

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here
Insert (in
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Applicant or
Applicants,
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Address (es).

XX (1) BASF CORPORATION
We
of 9 Campus Drive, Parsippany, N.J. 07054, United States
of America

(2) Here
Insert Title
of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)

FLUID LOSS CONTROL ADDITIVES FOR OIL WELL CEMENTING COMPOSITIONS

(3) Here insert
number(s)
of basic
application(s)

which is described in the accompanying complete specification. This application is a
Convention application and is based on the application numbered (8)

195,807

(4) Here insert
Name of basic
Country or
Countries, and
basic date or
dates

for a patent or similar protection made in (4) United States of America
on 19th May 1988

~~xxx~~ Watermark Patent & Trademark Attorneys
Our address for service is Messrs. Edward Waters & Sons, Patent Attorneys,
50 Queen Street, Melbourne, Victoria, Australia.

DATED this 17th day of May 1989

BASF CORPORATION

(5) Signa-
ture of
Applicant (or
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Seal of
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Signatures of
its Officers as
prescribed by
its Articles of
Association

Louis C. Gebhardt

Registered Patent Attorney

To:

THE COMMISSIONER OF PATENTS.

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1962

DECLARATION IN SUPPORT OF A CONVENTION
APPLICATION FOR A PATENT OR PATENT OF ADDITION(1) Here
insert (in
full) Name of
Company.

In support of the Convention Application made by⁽¹⁾ BASF Corporation, a corporation organized and existing under the laws of the State of Delaware, with a registered office at 9 Campus Drive, Parsippany, N.J. 07054, United States of America,
(hereinafter referred to as the applicant) for a Patent

(2) Here
insert title
of Invention.

for an invention entitled:⁽²⁾ FLUID LOSS CONTROL ADDITIVES FOR OIL WELL CEMENTING COMPOSITIONS

(3) Here
insert full Name
and Address,
of Company
official
authorized
to make
declaration.

I,⁽³⁾ Werner Kuesters,
of BASF Corporation, 1419 Biddle Avenue,
Wyandotte, MI 48192-3736

do solemnly and sincerely declare as follows:

1. I am authorised by the applicant for the patent
to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was
made in⁽⁴⁾ United States of America under Serial No. 195,807

(4) Here
insert basic
Country or
Countries
followed by
date or dates
and basic
Applicant or
Applicants.

on the 19th day of May 1988, by CLARE H. KUCERA, STEFANO C. CREMA, MICHAEL D. ROZNOWSKI, GERD KONRAD and HEINRICH HARTMANN
XXXXXXXXX XXXXXXXXX XXXXXXXXX

3. (5)

(5) Here
insert (in
full) Name
and Address
of Actual
Inventor or
Inventors.

CLARE H. KUCERA, a citizen of the United States of America, residing at 21314 Canterbury, Grosse Ile, Michigan 48138, U.S.A.; STEFANO C. CREMA, a citizen of Australia, residing at 1427 East Park Pl., Ann Arbor, Michigan 48104, U.S.A.; MICHAEL D. ROZNOWSKI, a citizen of the United States of America, residing at 1740 N. Trenton Drive, Trenton, Michigan 48183, U.S.A.; GERD KONRAD and HEINRICH HARTMANN, citizens of the Federal Republic of Germany, residing, respectively, at 33 Albert-Einstein-Allee, 6703 Limburgerhof; and 46 Weinheimerstrasse, 6703 Limburgerhof, Federal Republic of Germany.

is/are the actual inventors of the invention and the facts upon which the applicant is entitled to make the application are as follow:

The applicant is the assignee of CLARE H. KUCERA, STEFANO C. CREMA, MICHAEL D. ROZNOWSKI, GERD KONRAD and HEINRICH HARTMANN.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Wyandotte, U.S.A.
this 15th day of March 1989

(6) Signature.

W. Kuesters
Werner Kuesters

(6) BASF CorporationTo: THE COMMISSIONER OF PATENTS.

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- (56) Prior Art Documents
US 4471097
US 3025234
US 4632186
- (57) Claim

1. A cementing composition useful in cementing oil, gas and water wells comprising:
- water;
 - hydraulic cement; and
 - a fluid loss additive in an amount effective to reduce fluid loss from the cement slurry to the surrounding rock formations, said fluid loss additive comprised of a copolymer of acrylamide type monomer and a basic vinylheterocyclic monomer and derivatives thereof in a weight per cent ratio of from 95:5 to 5:95, said copolymer having a molecular weight range of from 10,000 to 3,000,000, said acrylamide monomer selected from the group consisting of acrylamide, methacrylamide, N,N-dimethyl(meth)acrylamide, dialkylaminoalkyl(meth)acrylamide and mixtures thereof, said basic vinyl heterocyclic monomer selected from the group consisting of 1-vinylimidazole, 2-vinylimidazole, 2-methyl-1-vinylimidazole, 4-methyl-1-vinylimidazole, 5-methyl-1-vinylimidazole, 2-ethyl-1-vinylimidazole, 2-propyl-1-vinylimidazole, 2-isopropyl-1-vinyl-

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imidazole, 2-phenyl-1-vinylimidazole, 1-vinyl-4, 5-benzimidazole, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine and mixtures thereof.

