaction that occurs when combining the inventive anionic sulfonated polymer with a cationic polygalactomannan. By utilizing these molecular and ionic forces, truly improved results are obtained as compared to those obtained when using homopolymer or blended nonionic polygalactomannans.

The inventors have also discovered that it is critical that the anionic polymer used be a sulfonated one which has groups derived from ethylenically unsaturated monomers containing sulfonate groups. Not all mixtures of anionic and cationic polymers yield blend compositions which are superior to the individual reactant compositions. For example, when blending either carboxymethyl guar or carboxymethylhydroxypropyl guar, both anionic polygalactomannans, with Jaguar C-14, a cationic polygalactomannan manufactured by Rhône-Poulenc Inc., a lower solution viscosity is obtained than the viscosity obtained by using the cationic or anionic polygalactomannans separately. It is hypothesized that this is because of shrinkage of guar molecules caused by the strong reaction between the cationic functional group with the anionic carboxymethyl group. This dramatically reduces the hydrophilic nature of the polygalactomannan starting materials. By stark comparison, when using the sulfonated mildly anionic polymers according to the present invention in combination with cationic polygalactomannans, a marked increase in viscosity occurs.

The novel compositions, including those obtained when blending with a cationic polygalactomannan, have a wide number of possible uses. Amongst them are as suspending agents for various solids, such as in oil field chemicals, for use in dyeing textile fibers, for use in foods, for use in cosmetics, for use with agricultural products, for use in explosives, for use in paper production, for use in personal care products and the like. Other uses will readily be appreciated by those skilled in the art.

A further feature of the inventive anionic sulfonated polymers is their insensitivity to salts such as KCl. This is particularly important when the compositions are used as thickeners in oil recovery procedures, as salt solutions such as KCl solutions are typically used in fracturing operations.

The invention is described in greater detail by the following non-limiting examples.

EXAMPLE 1

174.4 parts of a 50% NaOH solution are dissolved in 373.8 parts of deionized water to make a 16% solution. The solution is cooled to room temperature. 452 parts of 2-acrylamido-2-methylpropane sulfonic acid monomer (AMPS) are added to the solution at between about 25 and about 30°C. After the AMPS has fully dissolved, the solution is cooled to 20°C and the pH is adjusted to 9.1. The solvent is removed to yield sodium 2-acrylamido-2-methylpropane sulfonate monomer.

322 parts of guar gum are dispersed in 1200 parts of toluene in a nitrogen gas environment. A solution of 4 parts of ammonium persulfate and 3 parts of disodium phosphate in 50 parts water is added dropwise and the mixture is heated to about 60-65°C. 382 parts of sodium 2-acrylamido-2-methylpropane sulfonate monomer solution (50% aqueous, pH=10.5) are added and the mixture is heated to 80°C for 30 minutes and maintained at 70°C for 3 hours. The mixture is then washed with 70% methanol for three times and with 99% methanol for one time. The yield of this product is 351 parts. The moisture content is 10% and the degree of substitution is about 0.42.

1 part of this material is dispersed in 100 parts water at 25°C. The viscosity measured two hours after hydration by a Brookfield Viscometer (RVT at 20 rpm) is 4500 cps. The same experiment is repeated except the solvent selected is an aqueous 2% KCl solution. The measured viscosity is 4000 cps.

To crosslink this material, a .48% solution of the experimental composition in water is prepared. The viscosity measured by a Brookfield Viscometer is 410 cps. 1 ml of a 5% aluminum acetate solution is added to the mixture. The addition causes the pH to lower to 4.8 while the viscosity remains essentially the same (420 cps). NaOH is added to the solution and the viscosity does not show a great increase until the pH exceeds 8. At a pH of 8.03, the viscosity dramatically increases to 17000 cps. At a pH of 8.7, the viscosity is about 35000 cps. The viscosity remains high throughout the basic pH range (pH between 8 and 11). The same experiment is repeated in an aqueous 2% KCl solution. Similar behavior is noted, with a dramatic increase in viscosity once the pH is greater than 8. (For example, at pH 7, the viscosity is 390 cps; at 7.5 the viscosity is 1300; at 8.03 the viscosity is 19000; and at 8.7, the viscosity is 37500).

Example 2

322 parts of guar gum are suspended in 1300 parts of toluene in a nitrogen gas environment. A solution of 4 parts of ammonium persulfate and 3 parts of disodium phosphate in 50 parts water is added dropwise and the mixture is heated to about 60-65°C. 372 parts of a sodium 2-acrylamido-2-methylpropane sulfonate monomer solution (pH adjusted to 10.0) are added and the resulting mixture is heated and maintained at 68-

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

2020
Bogotá D.C., Septiembre 16 de 2005

Doctor
EMILIO FERRERO
Apoderado **AKZO NOBEL N.V.**

ASUNTO	Radicación	00-25853
	Trámite	002
	Evento	001
	Actuación	430
	Oficio	
	Folios	023

8575

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados:

A. Para el presente estudio se tuvo en cuenta el capítulo descriptivo, comprendido en los folios 184 a 228 del expediente correspondiente a la solicitud en estudio, el cual reemplazó al que fue radicado al inicio del trámite.

