

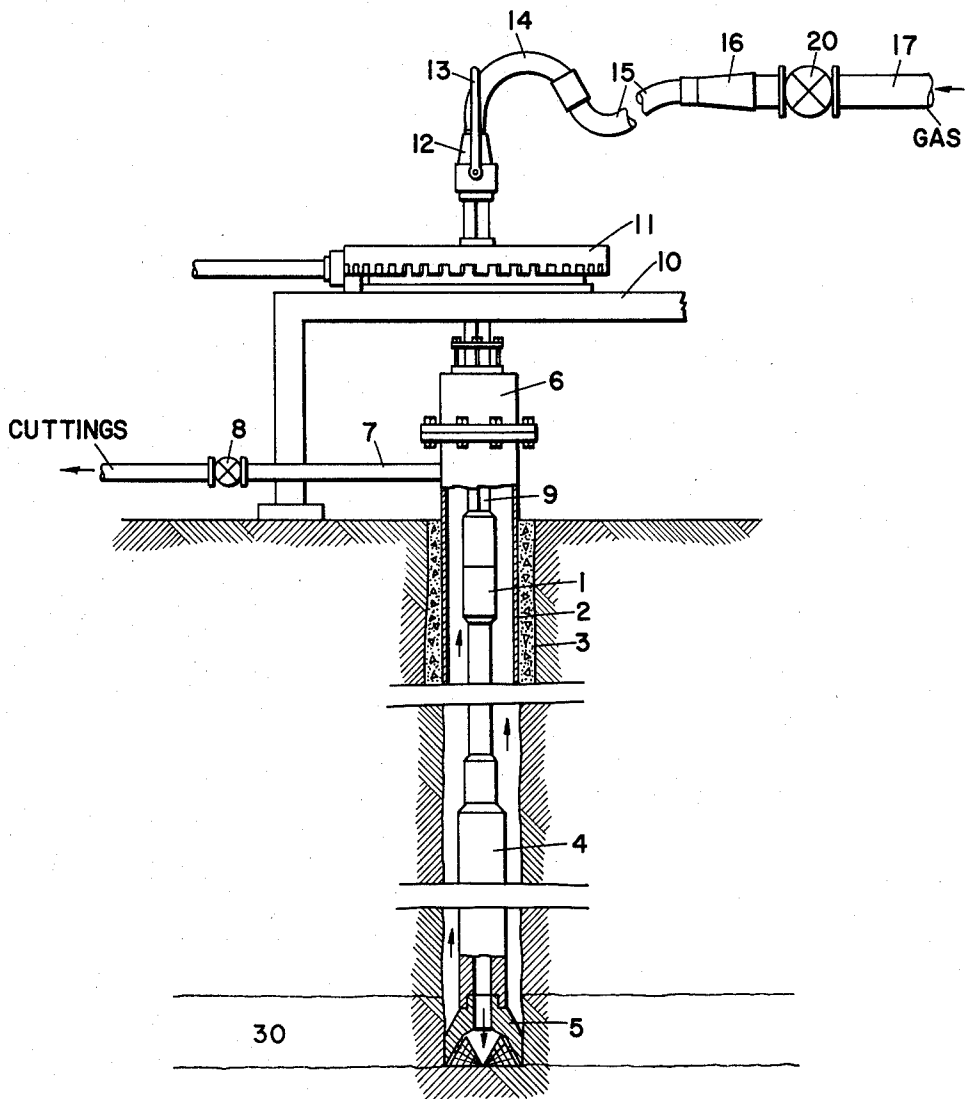
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RESINOUS SEAL FOR A BOREHOLE

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RESINOUS SEAL FOR A BOREHOLE

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The present invention is concerned with an improved technique for drilling boreholes into the earth's substrata. While the invention can be employed in all types of drilling operations for the sealing off of undesirable fluids from the borehole, the invention is more particularly concerned with an improved method wherein a gas is used to remove cuttings from the bottom of the borehole and wherein the hole penetrates areas where there exists water seepage into the hole. In accordance with the present process, resins prepared from styrene-polyester copolymers are utilized for sealing off the flow of undesirable water from entering the hole when utilizing a gas to remove cuttings to the surface.

