

[54] **PROCESS FOR FORMING BOREHOLE PLUGS**

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[57] **ABSTRACT**

A process for making plugs for boreholes. The process uses dispersions of water soluble polymers and cross-linking agents, the cross-linking activity of which is retarded. The dispersion is positioned while in a low viscosity state and subsequently high viscosities develop.

[56] **References Cited**
UNITED STATES PATENTS
 3,227,212 1/1966 Black et al. 166/294

6 Claims, No Drawings

PROCESS FOR FORMING BOREHOLE PLUGS

This invention relates to a process for placing strong substantially impermeable, relatively inexpensive temporary plugs in boreholes. More particularly, this invention relates to positioning aqueous dispersions of polymers and selected cross-linking agents in boreholes and causing the predominant portion of the cross linking to occur after the dispersion has been put in the desired position.

Operating fluid is used in boreholes for: one, carrying cuttings to the surface during drilling; two, treating during cleaning; and three, stimulating treatment. Plugs are used in drilling boreholes primarily to prevent the flow of operating fluid from the borehole into the surrounding rock or earth formation. This is a common problem encountered in oil well drilling. The leakage ordinarily occurs in particular areas of the borehole. The plug acts as a patch over that particular rock or earth stratum. Sometimes plugs are used to prevent the flow of fluids, such as water, from the surrounding rock or earth formations into the borehole. This is sometimes a problem in core drilling. Generally the plug is an aqueous solution or dispersion of a thickener, i.e. starch. The solution or dispersion is pumped into the borehole and impregnates and seals the pores in the rock or earth radial to the borehole. The plug may literally smear the surface of the borehole.

Various methods have been used in the past to devise plugs. One method consists of pumping dispersions of gums such as guar in concentrations of about 5% to 20% by weight into boreholes. This method has several disadvantages. First, because the dispersion is initially very viscous it is extremely difficult to pump and requires equipment capable of operating at pressure of the magnitude of about 500 to 3,000 psi. Secondly, because the gum is not cross linked, there is no gel structure present. The dispersion forms a paste in the environment of the borehole and is not very strong or impervious to fluid flow. Third, using gums at such high concentrations is expensive. A second method of devising a plug has been to inject a solution of cross-linking agent into a dispersion of guar at the outlet of the pump just before the dispersion is moved down the pipe in the borehole. The disadvantage in this method is that cross linking occurs very quickly. Therefore, only a small amount of cross linking can be tolerated or the gum will gel in the pipe and cannot be moved. Because only a small amount of cross linking can be tolerated, the plug itself is weak and fairly easily penetrated by fluids.

It has now been found that, by using water soluble polymers and selected cross-linking agents having retarded cross-linking action, dispersions of polymers can be put into place while in a reasonably low viscosity, fluid state and the viscosity or gelling of the dispersion developed after the dispersion is in position. The polymer dispersion when cross linked is not a true gel but a viscoelastic fluid. Viscoelastic fluids will flow but extremely slowly. For purposes of convenience, viscoelastic fluids having viscosities greater than 20,000 centipoise will be referred to as gels in the following description of my invention.

The advantages of this process over previously used processes are numerous. First, the dispersions contain relatively low concentrations of polymer and therefore can be pumped through the system without using excessively high pressures. For example, a 1% by weight

guar dispersion can be pumped at pressure less than 100 psig. Secondly, because the polymer concentration is much lower than in those processes which depend upon limited solution and high gum concentrations in the order of 5% to 20%, the process is much more inexpensive. Third, because the polymer is not substantially cross linked until the dispersion is in place, relatively heavy cross linking can be used thus creating more viscous, stiffer and less penetrable gelled plugs than heretofore possible.

In the practice of this invention the preferred polymers are polygalactomannan gums, hydroxyalkyl ethers of polygalactomannan gums, carboxyalkyl ethers of polygalactomannan gums, their depolymerized counterparts, polyvinyl alcohol and mixtures thereof. The term "polygalactomannan" as used herein includes the general class of polysaccharides containing both galactose and mannose units. The "polygalactomannans" are usually found in the endosperm sections of leguminous seeds such as guar, locust bean, tara, honey bean, flametree and cassia occidentalis.