B. El capítulo reivindicatorio tomado en cuenta para el presente estudio comprende 28 reivindicaciones y se encuentra en los folios 229 a 237, el cual reemplazó al que fue radicado al inicio del trámite.

C. Conforme lo establecen los artículos 9, 10 y 11 de la Decisión 486 de la Comisión de la Comunidad Andina, la presente solicitud en estudio fue presentada el 07 de abril de 2000, en el momento de la radicación se reclamó prioridad. La copia certificada de la solicitud cuya prioridad fue reivindicada (US 09/287.903 del 7 de abril de 1999 y CA 2.268.734 de abril 7 de 1999) aparece junto con la traducción de las reivindicaciones en los folios 90 a 177.

2. Objeto de la invención:

A. Las reivindicaciones 1 a 28 de la solicitud en estudio se refieren a: una composición de fluido de perforación basado en agua que comprende: a) agua como componente principal; b) 5 – 100 kg/m3 de uno o más formadores de viscosidad; c) 0,01 – 10 kg/m3 de uno o más agentes reológicos, donde dicho agente reológico de control es un polímero anfotérico, donde los grupos catiónicos de dicho polímero anfotérico son grupos de amonio cuaternario.

B. El objeto de la solicitud se puede clasificar según la clasificación internacional como C 09 K 7/07.

3. Claridad de la Solicitud:

A. En el artículo 30 de la decisión 486 de la Comisión de la Comunidad Andina se establece: "Las reivindicaciones definirán la materia que se desea proteger mediante la patente. Deben ser claras y concisas y estar enteramente sustentadas por la descripción. Las reivindicaciones podrán ser independientes o dependientes. Una reivindicación será independiente cuando defina la materia que se desea proteger sin referencia a otra reivindicación anterior. Una reivindicación será dependiente cuando defina la materia que se desea proteger refiriéndose a una reivindicación anterior. Una reivindicación que se refiera a dos o más reivindicaciones anteriores se considerará una reivindicación dependiente múltiple." En el artículo 51 se establece además: "El alcance de la protección conferida por la

patente estará determinado por el tenor de las reivindicaciones."

i. En la reivindicación 3 aparece la palabra "carboximetilalmióne" que debe ser una mala trascripción de "carboximetilalmidón". Se requiere la corrección especifica por parte del solicitante.

De acuerdo con lo anterior, el capítulo reivindicatorio no cumple con el requisito de claridad según lo establecido en el artículo 30 de la Decisión 486. El solicitante deberá anexar un nuevo capítulo reivindicatorio con todas las correcciones aquí requeridas.

4. Evaluación de la unidad de invención

El artículo 25 de la decisión 486 de la Comisión de la Comunidad Andina establece: "La solicitud de patente sólo podrá comprender una invención o un grupo de invenciones relacionadas entre sí, de manera que conformen un único concepto inventivo."

La presente solicitud carece de unidad de invención toda vez que configura dos objetos diferentes. Las reivindicaciones 1 a 25 se tratan de una composición que tiene como agente de control reológico un polímero anfotérico. Las reivindicaciones 26 a 28 se tratan de una composición que tiene dos polímeros, uno catiónico y otro aniónico, como agente de control reológico. Los otros componentes, agua y los formadores de viscosidad, ya eran conocidos en el estado de la técnica.

De acuerdo con lo anterior, la presente solicitud no cumple con el requisito de unidad de invención según el artículo 25 de la Decisión 486.

5. Determinación del estado de la técnica:

El artículo 16 de la Decisión 486 de la Comisión establece que: "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

"Solo para el efecto de la determinación de la novedad, también se considerará dentro del estado de la técnica el contenido de una solicitud de patente en trámite ante la oficina nacional competente, cuya fecha de presentación o de prioridad fuese anterior a la fecha de presentación o de prioridad de la solicitud de patente que se estuviese examinando, siempre que dicho contenido esté incluido en la solicitud de fecha anterior cuando ella se publique o hubiese transcurrido el plazo previsto en el artículo 40"

La fecha para determinar el estado de la técnica es el 7 de abril de 1999, tomando en cuenta la prioridad reivindicada.

Consultadas las bases de datos y los archivos con que cuenta la entidad, especialmente bajo las clasificaciones C 09 K 7/07, se encontró que antes del 7 de abril de 1999 habían sido publicados los documentos enumerados en la siguiente tabla.