Rotary drilling methods wherein a drill bit positioned at the end of a string of drill pipe is rotated against the formation are well known in the art. In this type of drilling, a drilling fluid or mud is circulated in the borehole, usually downwardly within the drill pipe and upwardly in the annular area between the drill pipe and the borehole wall. This drilling fluid or drilling mud serves a number of functions as, for example, to remove to the surface the drill cuttings to secure a hydrostatic head as the pressure formation is encountered and thus prevent blowouts, and also to form a mud cake on the borehole wall, thus helping to prevent undesirable entry of water and sand into the well being drilled. Conventionally, this drilling fluid is a thick suspension of bentonite or other clay in a water or oil base to which various chemicals may have been added in order to adjust viscosity, surface tension and similar properties.

In recent years it has been recognized that the hydrostatic pressure at the bottom of the borehole caused by the high densities of conventional drilling "muds" has a detrimental effect upon the cutting action of the drill bit, thereby lowering drilling rates. Thus, efforts have been made to develop drilling methods by means of which this high hydrostatic pressure can be avoided and drilling rates of penetration improved. The most successful of these methods has been the use of a gaseous drilling fluid in place of the conventional drilling mud. It has been found that if a gas is circulated in the borehole at sufficiently high velocities, it will entrain the cuttings produced by the bit and carry them to the surface, perform most of the other functions of a conventional drilling mud, and at the same time permit considerably higher drilling rates than can otherwise be obtained.

Although the use of gaseous drilling fluids thus makes possible faster and more economical drilling, it has been found that such gaseous fluids cannot be used effectively in wet formations and therefore their utility is somewhat limited. The entry of small amounts of water into the borehole during a gaseous drilling operation causes the cuttings at the bottom of the borehole to agglomerate into sticky masses which cannot be entrained by the gas and instead adhere to the drill stem and the walls of the borehole. This interferes with the cutting action of the bit, prevents the circulation of the drilling fluid and in time may "freeze" the drill stem in the hole. Large amounts of water entering the borehole may accumulate and in time flood the well because the gas stream is not efficient for the entrainment and removal of water. For these and similar reasons, it is usually necessary to revert to the use of conventional drill muds whenever water-bearing

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formations are encountered in a gas or air drilling operation.

Various methods have been proposed for overcoming these difficulties. A number of different additives have been suggested for use in gaseous drilling fluids in order to prevent the agglomeration of cuttings. These are generally effective, however, only where the cuttings are merely moist, as in the case of certain clay formations, and are of little benefit where sizeable quantities of water are present. For example, it has been proposed that various materials be added to the gas stream, such as foaming agents to remove the water as a foam from the well. Sealing agents also have been employed in order to seal the borehole against the influx of water. As a matter of fact, a number of compounds have been developed by industry for shutting off water in air drilled wells. Two of these are resins that are based on the polymerization of water soluble monomers or an isocyanate polymer. Another process utilizes the in situ precipitation of insoluble metal hydroxides. A still older method employs a mixture of soluble elements and strong mineral acids that form weak gels after a predetermined interval. Unfortunately, the compounds that have been developed do not meet all requirements for a superior water shut-off chemical. Thus, as a compromise measure, conventional muds have been mixed with gases in order to decrease the density, but the full benefits to be derived from gaseous drilling fluids cannot be obtained in this matter. Thus, for the reasons given, the use of gaseous drilling fluids has remained of limited application.

As pointed out heretofore, this is unfortunate since the unique advantages of air drilling are very great. Therefore, air drilling is employed in dry areas where there is little likelihood of water seepage into the hole. The use of air as a replacement for mud in drilling wells could save as much as \$20,000.00 on a 6,000 ft. well. Thus, if air drilling could be made a practical, routine operation, savings by the drilling industry would amount to millions of dollars annually. Other less tangible benefits would include a continuous hydrocarbon log of the subsurface formations being drilled.

In accordance with the present process, resins prepared from styrene-polyester copolymers are utilized to effectively prevent the seepage and flow of water from the surrounding formations into the borehole. These resins are caused to flow into the water producing interval wherein they set as a strong gel or hard solid within a predetermined time and thus prevent the flow of water into the borehole. The styrene may comprise styrene or its homologues, such as vinyl toluene, vinyl naphthalene and the like. The polyester is a polymer of phthalic acid, maleic acid and diethylene glycol. The phthalic anhydride and the maleic anhydride may be utilized in lieu of the acids.

