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3,249,535

METHOD OF RETARDING PARAFFIN CLOGGING IN PETROLEUM CONTAINERS

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9 Claims. (Cl. 252—8.3)

This invention relates to a method of preventing or retarding paraffin build up on the walls of petroleum conduits or containers, thereby reducing or preventing clogging.

The problem of paraffin clogging has plagued the oil industry for years. When oil is pumped to the surface it cools and the pressure on the oil is reduced due to gas release. Many crude oils have a high concentration of dissolved paraffins, and, upon cooling, and pressure reduction, these paraffins are likely to precipitate. The paraffin then collects in a clogging mass on the walls inside the oil pipes or oil containers.

A good deal of work has been done in the field of pipe linings to retard paraffin clogging. Plastics, for example, are used to line crude oil transmission pipes after the oil has been brought to the surface, but this method cannot be used for oil well pipe because of the abrasive action of sand and other particles that are brought up along with the crude oil. Also it is expensive.

Another technique used is to place immersion heaters into the well shaft to heat the oil and redissolve the paraffin.

Also, many oil wells are periodically closed down and the paraffin is bored out. This cleaning operation is a full-time profession for a number of people. Similarly, hot oil is sometimes recirculated into the well shaft with the same end in mind.

The objective of applicant's invention is to prevent or retard the deposition of paraffin in petroleum conduits and containers. This invention, however, can be used to prevent deposition on the walls of containers and conduits with other solutions, suspensions, dispersions and emulsions than crude oil.

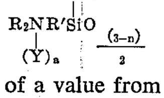
This is done by either coating the conduit or container surface with the below-described copolymers, or by introducing small amounts of said material into the petroleum itself, either by placing it into the pipe or container along with the petroleum, or by continuously introducing it into a moving flow of petroleum. The amount of copolymer used is not critical so long as there is sufficient material to retard the deposition of paraffin. It has been found that this greatly inhibits the growth of paraffin deposits.

This invention represents a substanital stride in the techniques of coping with paraffin in piping. It prevents paraffin deposition and saves many man-hours of labor, when compared with the various paraffin-removal techniques.

It is an advance over plastic-coated pipe in that it can be used in the well itself; it can be easily applied to pipe that is already in place and operating; and it can be much cheaper.

The material that is used by this invention is a siloxane copolymer consisting essentially of from 0.25 to 10 mol percent, siloxane units of the formula

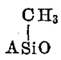
(1)



$$R_2\underset{(Y)_a}{N}R'\overset{R''_n}{Si}O_{\frac{(3-n)}{2}}$$

where n is an integer of a value from 0 through 2, R is a hydrogen, alkyl, alicyclic, or aminoalkyl group; R' is a divalent hydrocarbon that separates the N and the Si atoms by at least three carbon atoms, R'' is a monovalent hydrocarbon radical with from one through 6 carbon atoms, Y is a molecule of a monovalent aliphatic carboxylic acid or cycloaliphatic carboxylic acid of from 1 to 10 carbon atoms, and a has a value from 0 to a value equal to the number of N atoms in (1); and from 99.75 to 90 mol percent, siloxane units of the formula

(2)

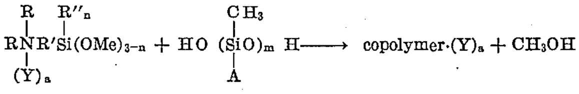


$$\underset{A}{\overset{CH_3}{Si}}O$$

where A is a monovalent hydrocarbon radical with from 1 through 3 carbon atoms.

The term "consisting essentially of" means that the copolymer is substantially as described but it can contain small amounts of other siloxane units which do not materially affect the property of retarding paraffin deposition.

This copolymer can be made in the following way:

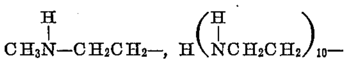


$$R\underset{(Y)_a}{\overset{R}{N}}R'\overset{R''_n}{Si}(OMe)_{3-n} + HO\ (\underset{A}{\overset{CH_3}{Si}}O)_m\ H \longrightarrow \text{copolymer}\cdot(Y)_a + CH_3OH$$

where m is an integer and the other symbols retain their former identities. This reaction will proceed at room tempeature or upon warming the mixture.

It should be stressed that Y need not be present (i.e., a may equal 0) in order for the copolymer to be useful in applicant's invention, nor, if it is present, is it necessary for every amine group to have a Y added to it.