9. A method of cementing a conduit in a borehole penetrating an earthen formation by introducing a cementing composition into the space between said conduit and said formation, wherein said cementing composition comprises:

- a) water;
- b) hydraulic cement; and
- c) a fluid loss additive in an amount effective to reduce fluid loss from the cement slurry to the surrounding rock formations, said fluid loss additive comprised of a copolymer of acrylamide/basic vinylheterocyclic monomer and derivatives thereof in a weight percent ratio of from 95:5 to 5:95, said copolymer having a molecular weight range of from 10,000 to 3,000,000, said acrylamide monomer selected from the group consisting of acrylamide, and acrylamide hydrolysis products, methacrylamide, N-N-dimethyl(meth)acrylamide, dialkylaminoalkyl(meth)acrylamide and mixtures thereof and said basic vinyl heterocyclic monomer selected from the group consisting of 1-vinylimidazole, 2-vinylimidazole, 2-methyl-1-vinylimidazole, 4-methyl-1-vinylimidazole, 5-methyl-1-vinylimidazole, 2-ethyl-1-vinylimidazole, 2-propyl-1-vinylimidazole, 2-isopropyl-1-vinylimidazole, 2-phenyl-1-vinylimidazole, 1-vinyl-4, 5-benzimidazole, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine and mixtures thereof.

614367

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

Class

Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

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Related Art:

Name of Applicant: BASF CORPORATION

Address of Applicant: 9 Campus Drive, Parsippany, N.J. 07054, United States of America

Actual Inventor: CLARE H. KUCERA, STEFANO C. CREMA, MICHAEL D. ROZNOWSKI, GERD KONRAD
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50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

FLUID LOSS CONTROL ADDITIVES FOR OIL WELL CEMENTING COMPOSITIONS

The following statement is a full description of this invention, including the best method of performing it known to us

FLUID LOSS CONTROL ADDITIVES FOR
OIL WELL CEMENTING COMPOSITIONS

The present invention relates to an aqueous cementing composition and a method of using the same in cementing oil and gas wells and the like. More particularly, the present invention relates to the incorporation into the cementing composition of copolymers, prepared by the copolymerization of acrylamide and vinyl imidazole in ratios of from about 95:5 to 5:95 by weight, as fluid loss additives in oil and gas well cementing operations.

The copolymerization of acrylamide and vinyl imidazole with a suitable third monomer generally does not affect the effectiveness of these materials as fluid loss additives for cement slurries. Partial substitution of vinyl imidazole with lower cost monomers which do not have deleterious effects on the stability of the polymer and rheology of the cement slurries can, in fact, be advantageously considered.

The incorporation of such copolymers and/or terpolymers as fluid loss additives for the cement slurries

used in the completion of oil and gas wells, greatly reduces the loss of water from the cement slurry to the rock formation.

Optionally, a dispersant such as polynaphthalene sulfonate may also be incorporated into the cement slurry with the copolymer and/or terpolymer. When polynaphthalene sulfonate is incorporated into the slurry with the fluid loss additive, there is a synergistic effect between the dispersant and the additive which results in an even greater reduction of fluid loss than could be achieved using either ingredient alone.

The incorporation of the fluid loss additives of the present invention into cement slurries greatly reduces fluid loss in oil and gas well cementing operations and allows for a more efficient bonding between the oil or gas well liners and the rock formations.

Oil well cementing and other underground cementing operations often require placement of a slurry of cement, water and other additives in a porous environment such as porous earthen or rock strata. For example, cement compositions are routinely used in the oil and gas industry to cement the annular space in the well bore between the

surrounding formation and the pipe or casing. Typically, the cement slurry is pumped down the inside of the casing and back up the outside of the casing through the annular space. The slurry is allowed to set up or harden in the annular space, thereby forming a rigid column which ideally forms a bond with the earth or rock formations as well as with the metal pipe or casing. To achieve a satisfactory primary cementing job, it is essential to achieve a tight bond to prevent vertical communication of fluids or gas along or within the column, which could contaminate the producing zone, or permit a loss of reserves.

The primary functions of the cementing process are to restrict fluid movement between geological formations and to bond and support the casing or metal pipe. In addition, the cement aids in protecting the casing from corrosion, preventing "blow-outs" by quickly sealing formations, protecting the casing from shock loads in drilling deeper wells and sealing off lost circulation or thief zones.

A common problem in petroleum well cementing is the flow of liquid from the slurry into the porous earth formations in contact with the cement. This fluid loss is undesirable since it causes thick filter cakes of cement solids which can ultimately plug the well bore. The fluid

loss can also damage rock formations and affect well production. Fluid loss from cement slurries is particularly a problem in a process known as "squeeze cementing".

Problems develop when water filters out of the slurry and into the porous media during the placement and setting period of the cement. As a result of the attendant rapid water loss, the cement experiences impaired qualities of strength and an uncontrolled setting rate. Also, the water loss from the cement frequently damages the porous rock formations. This problem cannot be solved by adding more water to the slurry as this approach only exacerbates the problem. In addition, serious placing and setting problems may occur.

