United States Patent Office 3,810,836
Patented May 14, 1974

3,810,836

NON-STAINING DRILL LUBRICANTS

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No Drawing. Filed June 1, 1972, Ser. No. 258,826
Int. Cl. C10m 3/08, 3/32
U.S. Cl. 252—8.5 C 6 Claims

ABSTRACT OF THE DISCLOSURE

A mineral-oil-based lubricant for use in drilling of mineral ore deposits, which is non-staining towards sample cores withdrawn during the drilling, can be prepared by combining a paraffinic oil, with minor amounts of a nonionic emulsifier package and a sulfur-containing extreme pressure agent. The nonionic emulsifier package can be a combination of an alkoxylated fatty acid ester and an alkoxylated alkyl phenol or a combination of fatty acid sorbitan polyesters which have been alkoxylated to varying extents.

FIELD OF THE INVENTION

This invention relates to a mineral-oil-based lubricant for use in drilling of ore deposits which is self-scouring and non-staining towards rock cores withdrawn during the drilling operation. This lubricant composition contains in addition to a major amount of a light colored, paraffinic mineral oil, minor amounts of a nonionic emulsifier package and a sulfur-containing extreme pressure agent.

BACKGROUND OF THE INVENTION

The present invention relates to a mineral-oil-based liquid lubricating composition. In general, it concerns a non-staining liquid lubricating composition particularly useful for diamond bit core drilling. In particular, it concerns a non-staining liquid lubricating composition containing both a nonionic emulsifier package and a sulfur-containing extreme pressure agent. In addition, this invention relates to the use of such a composition in the drilling of earth formations with a diamond drill coring bit.

In many industrial lubricating applications, staining of surfaces coming in contact with the lubricant is a problem. For example, in the Canadian mining industry where exploratory drilling is carried out using diamond bit core drilling apparatus to search for ore bodies, lubrication of the apparatus with conventional lubricants generally results in staining of the cores of rock and ore that are bored out by the diamond drill bit. Diamond bit coring is conventionally conducted by rotating a reamer and diamond bit on a string of drill pipe in a bore hole. It is the rotary action of the diamonds grinding against the rock and the weight of the drill rod assembly bearing down on the rock at the bottom of the hole which causes the assembly to penetrate into the rock. The doughnut-shaped diamond drill bit grinds out a smooth-surfaced cylindrical rock core (about one inch in diameter) which is pushed up into the inner core tube. The drill pipe is removed from the hole after every 10 to 20 feet of drilling to recover the rock cores. Recently a new technique has been perfected whereby a line equipped with a special clamp to fasten onto the core samples is lowered down through the drill pipe and the core samples are recovered without the necessity of raising and uncoupling the many feet of drill pipe. This new technique makes it especially mandatory that a lubricant that is non-staining toward the rock cores be used.

In diamond bit core drilling, water, usually called "fresh sludge water," is pumped down the drill pipe to flush the debris formed around the diamond bit back up through the annulus between the drill pipe and the walls of the hole

and to serve as a coolant for the cutting diamonds. It also provides such lubrication to the rotating drill line. A string of drill rods or pipe which is not properly lubricated will cause the inherent vibrations common to a long rod or pipe to become severe. This condition creates impact forces that are transmitted to the diamond bit with damaging effects. The recovery of the cores is also adversely affected under such conditions, since the vibration breaks the cores into smaller pieces. The rate of penetration of the bit is greatly reduced and will cease if the vibrations become too severe.

For some years a special grease has been marketed to coat the outside of the drill pipe to provide extra lubrication and to seal the hole where caving conditions are encountered due to fragile rock. The use of this grease permitted greater drilling speeds and also provided some rust protection to the rods under these conditions. The use of a grease applied to the drilling apparatus so as to lubricate only the external surface of drill rods or pipe will result in non-staining of the cores, but at the same time neither the internal surface of the core barrel or tube nor the diamond drill bit is lubricated with the grease; thus, there is no internal lubrication and, as a result, the life of the bit is decreased. In a like manner, when water alone is used as a lubricant, no core staining occurs. However, lubrication, both external and internal, is very poor and in many instances vibrations are so great that drilling must be stopped.

More recently it was found that a soluble oil, e.g. an emulsifiable oil comprising a major proportion of a mineral lubricating oil and minor proportions of one or more anionic emulsifiers, when metered into the fresh sludge water, markedly increased the cutting speed and bit life.

In most instances, however, use of the soluble oils caused deposition of a tenacious insoluble film on the surface of the rock cores. This film prevented the geologist from identifying by visual inspection the ores and rocks contained in the core. An analysis of the deposit showed that it was composed of 50% of a black magnetic iron oxide (of such fine crystalline structure as to make identification by X-ray diffraction techniques difficult), and 50% of a resinous organic binder. The iron oxide appeared to have been ground into the pores of the rock core.

