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Gannon et al.

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[54] PURGE FOR PREVENTING PIPELINE CONTAMINATION

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[52] **U.S. Cl.** ..... **252/8.3**, 252/8.55 B

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[58] **Field of Search** ..... 252/8.3, 8.55 B, 152, 89, 526, 252/545; 260/923, 924; 166/304

[56] **References Cited**

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[57] **ABSTRACT**

Surface active contaminants adsorbed on the interior surface of a pipeline can be desorbed therefrom and effectively removed by introducing into the line an effective quantity of wet aliphatic alcohol (C_2–C_4 alcohol) containing a small amount of either a dimer acid of a C_{16}–C_{20} ethenoid fatty acid or a C_4–C_{20} alkyl amine salt of a partially esterified phosphoric acid.

9 Claims, No Drawings

PURGE FOR PREVENTING PIPELINE CONTAMINATION

BACKGROUND OF THE INVENTION

1. Field

The present invention relates to an improvement in transportation of liquid petroleum products through pipelines and their corresponding equipment such as valves, pumps, etc. In particular, the present invention is concerned with an improvement in the transportation of petroleum products containing additives which are surface active and adsorb to the interior walls of the pipeline, thereby leading to possible contamination of a subsequent petroleum product stream through the pipeline.

2. Prior Art

It is common practice to introduce at the refinery relatively minor amounts of additive materials into a hydrocarbon stock or fraction intended for use as fuel in order to impart thereto certain desirable characteristics. Many of these additives are surface active. For instance, it is particularly desirable to add detergent-action hydrocarbyl amines or polyamines in minor amounts in gasolines to reduce engine deposits. See, for example, U.S. Pat. No. 3,438,757. Also, acyclic amino alkylene amides, described in U.S. Pat. No. 2,839,372, are useful as detergents in gasoline. Likewise, derivatives of various carboxylic acids, organic phosphorus containing compounds, polymeric materials, and other surface active additives are combined with petroleum hydrocarbon stocks such as gasoline.

The surface active constituents in petroleum hydrocarbon fuels tend to become adsorbed on the interior surface (wall) of the pipe. When a particular delivery of a "tender" of a fuel is completed and a new tender of a different stock is sent through the line, the adsorbed surface active materials are gradually removed (desorbed) from the surface of the line, passed into the stream of the new tender of fuel and are carried away with it.

The contamination of the subsequent fuel tender with the desorbed surface active materials cannot generally be tolerated. If the second tender is of a similar composition as that of the first tender, then the additive level in the second tender could be higher than that desired. If, as is generally the case, the second tender is of a different petroleum product than that of the first tender, the surface active materials which are desorbed into the second tender may have an extremely adverse effect upon the characteristics of the second tender. Thus, for example, if the second tender is a jet fuel, the presence of surface active contaminants will have an adverse effect on the water tolerance properties of the jet fuel and will be responsible for the rejection of such fuels by both private industry and the military.

SUMMARY OF THE INVENTION

The present invention significantly reduces contamination of petroleum fuels during their transportation through pipelines by providing a method for effective removal of substantial proportions of surface active contaminants from the walls of the pipelines. The surface active contaminants adsorbed on the interior surface of a pipeline can be desorbed therefrom by introducing into the line an effective quantity of a wet C_2–C_4 aliphatic alcohol, preferably isopropanol, containing from 1 to 20 volume percent of either (1) dimer acids of C_{16}–C_{20} ethenoid aliphatic monocarboxylic acids (fatty acids), preferably dimer acids of C_{18} di- and triethenoid alkyl monocarboxylic acids, or (2) C_4–C_{20} aliphatic amine salts of partially esterified phosphoric acid, preferably dialkyl phosphate salts of C_4–C_{20} alkyl amines, or combinations thereof.

DETAILED DESCRIPTION OF THE INVENTION

Following transportation of a tender of a petroleum fuel containing a surface active material through a pipeline whereby contamination of the interior surface wall of the pipeline occurs as a result of adsorption of the surface active material, the pipeline is purged to remove adsorbed surface active materials prior to transportation of a second tender of a petroleum fuel. The purge is accomplished using a C_2–C_4 aliphatic alcohol in an amount of from about 0.0001 to 0.01 barrels per 1,000 square feet of internal surface of the pipeline.

Normally, from about 1 to 25 barrels of the purge will be introduces as a tender, more usually from about 5 to 20 barrels. The amount of the purge will depend on the distance the previous tender is to travel, the volume of the previous tender, the amount of surface active material present in such tender, and the effectiveness with which the purge is able to remove the surface material from the surface of the pipe. Also to be considered is the rate at which the purge becomes diluted with the prior and subsequent tenders, since excessive dilution will reduce the purge's effectiveness in removing adsorbed surface active materials from the pipe surface.

The C_2–C_4 aliphatic alcohol will contain a compound in an amount of from 1 to 20 volume percent based on the alcohol either of (1) the dimer acids of C_{16}–C_{20} ethenoid fatty acids or (2) C_4–C_{20} alkyl amine salts of partially esterified phosphoric acid, or combinations thereof.