It is therefore of utmost importance that fluid loss control be achieved in order to insure satisfactory primary cementing. Inadequate fluid loss control can result in the formation of a bridge in the annulus opposite a permeable zone, thus isolating a lower zone from the hydrostatic pressure above the bridge. Only a small amount of filtrate loss beneath such a bridge is then necessary to drop the annular pressure to beneath that of the formation. The result is an influx of formation fluids and pressure, thereby creating flow channels and the need for often times expensive remedial work.

In order to attempt the control of fluid loss from the cement slurry to the surrounding rock formation, the cement matrix permeability must be reduced. This reduction allows the retention of a greater amount of water during the initial set, thereby effectively blocking the porous strata from the cement. The art is replete with examples of methods to achieve this goal. One way is to reduce filtrate mobility by increasing the filtrate viscosity to counter the normal thinning of the cement slurry which occurs at down hole temperatures. An increase in filtrate viscosity at down hole temperatures minimizes thermal thinning and increases the retention of the filtrate within the cement matrix. Conventional fluid loss additives do not satisfactorily address the problem of thermal thinning with increased temperature, thereby allowing increased fluid loss from the slurry to the formation and promotion of stratification of solids within the cement slurry column.

Accordingly, there is a greatly felt need for new materials which, when added to the cement slurries, reduce fluid loss to the surrounding rock formations.

Fluid loss additives in cementing compositions are old and well known in the art. Fluid loss additives have been discussed in the following articles:

Carter, Gregg and Slagle, Knox, "A Study of Completion Practices to Minimize Gas Communication", Society of Petroleum Engineers, Paper No. 3164, November 1970.

Christian, W.W., Chatterji, Jiten and Ostroot, Warren, "Gas Leakage in Primary Cementing - A Field Study and Laboratory Investigation", Society of Petroleum Engineers, Paper No. 5517, October, 1975.

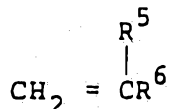
Cook, C. Cunningham, W., "Filtrate Control: A Key in Successful Cementing Practices", Journal of Petroleum Technology, August, 1977, page 951.

Smith, Dwight, "Cementing: SPE Monograph Volume 4, published by Millet the Printer, Inc., Dallas, Texas, 1976.

The patent literature is also replete with many attempts to overcome the fluid loss control problems associated with oil and gas well cementing operations. There are many references directed to protecting potable water by isolating hydrocarbon bearing strata by efficient cementing operations.

Uhl, U.S. Patent No. 4,471,097 relate to auxiliary agents for chemical flooding of petroleum deposits and auxiliary agents used in well drilling fluids. These agents are water-soluble copolymers containing 20 to 80 percent by

weight of unsaturated olefinic sulfonic acid, 5 to 15 percent by weight vinylacrylamine, 0 to 40 percent by weight acrylamide and/or methacrylamide, 5 to 50 percent by weight vinylimidazole, 0 to 10 percent by weight of



wherein R⁵ is hydrogen or methyl, and R⁶ represents hydroxy, alkoxy carbonyl with 1 to 12 carbon atoms in alkoxy moiety, cycloalkoxy carbonyl with 6 to 10 carbon atoms in cycloalkoxy moiety, phenyl, alkanoyloxy with 1 to 4 carbon atoms, or β-hydroxyalkoxy carbonyl with 2 or 3 carbon atoms in hydroxyalkoxy moiety; and 0 to 25 percent by weight of a cross-linking agent containing at least two olefinic double bonds.

These copolymers are used in drilling fluid additives during drilling operations. WP 8302449, which is the equivalent of U.S. Patent 4,471,097 discloses the use of these copolymers in deep bore cement compositions to act as rheology additives.

No showing is made in Uhl et al of using these copolymers as fluid loss additives in cement slurries to avoid fluid loss from the cement to surrounding rock

formations, and without adversely affecting the viscosity of the cement slurry.

Siegle, U.S. Patent No. 3,197,428 discloses compositions comprising cement and copolymers of acrylamide and acrylic acid to improve well cementing operations and reduce fluid loss from the cement to the rock formations. However, the compositions of Siegle are not entirely satisfactory because they retard cement setting at high temperatures and so cannot be used at elevated temperatures and pressures such as are encountered in deep oil and gas well operations.

Weisend, U.S. Patent No. 3,359,225 discloses cement additives containing polyvinylpyrrolidones and a condensate of sodium naphthalene sulfonate and formaldehyde. The polyvinylpyrrolidone reduces the separation of water from the cement slurry. The naphthalene sulfonate condensate is the dispersant. There is no teaching of the copolymers and/or terpolymers of the present invention.

Gibson et al, U.S. Patent No. 3,491,040 disclose an aqueous hydraulic cement slurry including hydraulic cement, water, a surfactant and a small amount of polyalkylenepolyamine, polyalkenimine or mixtures thereof. Gibson et al also disclose a sulfonated naphthalene conden-

sate dispersant as an additional additive to the cement slurry which cooperates with the polyamine additive to provide satisfactory fluid loss in cement slurries used at about 200°F and below. The sulfonated naphthalene dispersant is typically a low molecular weight material, e.g., in the range of about 1,000 to 3,000.