DESCRIPTION OF THE PRIOR ART

U.S. Pat. 3,425,940 discloses a lubricant composition for use in the above-described drilling operations which is free of mineral oil and contains as a lubricity additive a metal salt of an alkyl aromatic sulfonic acid together with a non-staining solubilizing agent and a non-staining rust inhibitor.

SUMMARY OF THE INVENTION

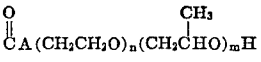
The composition of the present invention comprises a major amount of a light colored, paraffinic mineral oil in combination with minor amounts of a nonionic emulsifier package and a sulfur-containing extreme pressure agent. This invention is an improvement over the invention disclosed in U.S. Pat. 3,425,940. Generally, the present invention permits the use of lower cost materials, and compositions made in accordance with it exhibit better low temperature storage properties than do those made according to the prior art.

DETAILED DESCRIPTION OF THE INVENTION

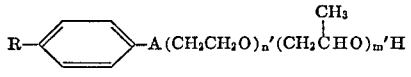
Nonionic emulsifier package

A preferred nonionic emuslifier package used in the compositions of this invention is a combination of (i) 75 to 95 wt. percent, preferably 80 to 90 wt. percent of

an alkoxylated fatty acid ester emulsifier of the general formula



wherein R is a C_{10} to C_{24} aliphatic group, A is an oxygen or sulfur atom, *n* and *m* are each numbers from 0 to 8 and the sum of $n+m$ is between about 4 to 8, with (ii) 25 to 5 wt. percent, preferably 20 to 10 wt. of an alkoxylated alkyl phenol emulsifier of the general formula



wherein R and A are as defined above, *n' and m'* are each numbers from 0 to 12, and the sum of $n'+m'$ is between about 6 and 12.

Another nonionic emulsifier package which can be used in the present invention is a combination of (iii) 25 to 75 wt. percent, preferably 40 to 60 wt. percent of a first fatty acid alkoxylated sorbitan polyester wherein said fatty acid contains 12 to 18 carbon atoms and said sorbitan is alkoxylated with 30 to 50 moles of a C_2 to C_3 alkylene oxide with (iv) 25 to 75 wt. percent, preferably 40 to 60 wt. percent of a second fatty acid alkoxylated sorbitan polyester wherein said fatty acid contains 12 to 18 carbon atoms and said sorbitan is alkoxylated with 10 to 30 moles of a C_2 to C_3 alkylene oxide.

The preparation of the alkoxylated alkyl phenol nonionic emulsifiers used in the compositions of this invention is well known to the art. For example, see Kirk-Othmer Encyclopedia of Chemical Technology, 2nd ed., vol. 19, pp. 532–536. Similarly, the preparation of the alkoxylated fatty acid ester emulsifiers used in the compositions of the present invention is also well known to the art (see ibid, pp. 541–545). The preparation of fatty acid akloxylated sorbitan polyesters is also known to the art (see ibid, pp. 545–548).

The lubricant compositions of this invention also include a sulfur-containing extreme pressure agent. Typical such agents are the following compounds which are conventionally employed for this purpose: sulfurized and phosphosulfurized synthetic acid and fatty acid ester oils of mono- and polyhydric compounds, such as sulfurized sperm oil, sulfurized lard oil, phosphosulfurized sperm oil, phosphosulfurized lard oil, sulfurized and phosphosulfurized tall oil; low molecular weight polysufides such as dibenzy disulfide or dialuaryl trisulfide; sulfurized and phosphosulfurized olefins and polymeric olefins such as sulfurized cracked wax olefins, sulfurized single olefins e.g., sulfurized octadene-1), sulfurized terpenic olefins having 10 to 32 carbons including those further sulfurized by treatment with sodium sulfide; sulfurized polyisobutylene, phosphosulfurized polyisobutylene, sulfurized isobutylene derivatives and phosphosulfurized polyisobutylene treated with sulfur chloride. Numerous other conventionally employed extreme pressure additives may be utilized either alone or in combination.

Sulfurization of the above-noted oils, olefins and polyolefins is usually carried out by simply heating them with free sulfur to about 180° to 250° C. The sulfur combines with the hydrocarbon portion of the molecule quite readily with an evolution of hydrogen sulfide. The reaction product may be blown with air or an inert gas to eliminate hydrogen sulfide, washed, and low boiling constituents evaporated or distilled off with steam. In many cases a small amount of free sulfur is present, not having reacted, and this may be separated by filtration. The sulfur may be either active or inactive as measured by tests for extreme pressure and corrosivity, as its state is immaterial for the purpose of the present invention.