Hydroxyalkyl ethers of polygalactomannans refer to derivatives obtained by reacting a polygalactomannan with an alkylene oxide in the presence of an alkaline catalyst. The alkylene oxide forms an ether linkage with a hydroxyl group of the galactomannan unit. In the case of guar gum each saccharide ring has an average of three hydroxyl groups with which the alkylene oxide can react. In addition, a new hydroxyl group is added with each alkylene oxide group and it too can react. Theoretically there is no limit to the amount of alkylene oxide that may be added to the guar gum. Molar substitution is the average of number of moles of the substituting material added to each mole of the anhydrohexose unit of polygalactomannan. As a practical matter, molar substitutions are of about 0.2 to 2.0. The preferred range is about 0.2 to 1.0.

In order for the reaction between the polygalactomannan and the alkylene oxide to proceed, the presence of an alkaline catalyst is necessary. Such catalysts are in general the alkali metal or alkaline earth metal hydroxides, such as sodium, potassium or calcium hydroxide. Ammonia may also be used, as well as more complex basic catalysts such as benzyl trimethyl ammonium hydroxide. No special advantage, however, is obtained by the use of more exotic basic or alkaline catalysts over the use of sodium hydroxide which is commonly available.

Very small amounts of catalyst may be employed, as low as 0.05% based on the weight of the polygalactomannan. It is generally not necessary to exceed 10% by weight of the polygalactomannan, although larger amounts might be used. In general, about 2% to 3% by weight of the polygalactomannan is employed.

The reaction can be conducted at room temperature or elevated temperatures. The temperature range in which the reaction is generally conducted is about 17° C. to 100° C. While higher temperatures can be used, such as up to 125° C., there is generally no advantage achieved.

The reaction can be conducted at atmospheric temperature, under reflux, or at elevated pressures, in a closed reactor. The exact pressure is not critical and while higher pressure may be employed, operation is normally conducted at whatever pressure develops during the reaction. Generally such developed pressures will be on the order of from about 30 to 125 psig.

The reaction may be conducted in the substantial absence of water or solvent (no water added) although the efficiency of the reaction is very low without the addition of water. Accordingly, the reaction is generally conducted in the presence of water to provide higher reaction efficiency. In the absence of other solvents, catalytic amounts of water on the order of about 3 to 8% based on the polygalactomannan are employed. These small amounts are generally used where higher temperatures and elevated pressures are employed, whereas larger amounts of water are used when lower temperatures and atmospheric pressure is employed. Further, other organic solvents, either water-miscible or water-immiscible organic solvents, can be employed. Illustrative of such organic solvents are isopropanol (water-miscible) and heptane (water-immiscible). Other unreactive organic solvents may be employed although the two mentioned are preferred. Such other organic solvents are the common aliphatic hydrocarbons having from 5 to 10 carbon atoms which are commercially available such as heptane and hexane. Alcohols higher than methanol, those having from 2 to 6 carbon atoms, may be employed also, such as *t*-butanol, the only requirement being that the solvent be substantially unreactive. Where higher water levels are employed, the water should be sufficient to swell the guar gum slightly, thereby making the gum more reactive. When employed with a solvent such as isopropanol or heptane, from about 10 to 80% water based on the weight of guar gum is employed. The preferred amount of water is from about 30 to 70% with the water-miscible solvents and about 20 to 30% with the water-immiscible solvents.

Where organic solvents are employed, they are generally present in an amount up to 8 times the amount of gum by weight, although larger amounts may be employed, if desired. Generally, with water-miscible solvents, an amount equal to one to three times the weight of gum are employed. With water-immiscible solvents, an amount of from 3 to 5 times the weight of gum is generally employed. With the organic solvents, the ratio by weight of water to organic solvent is preferably within the range of about 0.05 to 0.5. A range of from about 0.2 to 0.45 is preferred with the water-miscible organic solvents and from about 0.1 to 0.2 is preferred with the water-immiscible organic solvents. In general, any unreactive, organic solvent may be employed. With the lower ratios of water to organic solvent, the reaction is slowed. With the higher ratios, the recovery of product by filtration is slowed. The preferred hydroxyalkyl ethers of guar are those in which the hydroxyalkyl group contains 2 to 3 carbon atoms.