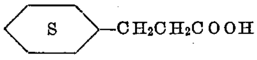
The two R groups do not have to be identical. In this invention R can be any alkyl or alicyclic radical such as methyl, decyl, isobutyl, cyclohexyl, cyclopentyl, methylcyclohexyl, or octadecyl; or R can be any aminoalkyl radicals such as $H_2NCH_2CH_2$—, $(CH_3)_2NCH_2CH_2$—,



$$CH_3\overset{H}{N}—CH_2CH_2—,\ H\left(\overset{H}{N}CH_2CH_2\right)_{10}—$$

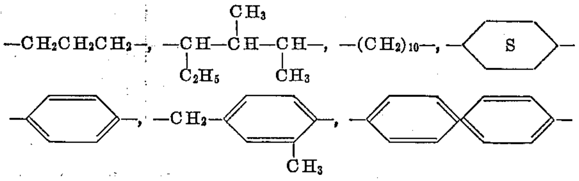
etc.

The Y group can consist of any of the defined carboxylic acids such as formic acid, acetic acid, isobutyric acid, decanoic acid,



cyclohexyl carboxylic acid, 4-methylcyclohexylcarboxylic acid, acrylic acid, methacrylic acid, butynoic acid, vinylacetic acid, crotonic acid, and $CH_2{=}CH(CH_2)_7COOH$.

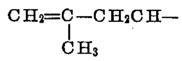
The R' group can be any divalent hydrocarbon radical such as



$$—CH_2CH{=}CH— \text{ and } —(CH_2)_{18}—$$

Preferably R' has from 1 through 10 carbon atoms.

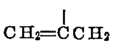
The R'' group can be any of the defined radicals such as methyl, hexyl, isopropyl,



$$CH_2{=}\underset{CH_3}{C}—CH_2CH—$$

cyclohexyl, phenyl, $CH_2{=}CHCH{=}CH$—, etc.

The A group can be methyl, ethyl, propyl, isopropyl, vinyl, allyl,



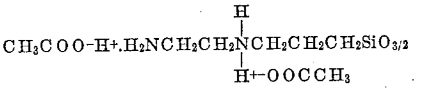
$$CH_2{=}\overset{|}{C}CH_2$$

etc.

The following examples are illustrative only and should not be construed as limiting the invention which is properly set forth in the appended claims.

Example 1

A polymer was made by reacting 2.7 mol percent of $H_2NCH_2CH_2NH(CH_2)_3Si(OMe)_3$ with 97.3 mol percent dimethylsiloxane with OH endblocks and an average chain length of 29 siloxane units and a small excess of acetic acid in an isopropanol solvent. The product was a copolymer of 2.7 mol percent



$$CH_3COO^-H^+.H_2NCH_2CH_2\overset{\overset{H}{|}}{\underset{\underset{H^+{}^-OOCCH_3}{|}}{N}}CH_2CH_2CH_2SiO_{3/2}$$

and 97.3 mol percent $(CH_3)_2SiO$. One-half gallon of this copolymer was diluted to 20 gallons with diesel fuel. The solution was fed into a flowing crude oil line a few feet before an oil-water separator, at a rate of about ten parts of polymer solution per million parts of crude oil that passed through the oil line. The separator was operated for three days continuously without being plugged up with paraffin. This separator normally operates for only two days before it ceases to function through paraffin clogging.

Example 2

One-half gallon of the polymer described in Example 1 was added to a well by "dump bailing" at 2500 feet depth. One-half gallon of a Humble Oil Company corrosion inhibitor, known as Corexit 801 was also added to the well.

Six days later the well was reopened to "cut the paraffin" and none was found. This well was habitually cleaned of its accumulated paraffin at weekly intervals.

The treatment of the well with silicon polymer and corrosion inhibitor was repeated, using the same quantities.

Seven days later the well was reopened, and still no paraffin was found.