The exact nature of the present invention may be readily understood by reference to the accompanying drawing in which the figure represents, diagrammatically, a drilling apparatus for the drilling of boreholes in accordance with the invention.

Referring to the figure, reference numeral 1 represents a string of drill pipe positioned in a borehole drilled into the earth's substrata. Surface casing 2 has been set and cemented in place in the upper part of the borehole in the usual manner, the cement being designated by reference numeral 3. Attached to the lower end of the string of drill pipe is drill collar 4, to which in turn is attached rotary bit 5. The drill collar and bit may be of any conventional design, the method of the invention being suitable for use with a wide variety of drilling tools. The drill pipe, collar and bit form a continuous conduit for the conveyance of fluids to the bottom of the borehole.

Connected to the end of casing 2 above the surface is

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well head 6 which may be any of the various types capable of maintaining a fluid tight seal about the drill string during drilling. Representative of such well heads is the Guiberson type EL pressure head shown on page 2057 of the "Composite Catalog of Oil Field and Pipeline Equipment," volume 1, 1957 edition. Connected to casing 2 below the well head is discharge line 7 which serves to convey gaseous fluids from the annular section of the borehole surrounding the drill string into a separation vessel which is not shown. Line 7 is fitted with valve 8 as a control means in the event that gases under high pressure enter the borehole from the formation.

The upper end of drill pipe 1 below the well head is connected to a kelly 9 which extends upward through the well head and through platform 10 and rotary table 11. The kelly and rotary table are of conventional design. Positioned atop kelly 9 is swivel 12 which permits the introduction of fluids into the kelly and drill pipe as they are rotated by the rotary table. The swivel is supported vertically by bail 13 which may be connected to the hook of a conventional hoisting cable. Gooseneck 14 extends out of the top of the swivel and is connected to hose 15. It will be understood that various items of equipment such as instrumentation devices have been omitted from the drawing and description since they are well known in the art and are not necessary for a complete understanding of the invention.

In carrying out a drilling operation in accordance with the preferred adaptation of the present invention, a stream of air, nitrogen, natural gas, methane, ethane, or the like is continually introduced into line 17 from a source not shown. The gas stream will normally be introduced at a rate in the range of about 100 to 2000 cu. ft. per minute, although the exact range for a particular drilling operation will depend upon the depth and size of the borehole and the conditions prevailing within the borehole.

If water is encountered from formation interval 30 and if the amount of water seepage is relatively small, a foaming agent comprising a surfactant, a protein composition or the like, may be introduced into the system continuously through a line not shown. However, if the amount of water is appreciable, the resin of the present invention is forced into water producing interval 30 about the periphery of the borehole and held there until it sets up as a gel or hard solid, thus preventing further entry of the water into the borehole.

If the drilling fluid being circulated comprises a drilling mud, the resin of the present invention is pumped down the borehole by conventional means to adjacent interval 30, pressure is applied both to the annular area and to within the drill string, thus forcing the resin into formation 30 about the periphery of the borehole. Other techniques of forcing the resin into the formation may be also applied. For example, a packer may be set immediately above formation 30 and pressure only applied within the drill string. The same techniques of forcing the resin into the formation may be applied if the drilling fluid comprises a gas. Generally, known techniques, such as sand consolidating techniques, cementing techniques and the like may be utilized for forcing the resin of the present invention into the water producing interval about the borehole.

As pointed out heretofore, the present invention is concerned with a superior composition or resin for sealing porous underground water producing formation which comprises a styrene-polyester polymer.

The resins of the present invention have:

- (1) A low viscosity which is maintained until set time thereby insuring pumpability;
- (2) A 2 to 3 hour delay in reaction thereby allowing time to pump the material into the water bearing formation;
- (3) A sealing reaction that takes place rapidly thereafter; and
- (4) High mechanical gel strength.

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In addition, the resins of the present invention are of low toxicity and are easy to handle.

The resins of the present invention comprise styrene or styrene homologues copolymerized with polyesters. The polyesters are copolymers of phthalic acid, maleic acid and diethylene glycol. Phthalic anhydride and maleic anhydride can be used instead of the acids.