Carboxyalkyl polygalactomannans are derivatives obtained by reacting polygalactomannan gum with halo aliphatic acid or salt of a halo aliphatic acid. Usually this is done by treating the polygalactomannan with aqueous solution of an alkali such as sodium hydroxide and then treating the alkali gum with a halo aliphatic acid or a halo aliphatic acid salt. One procedure calls for the following steps. The gum is dispersed in the aqueous alkali solution and the mixture is heated to an elevated temperature such as 60° to 90° C. The reaction mixture frequently becomes a semi-solid. This mass is cooled and broken up into fine particles and treated with the etherifying agent, usually in the form of a halo aliphatic acid or salt thereof. This reaction mixture is heated to a temperature of 80° to 85° C. for

a period of about 1 to 2 hours with mixing. The reaction mixture is then cooled and acidified. The product is filtered and dried. A method of preparing carboxyalkyl ethers of carbohydrate gums is set out in U. S. Pat. No. 2,520,161. Alternate methods of synthesis include hydrolysis of carbamoyl alkyl ethers of polygalactomannan. The preferred carboxyalkyl ethers are those in which the carboxyl alkyl group contains 1 to 3 atoms. The molar substitution is the average number of moles of halo aliphatic acid substituted per mole of anhydrohexose unit of polygalactomannan gum. The preferred range is about 0.1 to 1.0.

The depolymerized counterparts of the above polygalactomannan gums and their derivatives are made by treating the gum with a mixture of an alkali such as sodium hydroxide and hydrogen peroxide or alkali metal peroxide and heating the mixture to a temperature of about 60° to 90° C. as in making the carboxyalkyl or hydroxyalkyl derivatives. When making depolymerized carboxyalkyl or hydroxyalkyl ethers of polygalactomannan gums, the polygalactomannan gum can be first depolymerized and subsequently reacted with the halo aliphatic acid or the alkylene oxide.

The hydrogen or alkali metal peroxide attacks the glycosidic linkages of the polygalactomannan chain breaking the very long chains into shorter chains. The shorter chains of the depolymerized gums develop less viscosity in dispersions than the longer chains of the initial gum. More of the depolymerized gum by weight can be put into a dispersion before the viscosity becomes too great for the dispersion to be handled. For the purposes of this invention, the degree of depolymerization is measured by the decrease in viscosity of the gum or its derivatives. The preferred amount of depolymerization yields modified gums and derivatives that require amounts of about 2% to 3% by weight gum in an aqueous dispersion to develop viscosities equivalent to dispersions containing 1% by weight of their non-depolymerized counterparts. Dispersions having the same initial viscosity but containing depolymerized gums and gums having original chain lengths, respectively, will upon cross linking produce very different gels. Due to the greater concentration of the depolymerized gum, the gel obtained from dispersions containing depolymerized gums will be much stiffer than that obtained from the original gum.

Polyvinyl alcohol is a well-known polymer usually prepared by hydrolyzing polyvinyl acetate. The polyvinyl alcohols generally useful in the practice of this invention are those in which about 75% to 95% of the acetate groups have been hydrolyzed to hydroxyl groups. The preferred hydrolyzed range is about 80% to 90%. The molecular weight of the polyvinyl alcohol should generally produce viscosities of about 1 to 200 centipoise at a temperature of 25° C. in an aqueous dispersion containing 4% by weight polyvinyl alcohol.

The above described water-soluble polymers are generally used in this invention in amounts of about 1% to 10% by weight based upon the weight of the polymer and water combination. The long chain polygalactomannan gums and their derivatives are preferably used in amounts of from about 1% to 3% by weight and their polymerized counterparts preferably in amounts of from about 2% to 4% by weight, both based on the weight of the gum-water combination. Polyvinyl alcohol is generally used in amounts of about 1% to 10% by

weight, based on the weight of the polymer-water combination and preferably in amounts of 2% to 10%.

The cross-linking agents used in my process all have at least one characteristic which can delay their cross-linking action under conditions obtainable in a borehole. This characteristic can be that the cross-linking agent is in a slowly soluble form. It can be that the cross-linking agent must react with another component of the dispersion before it has cross-linking capacity and the other component acts slowly. The delaying characteristic may be that at certain pH values the cross-linking action of a particular cross-linking agent is very slow. Finally, the characteristic can be that at temperatures to which the dispersion is heated in the borehole only slow cross-linking action occurs. Any cross-linking agent can be used in the practice of this invention which can develop viscosities in excess of 20,000 centipoise in the polymer dispersion and which has a characteristic which is critical to the speed of reaction and can be manipulated.

Suitable cross-linking agents for members of the above-described water soluble polymers include borax glass, sodium and potassium pyroantimonate, antimony oxide and chromium salts. Borate, antimony and chromic ions are known cross-linking ions. Their usefulness in this process is that they can be used under conditions in which their cross-linking activity is retarded sufficiently to permit the positioning of the dispersion in the borehole before substantial gelling of the polymer occurs.