Harrison, U.S. Patent No. 3,409,080 discloses an aqueous cementing composition which is adapted to high turbulent flow. The disclosure teaches the polyvinyl alcohol and polyvinyl acetate can be used as fluid loss additives in oil well cements.

Perisinski et al, U.S. Patent No. 4,015,991, discloses a fluid loss additive for cement compositions which is a copolymer of acrylamide/2-acrylamido-2-methylpropane sulfonic acid derivative. These copolymers are useful only in operations where the bottom hole circulation temperature ranges from 90° to 125°F. Further, these copolymers have a salt tolerance of only up to 10 percent.

Cellulose-based fluid loss additives such as methyl cellulose, carboxymethylcellulose (CMC) and hydroxyethylcellulose (HEC) may be employed with or without a dispersant such as polynaphthalenesulfonic acid salts. However, there are several disadvantages to the use of CMC

or HEC as cement fluid loss control additives. These materials are solid and as a result are difficult to handle in offshore operations. In addition, they tend to considerably increase slurry viscosity, thereby preventing its movement under turbulent flow conditions and retard the set of the cement. Also, these materials lose effectiveness in the presence of soluble calcium salts and at elevated temperatures.

Hence, the industry desires a fluid loss additive that has as little effect on cement properties as is possible and still provides for the fluid loss properties which are necessary for the cementing of casings to rock formations. Further, any fluid loss additives should be compatible with as many other additives as possible and should be useable over as wide a range of temperatures and other environmental conditions as is possible.

The present invention relates to cementing compositions and more particularly to fluid loss additives which may be incorporated into the cement compositions. The cement compositions are useful in cementing operations in oil and gas wells and are comprised of water, hydraulic cement and copolymers and/or terpolymers. When a copolymer

of acrylamide and ~~vinyl imidazole~~ ^{a basic vinylheterocyclic monomer} is used, they are present in a ratio of 95:5 to 5:95, and more preferably in a ratio of from about 80:20 to 20:80. When a terpolymer is to be used, it may consist of acrylamide and ~~vinyl imidazole~~ ^{a basic vinylheterocyclic monomer} and any other suitable monomer. The terpolymer is comprised of 5 to 95 to 95 to 5 weight percent of acrylamide and vinyl imidazole, and 0 to 60 weight percent additional monomer. The copolymer has a molecular weight range of from about 10,000 to 3,000,000 and preferably between 100,000 to 1,000,000 where the molecular weights have been determined by GPC using polyethylene glycol standards. When a terpolymer is employed, it has a molecular weight range of from about 10,000 to 3,000,000, and preferably between 100,000 to 1,000,000. The copolymer and/or terpolymer function as fluid loss additives and are present in an amount effective to reduce fluid loss from the cement slurry to surrounding rock formations.

Optionally, the cementing composition may contain an effective amount of a dispersant such as polynaphthalene sulfonate. When this dispersant is present, there is a synergistic effect between the dispersant and the fluid loss additive which results in greater effectiveness of the system in reducing fluid loss than could be expected when



using the dispersant and copolymer and/or terpolymer separately. The dispersant also further decreases the viscosity of the slurry, thereby aiding in pumping of the slurry into the annular space.

5 The fluid loss additive may be used in any amount which is effective in reducing the fluid loss from the cement slurry to the surrounding rock formations. Ideally, the fluid loss additive should be present in an amount of about 0.05 to 2.0 percent by weight of the cement, and
10 preferably in an amount of about 0.125 to 1.0 percent by weight of the cement.

Cementing compositions are disclosed which provide for fluid loss control and use over a wide range of temperature and well conditions. The cementing compositions are
15 comprised of water, hydraulic cement, a fluid loss additive comprising a particular copolymer of an acrylamide type monomer and a basic vinylheterocyclic monomer such as vinylimidazole, vinylpyridine their derivatives, and mixtures thereof, or a terpolymer of acrylamide, vinyl
20 imidazole and any other suitable monomer, and optionally, a dispersant such as polynaphthalene sulfonate. The use of a dispersant has a synergistic effect on the copolymer or

terpolymer and results in an unexpected increase in its effectiveness as a fluid-loss additive.

The copolymer used in the cementing compositions of this invention include an acrylamide and associated
 5 acrylamide derivatives selected from the group consisting of acrylamide, methacrylamide, N,N, dimethyl(meth)acrylamide, N,N, dialkylamino- alkyl(meth)acrylamide, and mixtures thereof. The other monomer of the acrylamide/^{basic vinyl heterocyclic monomer}~~vinyl~~
 10 ~~imidazole~~ copolymer is a basic vinyl heterocyclic monomer selected from the group consisting of 1-vinylimidazole, 2-vinylimidazole, 2-methyl-1-vinylimidazole, 4-methyl-1-vinylimidazole, 5-methyl-1-vinylimidazole, 2-ethyl-1-vinylimidazole, 2-propyl-1-vinylimidazole, 2-isopropyl-1-vinylimidazole, 2-phenyl-1-vinylimidazole, 1-vinyl-4, 5-benzimidazole, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine and mixtures thereof. Preferred is 1-vinylimidazole. These are copolymerized in a weight ratio of from about 95:5 to 5:95 and preferably 80:20 to 20:80. The
 15 copolymer has a molecular weight of from about 10,000 to 20 3,000,000 and preferably between 100,000 to 1,000,000.