The lubricant composition of this invention contains a major proportion of a mineral oil which has a viscosity at 100° F. of at least 100 SUS and no more than 2000 SUS at 100° F. Preferred oils are paraffinic oils which

have been refined so as to be light colored and non-staining. Oils such as pale oil 300 and pale oil 400 can be used.

An example of such an oil is a paraffinic SAE grade 20 base oil which has been solvent refined, dewaxed and hydrofined from a mineral oil originating from Western Canada. This oil has a viscosity at 100° F. of 300 SUS, a viscosity at 210° F. of 50 SUS and a viscosity index of 80.

In general, the lubricating composition of the present invention will comprise the above-described components in the following general proportions:

Component	Parts by wt. per 100 parts by wt. oil	
	General	Preferred
Fatty acid ester emulsifier	2.0 to 20.0	4.25 to 8.5.
Alkylphenol emulsifier	0.25 to 3.5	0.75 to 1.5.
Sulfurized extreme pressure agent	1.0 to 20.0	5.0 to 10.0.

In certain embodiments of this invention, the fatty acid ester/alkyl phenol emulsifier package can be replaced by 2.0 to 20.0, preferably 5.0 to 10.0 parts by weight per 100 parts by weight of oil of the aforedescribed fatty acid alkoxylated sorbitan polyester combination.

Various other ingredients may be added to the compositions of the present invention. For example antifoamants such as silicone fluid DC 200 (350 centistokes), dyes such as Disulphine Blue VN 150, and other conventional additives may be employed for their known effects.

As noted above, drilling lubricants are normally used in conjunction with relatively large amounts of sludge water. When the lubricating compositions of this invention are used with water in the proportion of 1 volume of the composition to about 100 to 1,000 volumes of water, there will be obtained a circulating fluid which will consist essentially of about 200 to 1,000 parts by weight of water, from 0.45 to 0.90 part by weight oil, from 0.02 to 0.004 part by weight of the fatty acid ester emulsifier, from 0.004 to 0.008 part by weight of the alkylphenol emulsifier, from about 0.025 to 0.005 part by weight of the extreme pressure agent, and from about 0.26 to 0.005 part by weight of the fatty acid alkoxylated sorbitan polyester package.

EXAMPLE

A non-staining lubricant composition of the present invention was prepared by combining 90 parts per weight of the above-described paraffinic SAE 20 base oil, 4.25 parts by weight of an ethoxylated oleic acid having an average ethylene oxide content of 6 units, 0.75 part by weight of an ethoxylated n-octadecyl phenol having an average ethylene oxide content of 8 units, and 5 wt. percent of sulfurized sperm oil having a sulfur content of 11 to 12 wt. percent. This lubricant composition had an API gravity of 25.7 and a viscosity at 100° F. of 250 SUS. This oil was evaluated at an operating mine with respect to its ability to lubricate the drilling rods as evidenced by rod vibration and speed and the tendency of the oil to stain the rock cores withdrawn from the drill holes.

This composition was found to be eminently suitable for use in diamond drilling operations by metering about 1 gallon of the composition into about 400 gallons of water. For example, when water is circulating through the drill pipe at 1,200 gallons per hour, 3 gallons per hour of the described composition is metered into the circulating water.

In a typical operation a rock formation in an exploration hole at a depth between 6,600 and 10,000 feet below the surface was cored with a diamond bit, using circulating water to which the above composition had been added in the proportion of 1 gallon per 400 gallons of water. There was essentially no staining of the recov-

ered cores and lubrication of the drill pipe was good, as evidenced by lack of vibration.

Control 1

A lubricating composition was prepared using 94 parts by weight of a paraffinic SAE 5 base oil having a viscosity at 100° F. of 100 SUS, a viscosity at 210° F. of 39 SUS, a viscosity index of 80, 5.1 parts by weight of the fatty acid ester described in Example 1 and 0.9 part by weight of the alkoxyalkylphenol described in Example 1. This composition had an API gravity of 29.1 and a viscosity at 100° F. of 110 SUS. When it was used in the above-described drilling test, it was observed that the lubrication of the rods was poor, as reflected by severe vibrations. The composition performed satisfactorily with respect to preventing the staining of cores.