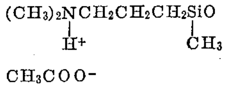
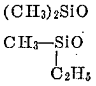
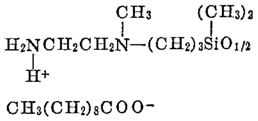
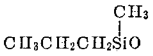
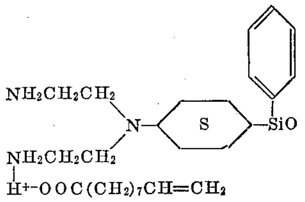
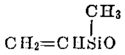
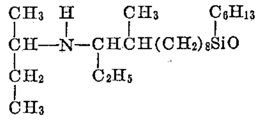
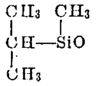
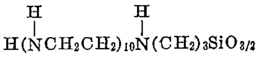
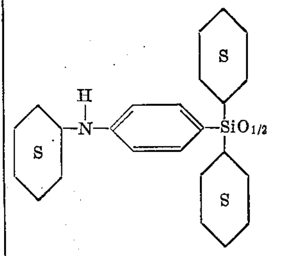
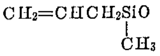
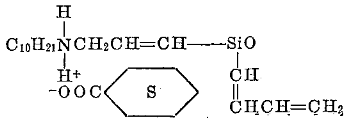
There was no further treatment of the well.

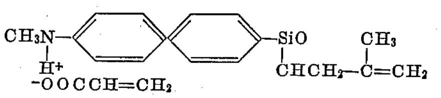
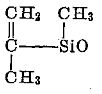
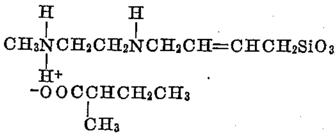
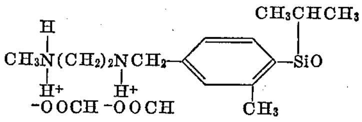
Seven days thereafter the well was again reopened, and still no paraffin at all was found.

This well continued normal production throughout the duration of the experiment.

Example 3

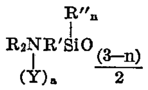
When copolymers of the following compositions are used to coat the inside of petroleum containers, or are added to the petroleum itself, effective retardation of the precipitation of paraffin on the container walls is noted:

Mol percent	Siloxane unit	Mol percent	Siloxane unit
0.5	$H_2NCH_2CH_2CH_2SiO_{3/2}$	99.5	$(CH_3)_2SiO$
10.0	 $(CH_3)_2\underset{\underset{H^+}{\vert}}{N}CH_2CH_2CH_2\underset{\underset{CH_3}{\vert}}{Si}O$ CH_3COO^-	90.0	 $CH_3{-}\underset{\underset{C_2H_5}{\vert}}{Si}O$
1.0	 $H_2\underset{\underset{H^+}{\vert}}{N}CH_2CH_2\overset{\overset{CH_3}{\vert}}{N}{-}(CH_2)_3\overset{\overset{(CH_3)_2}{\vert}}{Si}O_{1/2}$ $CH_3(CH_2)_8COO^-$	99.0	 $CH_3CH_2CH_2\overset{\overset{CH_3}{\vert}}{Si}O$
1.9		98.1	 $CH_2{=}CH\overset{\overset{CH_3}{\vert}}{Si}O$
4.5	 $\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{\underset{\underset{CH_2}{\vert}}{C}H}}{-}\overset{\overset{H}{\vert}}{N}{-}\overset{\overset{CH_3}{\vert}}{\underset{\underset{C_2H_5}{\vert}}{C}H}CH(CH_2)_8\overset{\overset{C_6H_{13}}{\vert}}{Si}O$	95.5	 $\overset{\overset{CH_3}{\vert}}{\underset{\underset{CH_3}{\vert}}{C}H}{-}\overset{\overset{CH_3}{\vert}}{Si}O$
8.1	 $H(\overset{\overset{H}{\vert}}{N}CH_2CH_2)_{10}\overset{\overset{H}{\vert}}{N}(CH_2)_3SiO_{3/2}$	92.9	$(CH_3)_2SiO$
3.5		96.5	 $CH_2{=}CHCH_2\underset{\underset{CH_3}{\vert}}{Si}O$
6.7		93.3	$(CH_3)_2SiO$

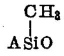
Mol percent	Siloxane unit	Mol percent	Siloxane unit
5.2		94.8	 $\underset{CH_3}{\overset{CH_2}{\overset{\parallel}{C}}}-\overset{CH_3}{Si}O$
0.25	 $CH_3\underset{\underset{^-OOC\underset{CH_3}{C}HCH_2CH_3}{H^+}}{\overset{H}{N}}CH_2CH_2\overset{H}{N}CH_2CH{=}CHCH_2SiO_{3/2}$	99.75	$(CH_3)_2SiO$
9.0		91.0	$(CH_3)_2SiO$