A very satisfactory polyester of the character described is manufactured by using approximately 2 mols of phthalic acid, 1 mol of maleic anhydride and about 2.4 mols of diethylene glycol.

One satisfactory method of manufacturing the polyester is to heat the diethylene glycol to about 100° C., then add the phthalic acid and the maleic acid and heat to a temperature in the range from about 170° to about 210° C. A preferred temperature range is in the range from about 190° to about 200° C. The time of heating ranges from about 6 to 16 hours, depending upon the particular ingredients used. It is preferred that the heating be done over an atmosphere of inert gas. Also while heating, it is desirable to flow an inert gas through the mixture in order to remove oxygen. Water is stripped off first through a warm reflux condenser and then through a relatively cool condenser. The resulting product is viscous and has a molecular weight in the range from about 800 to about 1200. A satisfactory polyester of the type described analyzes as follows:

Carbon	58.58
Hydrogen	5.04
Oxygen	36.36
Nitrogen	---
Sulfur	---
Ash	0
Molecular weight	1011
Saponification number	591
Acid number	45.7

As pointed out above, the mixture is heated for about 6 to 16 hours, depending upon the nature of the particular acid and the particular glycol used. Generally speaking, the mixture is heated to the lowest acid number without getting gelation. Generally, the mixture is heated to an acid number less than 60 and to an acid number in the range of about 5 to 50.

The mixture is then cooled to about 100° C. and a polymerization inhibitor added, generally in the concentration of from about 0.01 to 0.1% by weight. A satisfactory polymerization inhibitor is hydroquinone.

The polyester is then cooled to about 70° C. and blended with styrene or a homologue of styrene. Various amounts of styrene are added and the proper amount of catalyst added. After a pre-set interval of time, a three-dimensional or "crosslinked" polymer is formed.

Under certain conditions, the polyester may comprise an equivalent unsaturated polybasic acid, such as fumaric acid, itaconic acid, etc., and other equivalent glycols, such as ethylene glycol, triethylene glycol, propylene glycol, etc. Also under certain conditions, other saturated polybasic acids may be used instead of phthalic acid, such as adipic acid and the like.

As pointed out above, the object of the present invention is an economical, simple, relatively mistake-proof composition that will stop the flow of water into a well, preferably, an air drilled well. In addition, the material is flexible enough to be placed into position by any of several methods, including Bradenhead or packer squeezes, dump bailing, explosive "tamps," temporary gel seals, or as a dispersed phase in an air or gas stream.

The present invention fulfills the major specifications for a superior water shut-off compound. In particular, freshly made up solutions of the composition described in this invention have:

- (1) A viscosity of 5 to 40 centipoises;
- (2) Do not increase materially in viscosity until after a delay time of from 1 to 3 hours;

- (3) Harden after a 2 to 3 hour delay time; and
 (4) Have good gel strength toward hydrostatic pressure.

On either a per volume or per foot basis, materials described in this invention are more economical to use than the organic resins now offered by the industry.

The present invention will be more readily understood by the following examples illustrating embodiments of the same.

Example 1

A mixture of the following composition was prepared:

	Parts by weight
Styrene-polyester blend ¹ -----	50
Styrene (inhibited) ² -----	50
Methylethyl ketone peroxide in dibutyl phthalate (60% peroxide)-----	0.36

¹ Polyester=polymer having a molecular weight of about 1000 prepared by copolymerizing phthalic acid, maleic acid and diethylene glycol. Blend contained 30% styrene. Also a trace of cobalt naphthenate.

² Inhibitor=tertiary butyl pyrocatechol.

This mixture maintained its initial viscosity of 8 centipoises for a period of 2.5 hours at 77° F. At the end of this time a strong gel was formed which became a hard solid after 3 hours.

Example 2

A mixture of the following composition was prepared:

	Parts by weight
Styrene-polyester blend ¹ -----	50
Styrene (inhibited) ² -----	50
Toluene (as a thinner)-----	100
Methylethyl ketone peroxide in dibutyl phthalate (60% peroxide)-----	0.15

¹ Same as in Example 1.

² Same as in Example 1.

This material formed a gel after 1.2 hours and set to a stiff gel after 2.3 hours.