The copolymer is made in a conventional copolymerization process such as solution, emulsion or bulk polymerization in the presence of conventional free radical



initiators. Such procedures are well documented and are well known to those skilled in the art.

The terpolymer may include any suitable monomer in addition to the copolymer mentioned above. These monomers

5 may include unsaturated acid monomers and alkali metal, ammonium or organic amine salts thereof, water soluble or dispersible derivatives of acrylic acid and acrylamide such as N,N-dialkylaminoalkyl(meth)acrylamide, N,N-dialkylamino-alkyl(meth)acrylate, ethyl acrylate, methyl acrylate, acrylamido methylpropane sulfonic acid sodium salt, hydroxypropylacrylate and other vinyl monomers with sufficient water solubility or dispersibility such as vinyl pyrrolidone, vinyl amine, vinyl formamide, sodium vinylsulfonate, acrylonitrile, vinylacetate. The quaternary salts of the appropriate amino containing monomers listed above are also suitable comonomers for the terpolymers in question.

In its terpolymer form, the range of the three components is from about 0 to 60 weight percent additional monomer, from about 5 to 95 weight percent acrylamide and from about ~~5 to 95~~^{95 to 5} weight percent vinyl imidazole.

The terpolymers are made by conventional polymerization techniques as are well known to those skilled in the art.



The polymers can be added to the cement composition in dry, solution or emulsion form.

The result of the inclusion of the fluid loss additives of the present invention are improved pumpability of the cement which generally improves drilling fluid removal and reduced possibility of lost circulation, when cementing a conduit penetrating a permeable earthen formation.

The cement component of the cement composition of this invention may be any of the API classes of cement or cement blends, as are defined in the American Petroleum Institute Bulletin entitled "API Specification for Material and Testing for Well Cements", Third Edition, dated July 1, 1986 ("API Spec. 10"), and incorporated herein by reference. These include cements defined as Classes A through H in API Spec. 10.

As previously stated, the cement compositions of this invention may optionally include dispersants such as any anionic surfactant i.e., any compound which contains a hydrophobic portion (e.g., any hydrocarbon substituent such as alkyl, aryl or alkylaryl group) and a hydrophilic portion (e.g., any negatively charged moiety, such as O^- , CO_2^- , or SO_3^-). Suitable dispersants include sulfonic acid deriv-

atives of aromatic hydrocarbons, such as naphthalene sulfonic acid formaldehyde condensation product derivatives, particularly their sodium or potassium salts. Examples of dispersants which may be used include lignosulfonates, sodium and potassium naphthalene sulfonate formaldehyde condensation products (such as LOMAR D commercially available from Diamond Shamrock Chemical Company), and sodium salts of ketone sulfonate formaldehyde.

The cement compositions may also include at least one inorganic salt. Suitable salts include inorganic monovalent and polyvalent metal salts, such as magnesium chloride, ammonium chloride, sodium and potassium chloride and calcium chloride.

Other additives conventionally added to cement compositions useful in cementing casings in the bore hole of a well can also be added to the cement compositions of this invention in the amount which are normally used by those skilled in the art. These additives may include, for example, (1) heavy weight additives, such as hematite, ilmenite, silica flour and sand; (2) cement retarders such as lignins and lignosulfonates; and (3) additives for controlling lost circulation; such as walnut hulls and cellophane flakes.

The fluid loss additives of the present invention will effect a substantial reduction in the rate of water loss by filtration and in the apparent viscosity of the cement slurries. They are easily mixable and result in good fluid loss control while still exhibiting good flow properties at 0.05 percent to 2 percent by weight addition to the cement, depending upon the type of cement. Under API standards, excellent fluid loss rates below 100 cc/30 min can be achieved by the addition of about 0.05 percent to 2 percent by weight of the cement of such fluid loss additive to cement slurry of average density. Typically, a fluid loss of between about 20 and 100 cc/30 min., can be observed with a 0.25 percent to 0.50 percent by weight of the cement (BWOC) addition of the additives of the present invention.

Fluid loss properties can be controlled in salt cement formulations (such as up to saturated NaCl and seawater) with the addition of 0.25 percent to 0.50 percent by weight of the cement of the additives of the present invention without affecting rheology adversely.

Fluid loss varies as a function of molecular weight (MW). The molecular weight is a significant determinant in the properties of a product. The viscosity of a solution increases at a fixed concentration with higher

MW of the solute. In addition, film and solution properties change with MW values. The molecular weight grades of various copolymers may be identified by a determination of, the intrinsic viscosities of the polymers which are defined
5 in the following equation:

$$\text{Intrinsic Viscosity} = K(MW)^a$$

10 where K and a are constant for a given series of polymers.

As the intrinsic viscosity increases, one may extrapolate that the molecular weight of the additive increases. Further, the higher the molecular weight of the additive presumably the more viscous the cement slurry becomes, and the better the fluid loss properties become.
15 However the data, as indicated in Example 2, reveals that there is an optimum acrylamide/vinylimidazole copolymer molecular weight after which no further improvement in fluid loss is possible.