That which is claimed is:

1. A method comprising retarding the deposition of paraffin in petroleum containers by contacting the inside of the container with a siloxane copolymer consisting essentially of 0.25 to 10 mol percent siloxane units of the formula

(1) 
$$\underset{(Y)_a}{R_2N}R'\overset{R''_n}{Si}O_{\frac{(3-n)}{2}}$$

and from 90 to 99.75 mol percent siloxane units of the formula

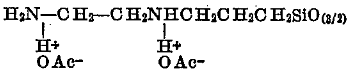
(2) 
$$A\overset{CH_3}{Si}O$$

where n is an integer of a value from 0 through 2, A is a monovalent hydrocarbon radical with from 1 through 3 carbon atoms, R is selected from the group consisting of H, alkyl, alicyclic, and aminoalkyl radicals, R′ is a divalent hydrocarbon radical with at least 3 carbon atoms, the N and the Si atoms being at least three carbon atoms apart, R″ is a monovalent hydrocarbon radical with from 1 through 6 carbon atoms, Y is selected from the group consisting of monocarboxylic, aliphatic, and cycloaliphatic carboxylic acids of from 1 through 10 carbon atoms, and a has a value from 0 to a value equal to the number of nitrogen atoms in (1).

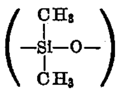
2. The method in accordance with claim 1 where A is CH_3.

3. The method in accordance with claim 1 where (1) contains at least one Y group of from 1 to 3 carbon atoms inclusive.

4. The method in accordance with claim 1 where the copolymer used consists of 0.25 to 10 mol percent of

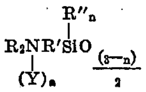

$$\underset{\underset{OAc^-}{H^+}}{H_2N}-CH_2-CH_2\underset{\underset{OAc^-}{H^+}}{N}HCH_2CH_2CH_2SiO_{(3/2)}$$

groups, and 90 to 99.75 mol percent of

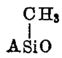

$$\left(-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right)$$

groups.

5. A method comprising incorporating in petroleum containing dissolved paraffin a copolymer consisting essentially of 0.25 to 10 mol percent siloxane units of the formula

(1) 
$$\underset{(Y)_a}{R_2N}R'\overset{R''_n}{Si}O_{\frac{(3-n)}{2}}$$

and from 90 to 99.75 mol percent siloxane units of the formula

(2) 
$$A\overset{CH_3}{Si}O$$

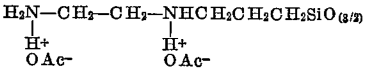
where n is an integer of a value from 0 through 2, A is a monovalent hydrocarbon radical with from 1 through 3 carbon atoms, R is selected from the group consisting of H, alkyl, alicyclic, and aminoalkyl radicals, R′ is a divalent hydrocarbon radical with at least 3 carbons atoms, the N atom and the Si being at least 3 carbon atoms apart, R″ is a monovalent hydrocarbon radical with from 1 through 6 carbon atoms, Y is selected from the group consisting of monocarboxylic aliphatic, and cycloaliphatic carboxylic acids of from 1 through 10 carbon atoms, and a has a value from 0 to a value equal to the number of N atoms in (1); in amount sufficient to retard deposition of paraffin on the walls of a container through which the petroleum is passed.

6. The method in accordance with claim 5 where the siloxane copolymer is continuously added to the petroleum stream passing through the container.

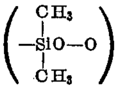
7. The method in accordance with claim 5 where A is CH_3.

8. The method in accordance with claim 5 wherein (1) contains at least one Y group of from 1 to 3 carbon atoms inclusive.

9. The method in accordance with claim 5 where the copolymer used consists of 0.25 to 10 mol percent of


$$\underset{\underset{OAc^-}{H^+}}{H_2N}-CH_2-CH_2-\underset{\underset{OAc^-}{H^+}}{N}HCH_2CH_2CH_2SiO_{(3/2)}$$

groups, and 90 to 99.75 mol percent of


$$\left(-\underset{CH_3}{\overset{CH_3}{Si}}O-O\right)$$

groups.

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