Example 3

A mixture of the following composition was prepared:

	Parts by weight
Styrene-polyester blend ¹ -----	50
Styrene (distilled) ² -----	50
Methylethyl ketone peroxide in dibutyl phthalate (60% peroxide)-----	0.32

¹ Same as in Example 1.

² Same as in Example 1.

This mixture was maintained in a constant temperature bath at 40° C. It formed a gel after 1 hour and hardened in 1.1 hours.

Example 4

A mixture of the following composition was prepared:

	Parts by weight
Styrene-polyester blend ¹ -----	48
Styrene (inhibited) ² -----	48
Petroleum solvent (boiling range 367-421° F.; API gravity 27° and 94% aromatics)-----	96
Isopropyl alcohol-----	32
Methylethyl ketone peroxide in dibutyl phthalate (60% peroxide)-----	0.8

¹ Same as in Example 1.

² Same as in Example 1.

After 3.5 hours, the mixture gelled. The material attained full strength after 24 hours.

Example 5

Into a column with a diameter of 3 centimeters and a length of 12 centimeters packed with 20-40 mesh Ottawa sand and saturated with a 1% sodium chloride brine was introduced under slight pressure, 27 cc. of a fluid of the following composition:

Parts by weight

Styrene-polyester blend ¹ -----	48
Styrene (inhibited) ² -----	48
6% cobalt naphthenate ³ -----	5
Methylethyl ketone peroxide in dibutyl phthalate (60% peroxide)-----	4

¹ Same as in Example 1.

² Same as in Example 1.

³ A 6% cobalt naphthenate in a solution of dibutyl phthalate or equivalent solvent.

- 10 The material was allowed to penetrate and displace the brine about $\frac{2}{3}$ of the length of the column. After the flow was stopped, the column was allowed to stand at room temperature for a period of 2 hours. At the end of this time fluids no longer would flow through the column, even under pressures of several pounds per square inch. When the material in the column was recovered and examined, it was found that the grains of the sand were firmly cemented together by an impermeable, hard resin.

Example 6

- In an approximately cylindrical core cut from quarried sandstone to dimensions of $9\frac{1}{4}$ inches diameter and 24 inches in length, a 2 inch diameter hole was drilled to a depth of 20 inches. After oven drying, the core was saturated with brine (3% sodium chloride in water) and placed in a pressure chamber provided with a packing element to isolate the 2 inch hole from the external surface of the core. The packer was provided with means for introducing fluids under pressure into the chamber. Simultaneously, fluids displaced from the core passed into the annular space around the core, thence to discharge. Into the core was introduced a resin solution of the following composition:

Styrene-polyester blend ¹ -----	2 lb. 10 oz. by weight.
Styrene (inhibited) ² -----	2 lb. 10 oz. by weight.
Cobalt naphthenate accelerator ³ ...	101 grams.
Methylethyl ketone peroxide in dimethyl phthalate (60% peroxide)-----	90 grams.
3% brine-----	25 ml.

¹ Polyester=polymer having a molecular weight of about 1000 prepared by copolymerizing phthalic acid, maleic acid and diethylene glycol. Blend contained 30% styrene.

² Inhibitor=tertiary butyl pyrocatechol.

³ A 6% cobalt naphthenate in a solution of dibutyl phthalate or equivalent solvent.

- The peroxide catalyst was added to the other ingredients just prior to use. The solution was pumped mechanically through $\frac{1}{4}$ " stainless steel lines, through the packer, and into the 2 inch hole. Four minutes were required to inject 1,500 ml. of the 8 cp. fluid into the pores of the rock.

- After one hour, the core was removed from the apparatus. The gelled resin was mechanically scraped from the hole and the core was replaced in the chamber. After 16 hours, the core withstood 500 p.s.i. of brine pressure before breakthrough.

- A second injection was carried out with a similar composition. After 3 minutes' injection, 1,100 ml. of the solution had been forced into the pores of the rock. The hardened resin was reamed out of the hole and the core was subjected to another pressure test. The fail pressure was 700 p.s.i.