20 The polymeric additives of the present invention exhibit some retardation effects on the cement slurry. The magnitude of the increase in thickening time of the cement slurries will depend on the temperature, pressures and

slurry composition. Also, the additives of the present invention do not excessively thicken the cement, which allows for the incorporation into the cement of other additives and ingredients as many be dictated by on-site use
5 conditions.

The following examples are presented in order to illustrate various aspects of the invention. Those skilled in the art will appreciate that the examples are not to be construed as limiting the scope and spirit of the invention.

10 In the following Examples, all cement slurries were prepared according to API Spec. 10, Third Edition, July 1, 1986.

Table I is an explanation of the symbols and abbreviations used in the tables containing the data of the
15 examples. The symbols and abbreviations used therein are standard in the art and are well known to those of ordinary skill in the art.

Table IExplanation of the Symbols Used in the Following Tables

5	AM/VI	Acrylamide/vinylimidazole copolymer Comp A: AM=80%; VI=20% by weight Comp B: AM=60%; VI=40% by weight Comp C: AM=40%; VI=60% by weight
	Dispersant	Sodium salt of condensed naphthalene sulfonate, Lomar D from Henkel
	BWOC	By Weight of Cement
	BWOW	By Weight of Water
10	Fluid Loss	Amount of water lost by the slurry over 30 min. under the conditions of the test.
	Compressive Strength	Pounds per square inch needed to crush the cement after 24 hour set at the test temperature.
15	Reference:	American Petroleum Institute, Specification 10, July, 1986.
	MAM/VI	methylacrylamide/vinylimidazole
	AM/MAM/VI	acrylamide/methylacrylamide/vinylimidazole
20	AM/VP/VI	acrylamide/vinylpyrrolidone/vinylimidazole

Example 1

Example 1, as depicted in Table II, shows the effectiveness of the acrylamide/vinylimidazole copolymers as fluid loss additives for oilfield cement. Slurries containing these materials at different concentrations are compared with neat cement slurries or cement slurries containing only the polynaphthalene sulfonate dispersant. An increase in the content of vinyl imidazole in the copolymers does not greatly affect the fluid loss of the slurry but considerably reduces the thickening times and improves the 24-hour compressive strength of the set cement.

Example 2

Example 2 shows how the molecular weight of the copolymers used affects, to a certain extent, the amount of fluid lost by the cement slurry. In Table III, the different molecular weights of the additives used are expressed by the "intrinsic viscosities", where increasing intrinsic viscosity values correspond to higher molecular weights. It is apparent from the data that there are optimal molecular weights at which the additives claimed in the patent perform the most effectively in controlling fluid loss from cement slurries.

Example 3

Example 3, as described in Table IV, shows the synergistic interaction of a sulfonated polynaphthalene dispersant with an acrylamide/vinylimidazole copolymer to
5 reduce the fluid loss of a Class H cement slurry containing 38% water. The data indicate that when no dispersant is used, an acceptable fluid loss is obtained at 0.5 percent additive BWOC but an almost ten fold increase in the fluid loss is experienced if the level of additive is reduced by
10 half. However, the addition of dispersant increases the effectiveness of the additive to such an extent that slurries containing 0.25 percent of the claimed additive and 0.5 percent of dispersant have a fluid loss similar to that of slurries containing 0.5 percent of the additive but no
15 dispersant.

Example 4

Example 4 shows the performance of the additives claimed in high salt content cement slurries. As seen from
20 Table V, the fluid loss of the cement slurry is not greatly affected by the amount of NaCl present in the slurry up to 9.0 percent BWOW. Only when 18 percent of salt BWOW is introduced in the slurry, the fluid loss increases. The

slurry is not retarded by the addition of high levels of salt (18% NaCl) contrary to what is seen with many commercial fluid loss additives.

Example 5

Example 5, as depicted in Table VI, shows that the use of acrylamide derivatives and/or the addition of a third monomer does not have deleterious effects on the effectiveness of the claimed additives. Some additives, however, tend to increase the viscosity of the cement slurries if an excessive amount of the third monomer is introduced in a terpolymer.

Table IIPerformance of Acrylamide/Vinylimidazole
Copolymers as Cement Fluid Loss Additives

API Tests, Class H Cement, 38% Water
180 Deg. F. 1000 psi

5

Test No.	% Additive BWOC	% Dispersant BWOC	Fluid Loss (ml)	Thickening Time (Hr:min)	Compressive Strength (psi)
10 1 Neat Cement	0.000	0.00	1628	01:45:00	5000
2 Neat Cement	0.000	0.50	775	N.A.	N.A.
3 Comp A	0.125	0.75	71	N.A.	N.A.
4 Comp A	0.250	0.50	62	N.A.	N.A.
5 Comp A	0.500	0.50	27	>5:00	No Set
15 6 Comp B	0.125	0.75	115	05:17:00	3842
7 Comp B	0.250	0.50	100	04:13:00	3841
8 Comp B	0.500	0.50	32	>4:00	3485
9 Comp C	0.500	0.50	24	N.A.	N.A.