There will normally be at least 0.5 volume percent water and not more than about 25 volume percent water, more usually in the range of 2 to 15 volume percent water, and preferably in the range of 3 to 10 volume percent water.

The C_2–C_4 aliphatic alcohol can be ethanol, n-propanol, isopropanol, n-butanol, isobutanol, and the like. Preferably isopropanol is used as the alcohol.

For practical purposes, the critical range of amounts of purge effective in accordance with the invention expressed in barrels extends from about 0.1 to about 10 barrels per each 100 miles of a smooth pipeline of 8 inch I.D. In other words, the purge will be introduced in amounts in a range from about 0.0001 to about 0.01 barrels per 1,000 square feet of the internal surface of pipeline.

The dimer acids used as a component of the purge are the dimer acids of C_{16}–C_{20} ethenoid aliphatic monocarboxylic acids, i.e., fatty acids, preferably the dimer acids of C_{18} di- and triethenoid aliphatic monocarboxylic acids (fatty acids). Suitable C_{16}–C_{20} ethenoid fatty acids which may be dimerized for use in the present inventive purge include the following:

C_{16}—triethenoid fatty acids
- hiragonic acid

C_{18}—diethenoid fatty acids
- linoleic acid
- lineolelaidic acid

C_{18}—triethenoid fatty acids
- linolenic
- elaidolinolenic
- pseudoeleostearic
- α-eleostearic
- β-eleostearic
- punicic

C_{18}—tetraethenoic fatty acids
- moroctic
- α-parinaric
- β-parinaric

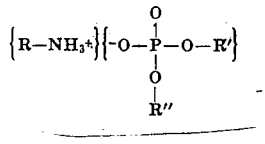
C_{20}—tetraethenoic fatty acids
- arachidonic acid

It is preferred to use the dimer acids of linoleic acid and linolenic acid. The most preferred dimer acid is that of linoleic acid. A dimer acid of linoleic acid is commercially available from Monsanto under the trade name of Santolene C.

Various procedures can be used to produce the dimer acids as, for example, thermopolymerization of the respective fatty acids. These procedures are generally known in the art. In producing the dimer acids, either a single fatty acid compound may be used or a mixture of two or more fatty acid compounds may be used to produce a mixture of dimers.

C_4–C_{20} alkyl amine salts of partially esterified phosphoric acids may also be used as a component of the purge. The organic substituent attached to the oxyphosphorous radical is an alkyl radical of from four to 20 carbon atoms, preferably from

six to 18 carbon atoms. Monoalkyl or dialkyl phosphates or mixtures thereof can be used. It is preferred that the alkyl substituent attached to the oxyphosphorous radical be straight chain. The C_4–C_{20} alkyl amine used to produce the salt is also preferably a straight chain alkyl amine. Preferably the alkyl amine will contain from six to 18 carbon atoms. A representative formula of the amine salts preferred as a component of the purge is:



wherein R is an alkyl hydrocarbon radical of from four to 20 carbon atoms, preferably straight chain, and where at least one of R′ and R″ is alkyl hydrocarbon radicals of from four to 20 carbon atoms, preferably straight chain, and the other may be hydrogen. When R′ and R″ are both alkyl hydrocarbon radicals of from four to 20 carbon atoms in length, they may be the same or different. The total number of carbons will be from eight to 40.

The dimer acid or amine salt should be present in the C_2–C_4 aliphatic alcohol in an amount, based on the alcohol, of from 1 to 20 volume percent, preferably 1 to 5 volume percent.

The subject matter of the present invention may be more fully understood by reference to the following examples.

EXAMPLE 1

A series of laboratory tests were carried out to simulate the conditions in a pipeline transporting petroleum fuels contaminated by adsorption of surface active materials. The test apparatus consisted of a 100 ml burette preceded and followed with a small plug of glass wool. The burette was filled with 60 grams of iron filings of 40 mesh. The surface of these iron filings was believed to be of iron oxide. The iron oxide surface of the particles in the burette, as determined by adsorption of nitrogen, corresponds to about 0.12 mile of a perfectly smooth 8-inch pipeline.

1,250 ml of gasoline containing from 1 to 1,000 ppm of a surface active material, i.e., a high molecular weight polybutene polyamine, was then passed through the burette. Thereafter, 50 ml of purge dissolved in 150 ml of isooctane was passed through the burette. After purging, an additional 50 ml of isooctane was passed through the burette to remove any traces of the purging solution. Finally, a 2,500 ml sample of jet fuel containing no polybutene polyamine was then passed through the burette. The jet fuel (JP–4) was subsequently tested to determine the water separating properties as measured by the modified water separometer index (WSIM). See ASTM 2550 for details of this test.

In two of the tests, the purge consisted of isopropanol containing 5 weight percent water. In another series of tests, the purge consisted of isopropanol, 5 weight percent water, and a dimer acid of linoleic acid (Santolene C) in various concentrations. In another series of tests, the purge consisted of isopropanol, 5 weight percent water, and a C_{12} alkyl amine salt of di-C_{13} alkyl phosphoric acid in various concentrations.