The borate ion can cross link any of the above-described polymers. For the purposes of this invention, the borate ion is in the form of borax glass. While in its solid state, borax glass is dispersed in the polymer dispersion. It dissolves in the dispersion in a time range of a few minutes to hours. The rate at which the borax glass dissolves and the borate ion becomes available for cross linking can be controlled by the mesh size of the borax glass particles. As shown in Example II, the gelling of guar gum can be delayed for hours using particle sizes of 100% passing through 20 mesh and 60% retained on 30 mesh U. S. Standard Sieve. Commercially, this particle size is classified as 18 mesh. Smaller particles of borax glass dissolve more rapidly causing gelling sooner. Borax glass is generally used in particle size distribution larger than about 90% through 100 mesh and 40% retained on 200 mesh U. S. Standard Sieves. Preferably borax glass is used in particle size distribution between about 100% through 20 mesh and 60% retained on 30 mesh U. S. Standard Sieve and 100% through 30 mesh and 20% retained on 100 mesh U. S. Standard Sieve. As the borax glass dissolves, it imparts alkalinity to the dispersion. Polygalactomannan gums generally are cross linked by borate ions when the pH of the dispersion is higher than about 7.5. Borax glass can be used in amounts of from 1% to 200% by weight of the polymer. Preferably, it is used in amounts of about 5% to 10% by weight of the polymer. When borax glass is dry blended and stored with polygalactomannan gum or its derivatives, the natural moisture in the gum tends to hydrate the borax glass. To retard such hydration, a small amount of an organic acid such as 1% citric acid by weight based on the weight of the gum, is usually included in the dry blend.

Potassium and sodium pyroantimonates can cross link polygalactomannans and their derivatives. These compounds are only slowly soluble in water based dis-

persions at slightly acidic and alkaline pH values. Cross-linking activity of the pyroantimonate ion is pH sensitive and occurs in the pH range of about 3 to 7. The cross-linking effect at pH values of about 3 is very fast. At the pH range of about 6 to 7, however, the cross-linking activity is very slow. By incorporating an acid into the polymer dispersion to achieve a given pH, the rate at which the pyroantimonate salt dissolves and the rate cross linking occurs can be controlled. The range of acids that can be used is very wide including organic acids such as acetic, citric and oxalic acid and mineral acids such as hydrochloric, sulfuric and nitric acid. The sodium or potassium pyroantimonate is usually used in amounts of about 1% to 10% by weight based upon the weight of the polymer.

Antimony oxide containing valentinite in the presence of an oxidizing agent can cross link polygalactomannan gums and their derivatives. Strong oxidizing agents such as dichromates induce almost immediate cross linking at appropriate pH values. Weak oxidizing agents such as hydrogen peroxide, sodium peroxide, nitric acid and potassium permanganate, induce cross-linking activity very slowly. The cross-linking activity is also pH sensitive being viable in the pH range of about 3 to 7. At pH values of about 6 to 7, the cross-linking reaction is slow. Antimony oxide containing valentinite is generally used in amounts of about 1% to 10% by weight of the gum.

Chromic ions can cross link carboxyalkyl ethers of polygalactomannan. The cross-linking activity is temperature sensitive. Dispersions being pumped down boreholes reach a temperature of from 5° C. to about 48° C. Chromic ions cross link carboxyalkyl ethers of polygalactomannan gums very slowly at these temperatures. Chromic ion salts such as chromic alum are usually used in amounts of about 1% to 10% by weight of the gum. In this particular combination it has been found that a small amount of calcium ion improves the stiffness of the gel. Generally, it is used at concentrations of about 100 ppm to the saturation concentration.

In the practice of this invention the distance from the entrance of the borehole to the desired position of the plug is measured. The available pumping pressure, the expected friction in the borehole and the viscosity of the polymer containing dispersion are determined. From this data, the time required to move the dispersion into position is calculated or estimated. A cross-linking agent which requires a greater period of time to gel the dispersion than the time required to position the dispersion in the borehole, is incorporated into the dispersion. Alternatively, the polymer and cross linking may be stored as a dry blend and the appropriate blend selected. The dispersion is then pumped down the pipe into the borehole. As shown in the following examples, borax glass and guar gum can require about 3½ hours to begin initial gelling under given conditions. Carboxyalkyl guar and hydroxyalkyl guar can require about ½ hour. The strength or viscosity of the cross-linked dispersions usually continues to increase for several hours after initial gelling begins. Maximum strength or viscosity is obtained about 16 to 22 hours after initial gelling.