- Plugs cut from typical sandstone cores before treatment with resin had dry air permeabilities of 297-411 millidarcies. The permeability to brine was 126-215 millidarcies, and the porosity averaged about 18%. The permeability of plug cut horizontally from the twice-injected core was 2.2 millidarcies, indicating that 98.7 of the original permeability had been blocked. The porosity of the plug had decreased from 18 to 12.7%. Examination of a section cut lengthwise from the core showed that the horizontal penetration of resin was approximately 3 inches.

Example 7

Using substantially the same technique as described in Example 6, another sandstone core was injected with a fluid of the following composition:

Styrene-polyester blend ¹ -----	2 lb. 10 oz. by weight.
Styrene (inhibited) ² -----	2 lb. 10 oz. by weight.
Cobalt naphthenate accelerator ³ ..	90 grams.
Methylethyl ketone peroxide in di-	
methyl phthalate (60% perox-	
ide) -----	100 grams.
1,1,2-trichloroethylene -----	300 ml.
3% brine-----	25 ml.

¹ Polyester=polymer having a molecular weight of about 1000 prepared by copolymerizing phthalic acid, maleic acid and diethylene glycol. Blend contained 30% styrene.

² Inhibitor=tertiary butyl pyrocatechol.

³ A 6% cobalt naphthenate in a solution of dibutyl phthalate or equivalent solvent.

Within a period of 5 minutes, 1,600 ml. of the above solution was injected into the pores of the rock sample.

After the resin had solidified, the resin was drilled out of the hole and the core was subjected to pressure tests as described above. On repeated tests, the pressure of failure was 800 p.s.i. A plug cut from the core indicated a permeability reduction of 88%. Examination of a longitudinal section of the core indicated that an irregular penetration of resin had been obtained.

Example 8

Using a procedure substantially as described in Example 6, another sandstone core was injected with a fluid of the following composition:

Styrene-polyester blend ¹ -----	3 lb. 15 oz. by weight.
Styrene (inhibited) ² -----	1 lb. 5 oz. by weight.
1,1,2-trichloroethylene -----	300 ml.
Methylethyl ketone peroxide in di-	
butyl phthalate (60% perox-	
ide) -----	100 grams.
6% cobalt naphthenate ³ -----	90 grams.

¹ Polyester=polymer having a molecular weight of about 1000 prepared by copolymerizing phthalic acid, maleic acid and diethylene glycol. Blend contained 30% styrene.

² Inhibitor=tertiary butyl pyrocatechol.

³ A 6% cobalt naphthenate in a solution of dibutyl phthalate or equivalent solvent.

The solution had a specific gravity greater than that of the brine and had a viscosity of 23 centipoises.

After 5 minutes injection, 1,600 ml. of the solution have been forced into the pores of the rock. Repeated back pressure tests of this core gave failure pressures of 2,400 to 2,500 p.s.i. At 300 p.s.i. differential pressure, the untreated core flowed brine at 51.5 g.p.h. After injection, the flow rate was reduced to 0.3 g.p.h. (permeability reduction of 99.4%). A small plug cut immediately below the packer zone had a permeability of 2.6 millidarcies or a permeability reduction of 99%.

A longitudinal slice of the core showed that a considerably more uniform degree of penetration than that in Example 7 had been obtained.

Example 9

Into a limestone which was cut to same dimensions as the core of Example 6, and whose permeability was approximately 6.6 millidarcies, was injected a fluid of the following composition:

Styrene-polyester blend ¹ -----	2 lbs. 10 oz. by weight.
Styrene (inhibited) ² -----	2 lbs. 10 oz. by weight.
Cobalt naphthenate	
accelerator ³ -----	100 grams.
Methylethyl ketone peroxide in	
dibutyl phthalate (60% per-	
oxide) -----	90 grams.
Brine -----	100 grams.

¹ Polyester=polymer having a molecular weight of about 1000 prepared by copolymerizing phthalic acid, maleic acid and diethylene glycol. Blend contained 80% styrene.

² Inhibitor=tertiary butyl pyrocatechol.

³ A 6% cobalt naphthenate in a solution of dibutyl phthalate or equivalent solvent.

After 6 minutes' injection, approximately 2,000 ml. of brine was displaced from the core by the fluid. A second injection of this core was made because the first injection sealed a high permeability zone without affecting a lower permeability zone in the core. A back pressure test after the resin placed by second injection had hardened gave 1,200 p.s.i. failure pressure. The permeability reduction in a small plug cut from the core was 96%. A longitudinal section of the core indicated a penetration of as little as $\frac{5}{32}$ inch.