The results are shown in Table I:

TABLE I

Purge	Concentration of Second Component (Wt. % Based on the Alcohol)	WSIM*
Wet isopropanol (no second component)		31, 40
Wet isopropanol dimer acid	2%	80, 78
	5%	83, 90, 86, 93, 95
	10%	84
	20%	97, 73, 77, 86
Wet isopropanol amine salt	1%	67, 74
	2%	70, 71
	5%	83, 81
	10%	79
	20%	94, 79, 95

*Each number represents a separate experiment.

As can be clearly seen from the table, the presence of the dimer acid or the amine salt with the isopropanol significantly increases the WSIM number. The WSIM number is an indication of the ease which a fuel or a fuel-additive combination will release entrained or emulsified water when passed through a coalescer-type water separator. The test provides a measure of the presence of surfactant agents in the fuel. The higher the WSIM number for the jet fuel, the greater the effectiveness of the purge in removing any surface active agents from the iron filings.

EXAMPLE 2

A 7,000 barrel tender of commercial automotive gasoline boiling in the range of about 120° to 440° F., containing as a detergent action additive, a high molecular weight polybutene polyamine in an amount of from 1 to 1,000 ppm was sent through an 8-inch pipeline over a distance of about 23 miles. Samples of the gasoline indicated reduction in the amount of surface active high molecular weight polybutene polyamine following flow through the pipeline.

A tender of jet fuel (JP–4) containing no high molecular weight polybutene polyamine was passed through the pipeline following the gasoline tender. For the first mile, no purge was used between the gasoline tender and the jet fuel tender. For the last 22 miles, a purge of five barrels of isopropanol containing 4 weight percent water was used between the gasoline tender and the jet fuel tender. It was found that the WSIM of the jet fuel suffered severe degradation during the first mile when no purge at all was used. Thus, the WSIM of the jet fell from 86 at the first measuring point to 75 at the end of the first mile. The WSIM of the jet fuel during the last 22 miles fell from 75 to 49.

In another field test, 8,000 barrels of gasoline were passed through the 23 mile, 8-inch pipeline. The gasoline contained the same detergent additive used in the above test. An isopropanol alcohol purge containing 4 weight percent water and 5 weight percent of a dimer acid of linoleic acid (Santolene C) was introduced in an amount of 5 barrels following the gasoline tender. Thereafter 15,200 barrels of jet fuel of the same specifications as that used above and containing no detergent was transferred through the pipeline. The degradation in the WSIM of the jet fuel was markedly less than that in the above field test. Thus, the WSIM of the jet fuel was 96 at the first measuring point, 95 after the first mile, and 90 after the next 22 miles for a total change of 6 WSIM numbers. This compares with the change of 37 WSIM numbers in the above test when no Santolene C was used with the purge.

We claim:

1. A process for removing adsorbed surface active material on the internal surface of a pipeline used for the transportation of liquid petroleum fuels which comprises introducing into said pipeline from about 0.0001 to about 0.01 barrels of a C_2–C_4 alcohol per 1,000 square feet of the internal surface of said pipeline, said alcohol containing from 1 to 20 volume percent, based on the alcohol, of a compound selected from the group consisting of (a) a dimer acid of a C_{16}–C_{20} ethenoid aliphatic monocarboxylic acid, and (b) a mono- or dialkyl phosphate salt of a C_4–C_{20} alkyl amine, the alkyl radical associated with the phosphate having from four to 20 carbon atoms, and from 0.5 to 25 volume percent water.

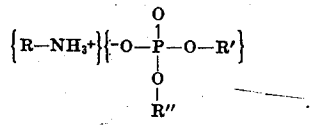
2. The process of claim 1, wherein said water is present in from 2 to 15 volume percent.

3. The process of claim 1, wherein said alcohol is isopropanol.

4. The process of claim 1, wherein said dimer acid is a dimer acid of linolenic acid.

5. The process of claim 1, wherein said dimer acid is the dimer acid of linoleic acid.

6. The process of claim 1, wherein the phosphate salt of the C_4–C_{20} alkyl amine is of the general formula



wherein R is an alkyl hydrocarbon radical of from six to 18 carbon atoms, R′ is an alkyl hydrocarbon radical of from six to 18 carbon atoms, and R″ is an alkyl hydrocarbon of from six to 18 carbon atoms or hydrogen.

7. The process of claim 6, wherein R is a C_{12} alkyl hydrocarbon radical and R′ and R″ are C_{13} alkyl hydrocarbon radicals.

8. A process for removing adsorbed surface active material on the internal surface of a pipeline used for the transportation of liquid petroleum fuels which comprises introducing into said pipeline in bulk, immediately after a tender of fuel containing a surface active material, from about 1 to 25 barrels of isopropanol containing from 1 to 20 volume percent of at least one of a dimer of a linoleic acid, or dodecyl amine salt of mono- or di-tridecyl phosphate and from 2 to 10 volume percent water.

9. A process according to claim 8 wherein said surface active material is aliphatic hydrocarbon substituted polyethylene polyamine of from two to 5 amine nitrogen atoms and said aliphatic hydrocarbon group is from 50 to 200 carbon atoms and wherein said surface active material was present in said fuel from 100 to 1,000 ppm.

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