No.	Documento	Título	Fecha de publicación
D1	US 5,663,123	Polymeric earth support fluid compositions and method for their use	1997-09-02
D2	US 5,387,675	Modified hydrophobic cationic thickening	1995-02-07
D3	EP 0 339 372	Method and composition for thickening or stabilizing aqueous media with polyamphoteric polysaccharides	1989-11-02

No.	Documento	Título	Fecha de publicación
D4	EP 0 632 057	Anionic sulfonated thickening compositions	1995-01-04

6. Evaluación de los requisitos de patentabilidad:

El artículo 14 de la Decisión 486 de la Comunidad Andina establece que: "*Los Países Miembros otorgarán patentes para las invenciones, sean de producto o de procedimiento en todos los campos de la tecnología, siempre que sean nuevas, tengan nivel inventivo y sean susceptibles de aplicación industrial*".

En cumplimiento del artículo 14 de la Decisión 486, se procedió a evaluar los requisitos de novedad, nivel inventivo y aplicación industrial con el fin de establecer la patentabilidad del objeto de la solicitud reivindicado en la solicitud en estudio.

A. Evaluación de la Novedad:

El artículo 16 de la decisión 486 de la Comisión de la Comunidad Andina establece:

"Una invención se considerará nueva cuando no esté comprendida en el estado de la técnica." "El estado de la técnica comprenderá todo lo que haya sido accesible al público por una descripción escrita u oral, utilización, comercialización o cualquier otro medio antes de la fecha de presentación de la solicitud de patente o, en su caso, de la prioridad reconocida."

En el documento D1 se divulga un polímero soluble en agua que se usa en fluidos de perforación como agente de control reológico. El fluido de perforación contiene arcillas, como la bentonita. El polímero es anfótero y contiene nitrógeno cuaternario. También se indica que el dicho polímero es polisacárido. En D1 se explica la acción del polímero anfótero así como también la de los polímeros catiónicos y aniónicos, en el control de fluidez. De esta manera, lo divulgado en D1 afecta la novedad del objeto de la solicitud en estudio.

B. Evaluación del nivel inventivo:

El artículo 18 de la Decisión 486 de la Comisión de la Comunidad Andina dispone que: "Se considerará que una invención tiene nivel inventivo, si para una persona del oficio normalmente versada en la materia técnica correspondiente, esa invención no hubiese resultado obvia ni se hubiese derivado de manera evidente del estado de la técnica".

Argumentar las razones por las cuales luego de comparar los documentos relevantes encontrados en el estado de la técnica y señalados en el numeral 8 el nivel inventivo podría verse afectado por ser obvio y derivarse de manera evidente. Si se trata sólo de algunas reivindicaciones indicar cuáles se podrían ver afectadas y demostrar estos hechos. Si existen oposiciones por parte de terceros señalar cómo estas afectan su nivel inventivo.

El documento D2 divulga un polisacárido con una fórmula que coincide con el polímero anfotérico que caracteriza la composición de fluido de perforación. De D1 ya se conoce que los fluidos de perforación tienen agua y formadores de viscosidad. El polímero anfotérico de D2 más las enseñanzas de D1 sugerían a un técnico medio en la materia la solución del problema planteado por el solicitante, es decir el control reológico en la perforación de pozos.

Así mismo, los polímeros de D3 son equivalentes a los que caracterizan al objeto de la solicitud en estudio. Por esta misma razón, la combinación de D3 y D1 también afecta el nivel inventivo de la solicitud en estudio.

Por último, el documento D4 también divulga polisacáridos anfóteros con nitrógeno cuaternario utilizados como espesantes y agentes controladores de viscosidad en campos de petróleo. Por tanto, lo que se revela en D4 en combinación con lo revelado en D1 también afecta el nivel inventivo de la solicitud en estudio.

Por lo tanto, la solicitud en estudio no cumple con el requisito de nivel inventivo establecido por el artículo 18 de la Decisión 486.

C. Resumen

En conclusión los requisitos de patentabilidad de la presente solicitud podrían encontrarse afectados así:

No.	Documento	Reivindicaciones afectadas	Requisito afectado
D1	US 5,663,123	1 a 28	Novedad y nivel inventivo
D2	US 5,387,675	1 a 28	Nivel inventivo
D3	EP 0 339 372	1 a 28	Nivel inventivo
D4	EP 0 632 057	1 a 28	Nivel inventivo

Se anexa copia de las anterioridades mencionadas.

7. Notificación

En cumplimiento del artículo 45 de la decisión 486 de la Comisión de la comunidad Andina, se le indica que debe dar respuesta dentro del término de sesenta días contados a partir de la fecha de la notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e) del capítulo quinto del título primero de la circular única No. 10 de 2001.

ALIX CARMENZA CESPEDES DE VERGEL
Jefe de la División de Nuevas Creaciones

El anterior requerimiento fue notificado por fijación en lista, de fecha 22 SET. 2005

CONCEPTO TÉCNICO Número: 1430	**EXAMINADOR TÉCNICO** Código: 202043