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Table III

Effect of MW as Expressed by "Intrinsic Viscosity" on the
Performance of AM/VI Copolymers as
Cement Fluid Loss Additives

5

API-Tests, Class H Cement, 38% Water
180 Deg. F, 1000 psi

Test No.	Intrinsic Viscosity (100 ml/g)	% Additive BWOC	% Dispersant BWOC	Fluid Loss (ml)
10 1 Comp A	1.13	0.25	0.5	102
2 Comp A	1.31	0.25	0.5	87
3 Comp A	1.71	0.25	0.5	62
4 Comp A	2.575	0.25	0.5	86
5 Comp A	2.87	0.25	0.5	97
15 6 Comp B	1.4	0.25	0.5	262
7 Comp B	1.68	0.25	0.5	153
8 Comp B	2.12	0.25	0.5	75
9 Comp B	2.61	0.25	0.5	74

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Table IV

Synergistic Effect of Polynaphthalene Sulfonate Dispersant
With AM/VI Copolymers as Fluid Loss Additives for Cement Slurries

Class H Cement, 38% H₂O
180 Deg. F, 1000 psi

5

Test No.	% Additive BWOC	% Dispersant BWOC	Fluid Loss (ml)	Thickening Time (Hr:min)	Compressive Strength (psi)
1 Comp B	0.50	0.00	70	02:48	N.A.
2 Comp B	0.25	0.00	619	N.A.	3829
10 3 Comp B	0.50	0.25	35	03:44	4300
4 Comp B	0.25	0.25	119	N.A.	3818
5 Comp B	0.50	0.50	32	06:41	4000
6 Comp B	0.25	0.50	74	05:31	4049

Table V
Performance of Acrylamide/Vinylimidazole
Copolymers as Cement Fluid Loss Additives in Salt Cement

API Tests, Class H Cement, 38% Water
180 Deg. F, 1000 psi

Test No.	% Additive BWOC	% Dispersant BWOC	%Salt(NaCl) BWOW	Fluid Loss (ml)	Thickening Time (Hr:min)	Compressive Strength (psi)
1 Comp B	0.5	0.5	0	32	05:00	3485
2 Comp B	0.5	0.5	5	26	02:44	4255
3 Comp B	0.5	0.5	9	28	02:41	4277
4 Comp B	0.5	0.5	18	101	01:33	3682

Table VI

Performance of Copolymers and Terpolymers Containing Vinyl
Imidazole and Acrylamide Derivatives as Cement Fluid Loss Additives

API Tests, Class H Cement, 38% Water
 180 Deg. F, 1000 psi

5

	Comonomers	Ratios Wt. %	% Additive	% Dispersant	Fluid Loss (ml)
			BWOC	BWOC	
	1 MAM/VI	80/20	0.5	0.5	88
	2 AM/MAM/VI	40/40/20	0.5	0.5	59
10	3 AM/MAM/VI	60/20/20	0.5	0.5	38
	4 AM/VP/VI	60/20/20	0.5	0.5	41
	5 AM/VP/VI	40/40/20	0.5	0.5*	
	6 AM/VP/VI	20/60/20	0.5	0.5*	

*Cement slurries too thick to mix.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A cementing composition useful in cementing oil, gas and water wells comprising:
 - a) water;
 - b) hydraulic cement; and
 - c) a fluid loss additive in an amount effective to reduce fluid loss from the cement slurry to the surrounding rock formations, said fluid loss additive comprised of a copolymer of acrylamide type monomer and a basic vinylheterocyclic monomer and derivatives thereof in a weight per cent ratio of from 95:5 to 5:95, said copolymer having a molecular weight range of from 10,000 to 3,000,000, said acrylamide monomer selected from the group consisting of acrylamide, methacrylamide, N,N-dimethyl(meth)acrylamide, dialkylaminoalkyl(meth)acrylamide and mixtures thereof, said basic vinyl heterocyclic monomer selected from the group consisting of 1-vinylimidazole, 2-vinylimidazole, 2-methyl-1-vinylimidazole, 4-methyl-1-vinylimidazole, 5-methyl-1-vinylimidazole, 2-ethyl-1-vinylimidazole, 2-propyl-1-vinylimidazole, 2-isopropyl-1-vinylimidazole, 2-phenyl-1-vinylimidazole, 1-vinyl-4, 5-benzimidazole, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine and mixtures thereof.
2. The composition of claim 1, wherein the fluid loss additive is present in an amount of from 0.05 to 2.0 percent by weight of the cement.
3. The composition of claim 1, wherein the copolymer has a molecular weight of from 100,000 to 1,000,000.
4. The composition of claim 1, further including a synergistic amount of a dispersant selected from the group



consisting of lignosulfonates, sodium or potassium salts of a sulfonated naphthalene formaldehyde condensate, sodium salts of ketone sulfonate formaldehyde condensate, and mixtures thereof.

5. The composition of claim 1, wherein the copolymer is comprised of a 80:20 to 20:80 weight percent ratio of acrylamide to basic vinylheterocyclic monomer.

6. The composition of claim 1, wherein the copolymer is polymerized with another monomer to create an acrylamide basic vinylheterocyclic monomer terpolymer having an average molecular weight range of from 10,000 to 3,000,000.