Optimized results can be obtained by using combinations of polymers and cross-linking agents. In addition to the polymer, water and cross-linking agents, it is frequently desirably to include oxalic acid or salts of oxalic acid in the dispersion to control the effects of hard water upon the rate or cross linking. Generally, oxalic

acid or its salts are included in amounts of 0.01% to 0.05% by weight of the dispersion. In addition to controlling water hardness, preservatives such as fatty amine salts or chlorophenols can be used to prevent microbiological spoilage of the gum.

Set out below are specific examples of polymers and various cross-linking agent combinations to demonstrate the fluid and cross-linking characteristics useful in forming plugs in boreholes.

EXAMPLE I

This example illustrates the gelling properties of guar gum and borax glass.

Five grams of a guar gum and borax glass blend having the following composition

	Percent by Weight
Guar Gum (90% through 200 mesh U.S. Standard Sieve)	94.0
Borax Glass (100% through 20 mesh, 60% on 30 mesh U. S. Standard Sieve)*	4.0
Borax Glass (90% to 100% through 60 mesh, 70% on 200 mesh U. S. Standard Sieve)**	1.0
Citric Acid (Anhydrous)	1.0

* Commercially graded 18 mesh
 ** Commercially graded 60 mesh

were added with agitation to 500 ml. of distilled water having a temperature of 25° C. The mixture was mixed for a period of two minutes in a 1 quart Waring Blendor operated at 1,500 to 2,000 rpm. Following the initial agitation the viscosity of the dispersion was continuously measured with a Brookfield RVF Viscometer using a No. 4 spindle at a speed of 10 rpm. When the viscosity of the dispersion reached 20,000 centipoise, the cross linking had progressed sufficiently to consider the dispersion gelled. The changes in viscosity measured from the beginning of the initial mixing to gela-

Time, minutes	Viscosity, centipoise
3	1,900
5	2,400
10	3,100
15	3,800
20	4,200
25	4,900
32	6,400
35	9,000 (gelling 35-40 minutes)
40	>20,000

EXAMPLE II

This example illustrates a variation of the guar gum and borax glass combination.

The formulation procedure and viscosity measurements set out in Example I were repeated using the following guar gum and borax glass blend.

	Percent by Weight
Guar Gum (90% through 200 mesh U. S. Standard Sieve)	94.0
Borax Glass (commercial mesh size 18)*	5.0
Citric Acid (Anhydrous)	1.0

*See footnote Example I.

Viscosity change was as follows:

Time hours	Viscosity, centipoise	pH
1.0	3,000	
1.5	3,000	
2.0	3,000	
3.0	5,000	6
3.5	10,000 (gelling)	7.4

3.7	time 3.5-3.7 hours) >20,000	7.6
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Comparing these results with those of Example I, it is apparent that the time period required for gelling can be varied by changing the mesh size of the borax glass thus changing the rate it dissolves in the dispersion and becomes available as a cross linker.

EXAMPLE III

This example illustrates the characteristics of a carboxyethyl ether of guar gum having a molar substitution of about 0.2 and borax glass. Ten grams of a blend having the following composition

	Percent by Weight
Sodium carboxyethyl guar	47.6
Borax glass (commercial mesh size 18)*	4.6
Citric Acid (Anhydrous)	4.8

*See footnote Example I.

were added to and mixed with 500 ml. of distilled water having a temperature of 25° C. Viscosity measurements were made as in Example I. The results are as follows:

Time, minutes	Viscosity, centipoise	pH
15	2,800	
20	15,000 (gelling time 20-22 minutes)	8.0
22	>20,000	8.5

EXAMPLE IV

This example illustrates the use of using two gums and two cross-linking agents in a blend. The particular gums used were sodium carboxyethyl ether of guar and hydroxypropyl ether of guar. The cross-linking agents used were borax glass and chromium alum [CrK(SO₄)₂·12H₂O]. Oxalic acid was included to simulate hard water control. Preservatives (sodium orthophenoxyphenol and sodium pentachlorophenylate, Dovicide A and G, Dow Chemical Co.) were included to simulate the protection of the gum from microbiological deterioration.

The composition of each blend is shown in Table 1. The amount of each blend used was 8.54 grams in 500 ml. of water having a temperature of 25° C. The viscosity change measurements and the time required for gelling are shown in Table 1. Gelling time corresponds to the time required to develop a viscosity of 20,000 centipoise.