Example 10

The polymer prepared in accordance with Example 8 was tested so as to determine flowability of brine through various cores before and after. The results of these tests are as follows:

	Flow gallons per hr./ft. ¹		Percent shut off
	Original	Treated	
Styrene-Polyester plus Pozzolan A ² -----	181	0.5	99.7
Styrene-Polyester-----	351	4.1	98.8
Styrene-Polyester-----	285	2.4	99.2

¹ At $\Delta P=300$ p.s.i.

² Equal parts by weight used.

From the above, it is apparent that excellent shut-off of the sand was secured.

Example 11

A polymer prepared in accordance with the present technique comprised 50 parts by weight of polyester, 50 parts by weight of vinyl toluene, 300 cc. of trichloroethylene, 6% of cobalt naphthenate solution, 21 grams of methylethyl ketone peroxide solution and 100 cc. of water. The core test with respect to this polymer was as follows:

	Flow gallons per hr./ft. ¹		Percent shut off
	Original	Treated	
Vinyl Toluene-Polyester, 34 cp.-----	136	3.4	98.2

¹ At $\Delta P=300$ p.s.i.

Example 12

A polymer prepared using 1000 grams of polyester, 1375 grams of vinyl toluene, 480 grams of trichloroethylene, 19 grams of 6% of cobalt naphthenate and 19 grams of methylethyl ketone and 100 cc. of water was core-tested as described above with the following results:

	Flow gallons per hr./ft. ¹		Percent shut off
	Original	Treated	
Vinyl toluene-Polyester, 18 cp.-----	438	3.3	99.2

¹ At $\Delta P=300$ p.s.i.

The present invention is concerned with an improved sealing technique, particularly, for the prevention of flow of water into a borehole, particularly, when using an air drilling operation by utilizing a particularly desirable type of a gelling resin. In essence, the resin prior to gelling comprises a blend of styrene and a polyester which has a molecular weight in the range from about 800 to 1200. The viscosity of the blend is in the range from about 5 to 40 centipoises, preferably, about 20 to 30 centipoises. The resin solution has a gelling time in the range from about 1 to 3 hours.

The polyester is prepared as described heretofore from phthalic anhydride, maleic anhydride and a glycol as, for example, diethylene glycol. The phthalic acid or the

maleic acid may be used in lieu of the anhydride. The polyester may comprise from 0.5 to 5.0 mols of phthalic anhydride, 0.5 to 3 mols of maleic anhydride and 1.0 to 5.0 mols of diethylene glycol. A particularly desirable polyester comprises about 2 mols of phthalic anhydride, about 1 mol of maleic anhydride and about 2.4 mols of diethylene glycol. The polyester is prepared by a technique heretofore described. The amount of polyester employed with respect to the styrene utilized to form the resin is about 20 to 40% by weight of the polyester and about 80 to 60% by weight of the styrene. A desirable ratio of polyester to styrene is about 1 part by weight of the polyester to 2 parts by weight of the styrene.

A gelling catalyst is employed to cause a reaction whereby on gelling the polyester is crosslinked with the styrene or a styrene homologue. The preferred catalyst comprises methylethyl ketone peroxide in a suitable solvent, such as dibutyl phthalate. Other gelling catalysts may comprise benzoyl peroxide which require a slightly higher temperature, such as 50° C. Other gelling catalysts comprises lauroyl peroxide or 2,4-dichlorobenzoyl peroxide. Generally, it is preferred that about 0.1 to 2.5% by weight of the catalyst be used based upon the total weight of polyester and styrene present. Under certain conditions, it may be desirable to use from 50 to 150% by weight of a thinner such as toluene or another aromatic type of oil.

Under certain conditions, it may also be desirable to use solubilizing agents such as isopropyl alcohol or other low molecular weight alcohols. The amount of solubilizing agent employed may vary from 20 to 60% by weight based upon the total amount of polyester and styrene present.