7. The composition of claim 6, wherein the monomer is selected from the group consisting of unsaturated acid monomers, alkali metals, ammonium, ammonium organic amine salts, N,N-dialkylaminoalkyl(meth)acrylamide, N,N-dialkylaminoalkyl(meth)acrylate, ethylacrylate, methyl acrylate, acrylamido methylpropane sulfonic acid sodium salt, hydroxypropyl acrylate, vinylpyrrolidone, vinyl formamide, sodium vinylsulfonate, acrylonitrile, vinylacetate and quaternary salts of the amino groups containing monomers, and mixtures thereof.

8. The composition of claim 6, wherein said terpolymer is comprised of from 0 to 60 weight percent additional monomer, from 5 to 95 weight percent acrylamide and from 95 to 5 weight percent basic vinylheterocyclic monomer.

9. A method of cementing a conduit in a borehole penetrating an earthen formation by introducing a cementing composition into the space between said conduit and said formation, wherein said cementing composition comprises:

- a) water;
- b) hydraulic cement; and
- c) a fluid loss additive in an amount effective to



reduce fluid loss from the cement slurry to the surrounding rock formations, said fluid loss additive comprised of a copolymer of acrylamide/basic vinylheterocyclic monomer and derivatives thereof in a weight percent ratio of from 95:5 to 5:95, said copolymer having a molecular weight range of from 10,000 to 3,000,000, said acrylamide monomer selected from the group consisting of acrylamide, and acrylamide hydrolysis products, methacrylamide, N-N-dimethyl(meth)acrylamide, dialkylaminoalkyl(meth)acrylamide and mixtures thereof and said basic vinyl heterocyclic monomer selected from the group consisting of 1-vinylimidazole, 2-vinylimidazole, 2-methyl-1-vinylimidazole, 4-methyl-1-vinylimidazole, 5-methyl-1-vinylimidazole, 2-ethyl-1-vinylimidazole, 2-propyl-1-vinylimidazole, 2-isopropyl-1-vinylimidazole, 2-phenyl-1-vinylimidazole, 1-vinyl-4,5-benzimidazole, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine and mixtures thereof.

10. The method of claim 9, further including a synergistic amount of a dispersant selected from the group consisting of lignosulfonate, sodium or potassium salts of sulfonated naphthalene formaldehyde condensate, sodium salts of ketone sulfonate formaldehyde, and mixtures thereof.

11. The method of claim 9 wherein said copolymer is polymerized with a suitable monomer to create an acrylamide/basic vinylheterocyclic monomer terpolymer having a molecular weight range of from 10,000 to 3,000,000.

12. The method of claim 11, wherein the monomer is selected from the group consisting of unsaturated acid monomers, alkali metals, ammonium, ammonium organic amine salts, N,N-dialkylaminoalkyl(meth)acrylamide, N,N-dialkylaminoalkyl(meth)acrylate, ethylacrylate, methyl acrylate,



acrylamido methylpropane sulfonic acid sodium salt, hydroxypropylacrylate, vinylpyrrolidone, vinylamine, vinylformamide, sodium vinylsulfonate, acrylonitrile, vinylacetate, quaternary salts of the amino groups containing monomers, and mixtures thereof.

13. The method of claim 11, wherein said terpolymer is comprised of from 0 to 60 weight percent additional monomer from 5 to 95 weight percent acrylamide and from 95 to 5 weight percent basic vinylheterocyclic monomer.

14. The method of claim 9 wherein said fluid loss additive is present in an amount of from 0.05 to 2.0 percent by weight of the cement.

15. The method of claim 9, wherein the terpolymer has a molecular weight of from 100,000 to 1,000,000.

16. Use of a cementing composition for cementing a conduit in a borehole penetrating an earthen formation by introducing the cementing composition into the space between said conduit and said formation, wherein said cementing composition comprises:

- a) water;
- b) hydraulic cement; and
- c)

a fluid loss additive in an amount effective to reduce fluid loss from the cement slurry to the surrounding rock formations, said fluid loss additive comprised of a copolymer of acrylamide/basic vinylheterocyclic monomer and derivatives thereof in a weight percent ratio of from 95:5 to 5:95, said copolymer having a molecular weight range of from 10,000 to 3,000,000, said acrylamide monomer selected from the group consisting of acrylamide, and acrylamide hydrolysis products, methacrylamide, N-N-dimethyl(meth)acrylamide,



dialkylaminoalkyl(meth)acrylamide and mixtures thereof and said basic vinyl heterocyclic monomer selected from the group consisting of 1-vinylimidazole, 2-vinylimidazole, 2-methyl-1-vinylimidazole, 4-methyl-1-vinylimidazole, 5-methyl-1-vinylimidazole, 2-ethyl-1-vinylimidazole, 2-propyl-1-vinylimidazole, 2-isopropyl-1-vinylimidazole, 2-phenyl-1-vinylimidazole, 1-vinyl-4, 5-benzimidazole, 2-vinylpyridine, 4-vinylpyridine, 5-methyl-2-vinylpyridine and mixtures thereof.

DATED this 16th day of May, 1991.

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