TABLE 1

Sample.....	Percent by weight				
	A	B	C	D	E
Carboxyethyl guar.....	37.0	37.0	36.65	36.65	36.65
Hydroxypropyl guar.....	37.0	37.0	36.65	36.65	36.65
Borax glass (100% through 30 mesh, 90-100% through 60 mesh U.S. Standard Sieve)*				6.65	13.3
Borax glass (commercial mesh size 60)**		13.3	13.3	6.65	
Borax glass (100% through 100 mesh and 40% retained on 200 mesh U.S. Standard Sieve)***	13.3				
Chrome alum.....	7.0	7.0	7.0	7.0	7.0
Oxalic acid.....	0.7	0.7	1.4	1.4	1.4
Sodium pentachlorophenylate (Dovicide G, Dow Chemical Co.).....	2.5	2.5	2.5	2.5	2.5
Sodium orthophenoxyphenyl (Dovicide A, Dow Chemical Co.).....	2.5	2.5	2.5	2.5	2.5
(gelling time minutes).....	4-5	8-10	10-12	20-22	>30

* Commercially graded 30 mesh.
 ** See footnote Example I.
 *** Commercially graded 100 mesh.

EXAMPLE V

This example illustrates the behavior of a blend of hydroxypropyl ether and carboxyethyl ether of guar and two cross-linking agents in the presence of mineral salts commonly found in water available for making dispersions in the field.

The composition of the gum blend is as follows:

	Percent by Weight
Carboxyethyl Ether of Guar (M.S. approx. 0.2)	35.0
Hydroxypropyl Ether of Guar (M.S. approx. 0.5-0.6)	35.0
Calcium Sulfate (anhydrous)	10.0
Ammonium Oxalate	6.0
Chromium Alum	5.0
Borax Glass (commercial mesh size 60 mesh)*	4.0
Borax Glass (commercial mesh size 30 mesh)**	4.0
Oxalic Acid	1.0

* See footnote Example I

** See footnote Example IV

Ten grams of the above blend were dispersed in 500 ml. of the solutions shown in Table 2. The solutions had a temperature of 25° C. The dispersion procedure was the same as described in Example I. Changes in viscosity were measured as in Example I. In addition, the stiffness of the resulting gels was measured with a penetrometer after a period of 16 hours from the beginning of the mixing. This test was run for 30 seconds with a Precision Penetrometer fitted with a 45° steel cone having a 2½ inch base diameter and weighing 94 grams. An additional 150 grams of weight was placed on the penetration arm.

Table 2

Sample	Salt	Concentration	Gelling Time, minutes	Penetrometer Reading, millimeters
A	pure water	—	10.0	37.6
B	calcium chloride	500 ppm	10.7	37.1
C	calcium chloride	1000 ppm	12.0	—*
D	magnesium chloride	50 ppm	12.7	—*
E	magnesium chloride	100 ppm	12.8	—*
F	magnesium chloride	200 ppm	18.3	—*
G	magnesium chloride	500 ppm	36.0	39.5
H	ferric chloride	10 ppm	—	11.7 36.3
I	sodium chloride	% by wt.	19.8	42.0
J	potassium chloride	% by wt.	14.3	41.1
K	calcium sulfate	saturated	9.5	35.9

* Measurement not taken

As can be seen from the above data, gelling time is generally increased in the presence of mineral salts.

EXAMPLE VI

This example illustrates the effect of the temperature of the aqueous media and the concentration of the blend of gums and cross-linking agents described in Example IV. The blend in amounts of 2% by weight was incorporated in water having the temperature shown in Table 3. Gelling time and penetrometer measurements were made as described in Examples I and IV. The results are as follows:

Table 3

Sample	Water Temp., °C.	Gelling Time, minutes	Penetrometer Readings
A	4.5	45	33.8
B	25.0	10	37.6
C	38.0	5	36.7

EXAMPLE VII

This example illustrates the effect of concentration of the gum and cross linker blend in the dispersion upon gelling time and gel stiffness. The blend described in Example IV was incorporated in water having a temperature of 25° C. at the concentrations shown below. The gelling time and penetrometer readings determined for these gels is also shown below.