A number of other compositions were prepared from commercially available emulsifiers in a manner similar to that described in Example 1. When evaluated in the above-described tests, they were found to be generally unsatisfactory with respect to staining and often with respect to rod lubrication. Among the emulsifiers thus found to be unsatisfactory were the following:

Supplier	Trade name	Chemical composition
Rohm & Haas	Triton X-207	Alkylaryl polyether plus a nonionic solubilizer.
Do	Triton X-45	Octyl phenoxy polyethoxy ethanol.
Do	Triton X-102	Do.
Gen. Anil. & Film	Emulphor VN-430	Polyoxyethylated fatty acid ester.
Do	Antara LF-205	Barium salt of a complex organic phosphate ester.
Do	Antara LM-400	Free acid of a complex organic phosphate ester.
Do	Antara LE-700	Do.
Do	Igepal CO 430	Nonyl phenoxypolyl (ethyleneoxy) ethanol.
Do	Igepal CO 530	Do.
Do	Igepal CO 630	Do.
Atlas Chem. Ind	Tween 81 +	Polyoxyethylene sorbitan monooleate.

It should be noted the Triton and Emulphor emulsifiers closely resemble the first and second components of the emulsifier combination of the present invention. Thus the data show that a combination of emulsifiers, rather than a single emulsifier above, should be used to obtain the results obtained by the present invention.

What is claimed is:

1. A lubricant composition that is non-staining toward rock when diluted with water and employed as a drilling lubricant and circulating fluid in the core drilling of earth formations which consists essentially of a major proportion of a mineral oil having a viscosity at 100° F. of from about 100 to 2000 SUS, to which have been added, per 100 parts by weight of said oil:

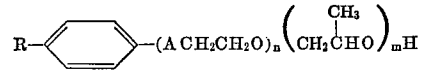
(a) from about 1 to 20 parts by weight of a sulfur-containing extreme pressure agent comprising a low molecular weight hydrocarbon sulfide or polysulfide or a sulfurized or phosphosulfurized olefin, polyolefin, terpene, or fatty acid ester oil; and

(b) a nonionic emulsifier selected from the group consisting of

(A) a combination of (i) 75 to 95 wt. percent of a nonionic alkoxylated fatty acid ester emulsifier of the general formula

$$R\overset{O}{\overset{\|}{C}}A_2(CH_2CH_2O)_n\left(\begin{matrix}CH_3\\|\\CH_2CHO\end{matrix}\right)_mH$$

wherein R is a C_{10} to C_{24} aliphatic group, A is an oxygen or sulfur atom, n and m are each numbers from 0 to 8 and the sum of $n+m$ is between about 4 to 8; and (ii) 25 to 5 wt. percent of a nonionic alkoxylated alkyl phenol emulsifier having the general formula



wherein R and A are as defined above, n' and m' are each numbers from 0 to 12 and the sum of $n'+m'$ is between about 6 and 12, and

(B) a combination of (iii) 25 to 75 wt. percent of a first fatty acid alkoxylated sorbitan polyester wherein said fatty acid contains 12 to 18 carbon atoms and said sorbitan is alkoxylated with 30 to 50 moles of a C_2 to C_3 alkylene oxide, and (iv) 25 to 75 wt. percent of a second fatty acid alkoxylated sorbitan polyester wherein said fatty acid contains 12 to 18 carbon atoms and said sorbitan is alkoxylated with 10 to 30 moles of a C_2 to C_3 alkylene oxide;

said combination (A) when used being present in an amount ranging from about 2.25 to about 23.5 parts per 100 parts by weight of said oil, and said combination (B) when used being present in an amount ranging from about 2 to about 20 parts per 100 parts by weight of said oil.

2. A composition as defined by claim 1 wherein said extreme pressure agent is present in an amount of from about 5 to 10 parts by weight, said alkoxylated fatty acid ester emulsifier (i) is present in an amount of from about 4.25 to 8.5 parts by weight, and said alkoxylated alkyl phenol emulsifier (ii) is present in an amount of from about 0.75 to 1.5 parts by weight, all parts being parts by weight per 100 parts of said oil.

3. A composition as defined by claim 1 wherein said alkoxylated fatty acid ester (i) emulsifier is an ethoxylated oleic acid, said alkoxylated alkyl phenol (ii) is an ethoxylated n-octadecyl phenol, and said extreme pressure agent is sulfurized sperm oil.

4. A composition as defined by claim 3 wherein said ethoxylated oleic acid has an average ethylene oxide content of about 6 units, said ethoxylated n-octadecyl phenol has an average ethylene oxide content of about 8 units, and said sulfurized sperm oil has a sulfur content of about 11 to 12 wt. percent.

5. A composition as defined by claim 1 wherein said extreme pressure agent is a sulfurized sperm oil.

6. A circulating fluid for the lubrication of a string of drill rods or drill pipe and an earth coring device suspended therefrom in an earth well bore which consists essentially of a mixture of from 100 to 1000 volumes of water and one volume of the lubricant composition defined by claim 1.

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HERBERT B. GUYNN, Primary Examiner

U.S. Cl. X.R.

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