A preferred method of manufacturing the gelling resin composition of the present invention is to use from 0.01 to 3.0% by weight of an accelerator based upon the amount of polyester and styrene present. The preferred accelerator comprises 6% solution of cobalt naphthenate. The solvent may be dibutyl phthalate, a medium-boiling petroleum distillate. The preferred accelerators comprise the cobalt and manganese salts of organic acids such as cobalt tallate, manganese naphthenate and the like. Another accelerator comprises N-phenyl morpholine. This latter accelerator is particularly desirable when the catalyst comprises benzoyl peroxide. It is preferred that the amount of accelerator used be in the range from .1 to 0.5% by weight based upon the amount of polyester and styrene present.

Under certain conditions as, for example, when it is necessary that a relatively high concentration of the accelerator be utilized, it is desirable to use from 0.5 to 2%, preferably, about 1% of a saturated brine solution as an inhibitor.

Also, under certain conditions, it is desirable to use a weighting agent, such as trichloroethylene, carbon tetrachloride or an active agent, such as dichlorostyrene. The amount used is preferably in the range from about 25 to 50% by weight of the weighting agent based upon the amount of polyester and styrene present. In general, the weighting agent should have a specific gravity greater than that of water up to about 1.6. The weighting agent will prevent the resin from accumulating at the top of the interval to be sealed off.

When the formation to be sealed up has relatively high permeability, it is desired to use a filter control agent such as Pozzolan. This agent has a specific gravity in the range from about 2.3 to 2.8. The properties of Pozzolan are described in "Engineering News Record," issue of April 5, 1951, in an article by Raymond E. Davis, entitled "What You Should Know About Pozzolan." This material controls rate of penetration of the resin into the formation surrounding the hole by forming a filter cake of lower permeability than that of the surrounding forma-

tion. Generally, it is preferred to use about 50 to 200% by weight of Pozzolan or equivalent, particularly, about an equal quantity of Pozzolan based upon the weight of polyester and styrene present.

While the present invention is specifically directed towards sealing off borehole walls in an air drilling operation, the composition may be used to seal off other formations exposed in other openings, such as mine shafts, underground gas and liquid storage reservoirs and the like.

What is claimed is:

1. Improved process for preventing the flow of fluids from a subterranean formation into a well borehole which comprises injecting into said formation a gel forming blend comprising a polyester secured by copolymerizing a phthalic organic compound, a maleic organic compound and a glycol; and a vinyl aromatic along with a gelling catalyst wherein said copolymerizing is carried out by heating the glycol to about 100° C., then adding said phthalic organic compound and said maleic organic compound and heating the mixture to a temperature in the range from about 170° to about 210° C. for a time period in the range from about 6 to 16 hours, and thereafter cooling said latter mixture to a temperature of about 70° C. and copolymerizing with said vinyl aromatic.

2. Process as defined by claim 1 wherein said polyester is secured by copolymerizing phthalic acid, maleic acid and diethylene glycol under conditions to secure a polymer having a molecular weight in the range of about 800 to 1200; and wherein said vinyl aromatic comprises styrene and wherein the amount of polyester present in the blend is about 20 to 40% by weight, wherein the amount of styrene present is about 80 to 60% by weight, and wherein the viscosity of the blend is in the range from about 5 to 40 centistokes.

3. In the drilling of a well bore into the earth's substrata wherein a gas is used to remove the cuttings to the surface and wherein a water producing subsurface interval is encountered, the improvement which comprises injecting into said water producing interval a gel forming blend comprising a polyester secured by copolymerizing a phthalic acid, a maleic acid and diethylene glycol; and a vinyl aromatic along with a gelling catalyst, wherein the amount of polyester in the blend is about 20 to 40% by weight and wherein the amount of styrene present is about 80 to 60% by weight and wherein the viscosity of the blend is in the range from about 5 to about 40 centipoises, maintaining said blend in said formation for a time interval, whereby said blend will gel and thereafter prevent the flow of water into the well bore.

4. Process as defined by claim 3 wherein an accelerator inhibitor, a weighting agent and a filter control agent is present.

5. Process as defined by claim 4 wherein accelerator inhibitor comprises brine wherein said weighting agent is selected from the class consisting of trichloroethylene and carbon tetrachloride and wherein said filter control agent comprises Pozzolan.

6. Process as defined by claim 3 wherein from about 20 to 60% by weight of a solubilizing agent selected from the class of low molecular weight alcohols is used.

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