Table 4

Sample	Concentration of Blend, % by Wt.	Gelling Time, minutes	Penetrometer Reading
A	1.4	17.2	41.3
B	2.0	10.0	34.7
C	2.6	4.3	37.6

EXAMPLE VIII

This example illustrates the use of depolymerized gums in the process of this invention. In general, depolymerized gums, because they have lower molecular weight than the natural gums, develop less viscosity at the same solids concentration than do natural gums while the dispersion is in an uncross-linked condition. Their dispersion having equivalent initial viscosities will contain a higher solids level of depolymerized gum than of natural gums. Because the solids level is higher, upon cross linking significantly stiffer and less mobile gels are obtained from the dispersions of depolymerized gum than that from the natural gum.

In the samples described below, Sample A is a hydroxypropyl ether of guar retaining its original chain lengths. Sample B is a hydroxypropyl ether of guar in which the chain lengths of the guar base have been shortened to the extent that 3% by weight of this depolymerized guar derivative is required to develop the same initial viscosity as 1% by weight of the hydroxypropyl ether of guar having the original chain lengths. Dispersions were prepared respectively by dispersing 3% by weight of the depolymerized guar derivative and 1% by weight of guar derivative having original chain lengths in 500 ml. of water having a temperature of 25° C. One gram of 30 mesh borax glass was then added to each dispersion and cross linking allowed to proceed to maximum gel strength. Each gel was then evaluated by penetrometer measurements as described above. The flow characteristic of each gel was also evaluated by a Baroid Cell. The efflux pressure from the Baroid Cell

was determined by packing the gel into the cell without using a screen or other barrier, closing the cell and slowly applying pressure with nitrogen. The pressure at which the gel began to flow out of the cell was recorded and shown below:

Table 5

Sample	Concentration of Gum	pH	Penetrometer Reading	Baroid Cell Flow Pressure psig.
A	1.0	9.2	38.0	5-10
B	3.0	8.9	33.6	35-37

As can be readily seen from the data, the gel formed from the depolymerized guar derivative was much stiffer and less mobile than the gel formed by the guar derivative having the original chain lengths.

EXAMPLE IX

This example illustrates the use of polyvinyl alcohol as a plug former.

An aqueous dispersion of 4% polyvinyl alcohol by weight was prepared using distilled water having a temperature of 75° to 80° F. After the completion of dispersion a dry mixture of 0.2 grams of 100 mesh (commercial graded mesh) borax glass, 0.8 grams of 30 mesh (commercial graded mesh) borax glass and 0.1 gram of anhydrous citric acid was added to 500 ml. of the dispersion. The viscosity development was measured as in Example I and is as follows:

Time, minutes	Viscosity, centipoise
0	30
8	50
10	300
12	4,000
13	20,000 (gelling time)

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for forming borehole plugs comprising: introducing into a borehole and positioning in the borehole an aqueous dispersion comprising a water soluble polymer selected from the group consisting of carboxyalkyl ethers of polygalactomannans in amounts of from about 1% to 3% by weight based on the weight of the water-polymer combination and depolymerized derivatives of carboxyalkyl ether of polygalactomannan in amounts of about 2% to 4% by weight based on the weight of the water-polymer combination, and a chromic salt, said aqueous dispersion having a low initial viscosity and said aqueous dispersion having a temperature of about 5° C. to 48° C. whereby the rate of cross-linking activity is such that the period of time between the introduction of the dispersion into the borehole and the development of viscosities in excess of about 20,000 centipoise is greater than the time between the introduction of the aqueous dispersion into the borehole and the positioning of the aqueous dispersion; and allowing the viscosity of the dispersion to exceed about 20,000 centipoise subsequent to the positioning of the aqueous dispersion.

2. A process for forming borehole plugs comprising: introducing into a borehole and positioning in the borehole an aqueous dispersion comprising a mixture of carboxyalkyl ether of polygalactomannan and hydroxyalkyl ether of polygalactomannan in amounts of from about 1% to 3% by weight based on the weight of the water-polymer combination, and a mixture of chromic

salt and borax glass, said aqueous dispersion having a low initial viscosity and said aqueous dispersion having a temperature of about 5° C. to 48° C. whereby the rate of cross linking activity is such that the period of time between the introduction of the dispersion into the borehole and the development of viscosities in excess of about 20,000 centipoise is greater than the time between the introduction of the aqueous dispersion into the borehole and the positioning of the aqueous dispersion; and allowing the viscosity of the dispersion to exceed about 20,000 centipoise subsequent to the positioning of the aqueous dispersion.

3. A process for forming borehole plugs comprising: introducing into a borehole and positioning in the borehole an aqueous dispersion comprising a water soluble polymer selected from the group consisting of polygalactomannans, carboxyalkyl ethers of polygalactomannans, hydroxyalkyl ethers of polygalactomannans in amounts of from about 1% to 3% by weight based on the weight of the water-polymer combination, depolymerized derivatives of polygalactomannan, carboxyalkyl ether of polygalactomannan, hydroxyalkyl ether of polygalactomannan in amounts of about 2% to 4% by weight based on the weight of the water-polymer combination, and a cross linking agent selected from sodium or potassium pyroantimonate, said aqueous dispersion having a low initial viscosity and said aqueous dispersion having a pH range of about 6 to 7, whereby the rate of cross linking activity is such that the period of time between the introduction of the dispersion into the borehole and the development of viscosities in excess of about 20,000 centipoise is greater than the time between the introduction of the aqueous dispersion into the borehole and the positioning of the aqueous dispersion; and allowing the viscosity of the dispersion to exceed about 20,000 centipoise subsequent to the positioning of the aqueous dispersion.

4. A process for forming borehole plugs comprising: introducing into a borehole and positioning in the borehole an aqueous dispersion comprising a water soluble polymer selected from the group consisting of polygalactomannans, carboxyalkyl ethers of polygalactomannans, hydroxyalkyl ethers of polygalactomannans in amounts of from about 1% to 3% by weight based on the weight of the water-polymer combination, depolymerized derivatives of polygalactomannan, carboxyalkyl ether of polygalactomannan, hydroxyalkyl ether of polygalactomannan in amounts of about 2% to 4% by weight based on the weight of the water-polymer combination, and antimony oxide in the presence of a weak oxidizing agent, said aqueous dispersion having a low initial viscosity, and the rate of cross linking activity being such that the period of time between the introduction of the dispersion into the borehole and the development of viscosities in excess of about 20,000 centipoise is greater than the time between the introduction of the aqueous dispersion into the borehole and the positioning of the aqueous dispersion; and allowing the viscosity of the dispersion to exceed about 20,000 centipoise subsequent to the positioning of the aqueous dispersion.

5. A process for forming borehole plugs comprising: introducing into a borehole and positioning in the borehole an aqueous dispersion comprising polyvinyl alcohol in amounts of from about 1% to 10% by weight based on the weight of the water-polymer combination and mixtures thereof, and borax glass, said aqueous dis-

persion having a low initial viscosity, and the rate of cross linking activity being such that the period of time between the introduction of the dispersion into the borehole and the development of viscosities in excess of about 20,000 centipoise is greater than the time between the introduction of the aqueous dispersion into the borehole and the positioning of the aqueous dispersion; and allowing the viscosity of the dispersion to exceed about 20,000 centipoise subsequent to the positioning of the aqueous dispersion.

6. A process for forming borehole plugs comprising: introducing into a borehole and positioning in the borehole an aqueous dispersion comprising a water soluble polymer selected from the group consisting of carboxyalkyl ethers of polygalactomannans and hydroxyalkyl ethers of polygalactomannans in amounts of from about 1% to 3% by weight based on the weight of the

water-polymer combination, depolymerized derivatives of carboxyalkyl ether of polygalactomannan, and hydroxyalkyl ether of polygalactomannan in amounts of about 2% to 4% by weight based on the weight of the water-polymer combination, and borax glass, said aqueous dispersion having a low initial viscosity and the rate of cross linking activity being such that the period of time between the introduction of the dispersion into the borehole and the development of viscosities in excess of about 20,000 centipoise is greater than the time between the introduction of the aqueous dispersion into the borehole and the positioning of the aqueous dispersion; and allowing the viscosity of the dispersion to exceed about 20,000 centipoise subsequent to the positioning of the aqueous dispersion.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,794,115 Dated February 26, 1974

Inventor(s) William E. Skagerberg

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 6, line 65, "desirably" should read --desirable--;
line 66, "or" should read --of--. Column 8, line 35,
"chromium" should read --chromic--; line 55, "class" should
read --glass--. Column 9, line 18, "Chromium" should read
--Chromic--; line 52, --11.7-- should be centered under the
column headed "Gelling Time"; line 53, "% by wt." should read
--5% by wt.--; line 54, "% by wt." should read --2% by wt.--.
Column 10, line 26, "Pentrometer" should read --Penetrometer--;
line 28, --1.4-- should be centered under the column headed
"Concentration of Blend" and "td" should be deleted; line 49,
"than that from" should read --than from--; line 54, "extend"
should read --extent--.

Signed and sealed this 24th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents