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CLEANING METAL SURFACES WITH HYDROCARBON SOLVENTS

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This invention relates to improvements in the cleaning of metal surfaces, particularly tank cars, but also, tanks, vessels, exchangers and lines, which have been contaminated by service in handling tarry or resinous products such as crude oil, fuel oil, asphalt and other petroleum residnal products.

Tank cars present unique cleaning problems since they may be used to transport such a range of materials. Service may vary from heavy black oil type products to easily contaminated clean products. A car that has been in black oil or "dirty" service often must be cleaned quickly for handling "clean" products such as gasoline, kerosine, solvents, edible oils, oxygenated organic chemicals and the like. Obviously any material remaining in the car after cleaning can cause serious contamination. On the other hand, time required for cleaning must be kept to the minimum necessary in order to avoid undue turn-around losses.

Conventionally, tank cars are often cleaned by spraying a hot hydrocarbon solvent, e.g. a light catalytic cycle oil, over the interior of the car under pressure. Usually, a recirculating system is employed for circulating oil from a storage tank to rotating high pressure nozzles in the car. The oil drains by gravity from the car to the storage tank and the oils is filtered before recirculation. Heating coils are usually provided in the storage tank to maintain elevated temperature. The cleaning with hot, recirculated solvent may be followed with hot and cold water spray cycles. After the cold water spray has cooled the car, permitting the entrance of laborers for manual cleaning as required, the cars are steamed before returning to service.

According to the present invention, it has been found that the effectiveness of hydrocarbon solvents for cleaning tank cars, heat exchangers, storage vessels and the like, is greatly imrpoved by incorporation of between 0.2 and about 2 weight percent of a fuel oil additive combination. The additive combination consists essentially of a detergent-dispersant comprising the neutralized reaction product of a phosphorus sulfide and a higher hydrocarbon (non-gaseous) and a stabilizer such as an oil soluble polyamine, e.g. an N-alkyl propylene diamine. It has been found that the detergent-dispersant is useful alone in approximately the above proportions in promoting cleansing action but, surprisingly, not at the level of effectiveness of the additive combination. The additive combination also may contain with particular advantage an anti-rust component, e.g. a carboxylic acid salt of an amine, or other compatible, oil soluble rust inhibitors.

Operation, according to the invention, is most readily described by reference to evaluation tests made with specific cleaning formulations. The evaluation tests were run on the cleaning racks of a tank car leasing company. Cars which had been in heavy asphalt service were used in the test since these are considered the most difficult to clean. The cleaning schedule provided circulation of a light catalytic cycle oil at 200° F. for about 1 hour.

In some of the runs, a longer circulation period was employed to see if this would be beneficial. The hot oil was sprayed over the interior of the car under a pressure of 200 p.s.i.g. by a cleaning rig equipped with high pressure nozzles rotating in both the horizontal and vertical plane so as to reach all parts of the car and dome. The oil circulation was followed by hot water for ¾ hour and then by cold water for ¼ hour. After manual cleaning, the cars were steamed. The effectiveness of the cleaning job was evaluated by visual observation inside the car and by visual observation of the oil and water in the storage tanks during circulation through the cars.

As noted above, the severest service is generally asphalt. When hot oil is used without any additive on cars that have been in asphalt service, the asphalt usually washes off the walls of the car, but collects in the bottom of the car. After cooling, the asphalt must be chipped out by hand. Ordinarily, 4 man-days are required to clean a car of this type. In the first additive test, 0.2% by weight of an additive combination consisting of 50 parts of a neutralized phosphorous sulfide-hydrocarbon reaction product, 40 parts of a substituted alkylene polyamine and 10 parts of an anti-rust was used. More specifically, the detergent-dispersant was a potassium hydroxide neutralized reaction product of phosphorus pentasulfide and a butylenes polymer having a molecular weight of about 1000. The polyamine was N-tallow propylene diamine (Duomeen T). The anti-rust was the monooleate of this amine.

After circulating the above composition for several hours, it was apparent that a concentration of 0.2% was too low to clean the car. The concentration was then raised by adding concentrate to the level of 1%. This concentration proved very effective. A considerable amount of asphalt was removed from the car during a circulation period of 2 hours. The asphalt that remained in the bottom of the car was plastic and could be shoveled readily from the bottom of the car instead of being hard, brittle and difficult to remove. Only 4 man-hours were required to clean the car. This is normal time for a car that has been in crude oil or residual fuel service and constrasts with the 4 man-days normally required for cars in asphalt service.

By comparison, 0.5% of the potassium neutralized phosphorus sulfide-hydrocarbon component was used alone. Although this proved quite effective in cleaning a total of 20 cars, it appeared to be less satisfactory than the additive combination. Foreign material remained around rivet and bolt heads on car sides and considerably more manual cleaning was required than in the case of the additive combination.

It was found that 2.5% of the potassium neutralized phosphorus sulfide-hydrocarbon detergent was too strong. After a number of cars had been cleaned, the solution caused emulsification of material washed from the car so that it could not be removed by filtration or by settling in the storage tank but was carried back into the car and sprayed onto the walls. To remove the emulsified material from the walls of the car, manual cleaning was required.

Further testing of the additive combination and the detergent alone confirmed that the 1% concentration level appeared to be about optimum. Compared to the use of light catalytic cycle oil alone, the use of the additives reduced cleaning time greatly and gave better results. Without additive, a dingy, greasy film was habitually left over the surface of the car whereas cars according to the invention were film free.

The detergent-dispersant of the invention may be obtained by reacting a phosphorus sulfide with a hydro-

carbon at a temperature of from about 200° F. to about 600° F., and preferably from about 250° F. to about 500° F., using from about 1 percent to about 50 percent, and preferably from about 5 percent to about 25 percent by weight, of the phosphorus sulfide in the reaction. It is advantageous to maintain a non-oxidizing atmosphere, such as for example, an atmosphere of nitrogen above the reaction mixture. Usually, it is preferable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification becomes necessary; however, an excess of phosphorus sulfide can be used and separated from the product by filtration or by dilution with a solvent, such as hexane, filtering and subsequently removing the solvent by suitable means, such as by distillation. The phosphorus sulfide-hydrocarbon reaction products contain both sulfur and phosphorus. The reaction may if desired be carried out in the presence of an additional sulfurizing agent or the phosphorus sulfide-hydrocarbon reaction product can be sulfurized, as described in U.S. 2,316,087 issued April 6, 1943, to James W. Gaynor and Clyarence M. Loane.

The hydrocarbon constituent of the reaction is preferably a mono-olefin hydrocarbon polymer resulting from the polymerization of low molecular weight mono-olefinic hydrocarbons or isomono-olefinic hydrocarbons, such as propylene, butylenes, and amylenes or the copolymers obtained by the polymerization of hydrocarbon mixtures containing isomono-olefins and mono-olefins or mixtures of olefins in the presence of a catalyst, such as sulfuric acid, phosphoric acid, boron fluoride, aluminum chloride or other similar halide catalysts of the Friedel-Crafts type.

The polymers employed are preferably mono-olefin polymers or mixtures of mono-olefin polymers and isomono-olefin polymers having molecular weights ranging from about 150 to about 50,000 or more, and preferably from about 300 to about 10,000. Such polymers can be obtained, for example, by the polymerization in the liquid phase of a hydrocarbon mixture containing mono-olefins and isomono-olefins such as butylene and isobutylene at a temperature of from about −80° F. to about 100° F. in the presence of a metal halide catalyst of the Friedel-Crafts types such as, for example, boron fluoride, aluminum chloride, and the like. In the preparation of these polymers there may be employed, for example, a hydrocarbon mixture containing isobutylene, butylenes and butanes recovered from petroleum gases, especially those gases produced in the cracking of petroleum oils in the manufacture of gasoline. U.S. 2,407,873 to Evering et al. describes a particularly suitable technique for polymerizing such olefins in the presence of an aluminum-chloride-hydrocarbon complex catalyst.

Essentially paraffinic hydrocarbons such as bright stock residuums, lubricating oil distillates, petrolatums or paraffin waxes may be used. The condensation products of any of the foregoing hydrocarbons or their halogen derivatives, with aromatic hydrocarbons can also be employed.

Examples of high molecular weight olefinic hydrocarbons which can be employed as reactants are cetene (C_{16}), cerotene (C_{26}), melene (C_{30}), and mixed high molecular weight alkenes obtained by cracking petroleum oils. Other olefins suitable for the preparation of the herein described phosphorus sulfide reaction products are olefins having at least 20 carbon atoms in the molecule of which from about 12 carbon atoms to about 18 carbon atoms, and preferably at least 15 carbon atoms, are in a long chain. Such olefins can be obtained by the dehydrogenation of paraffins, such as by the cracking of paraffin waxes, or by the dehalogenation of alkyl halides, preferably long chain alkyl halides, particularly halogenated paraffin waxes. Also, olefins derived from the synthol or hydrocarbon synthesis process may be employed. These are essentially straight chain compounds varying widely in molecular weight.

Also contemplated within the scope of the present invention are the reaction products of a phosphorus sulfide with aromatic hydrocarbons such as benzene, naphthalene, anthracene, toluene, diphenyl, etc. and alkylated aromatic hydrocarbons such as, for example, an alkyl benzene characterized by having at least one alkyl group of at least four carbon atoms, and preferably at least eight carbon atoms such as a long chain paraffin wax.

The phosphorus sulfide reactant can be any phosphorus sulfide, such as for example, P_2S_3, P_4S_3, and preferably P_2S_5.

The phosphorus sulfide-hydrocarbon reaction product normally shows a titratable acidity which is neutralized by treatment with a basic reagent. The phosphorus-sulfide-hydrocarbon reaction product when neutralized with a basic reagent containing a metal constituent is characterized by the presence or retention of the metal constituent of the basic reagent. Other metal constituents such as a heavy metal constituent can be introduced into the neutralized product by reacting the same with a salt of the desired heavy metal.

The term "neutralized phosphorus sulfide-hydrocarbon reaction product" as used herein means a phosphorus sulfide hydrocarbon reaction product having at least about 1 percent of its titratable acidity neutralized by the reaction with a basic reagent and includes the neutralized phosphorus sulfide-hydrocarbon reaction products containing a metal constituent resulting from said neutralization or resulting from the double decomposition of the phosphorus sulfide-hydrocarbon reaction product treated with a heavy metal salt.

The neutralized phosphorus sulfide-hydrocarbon reaction product can be obtained by treating the reaction product with a suitable basic compound such as a hydroxide, carbonate, sulfide, or an oxide of an alkaline earth metal, e.g. calcium or barium, and preferably the latter, or an alkali metal such as, for example, potassium hydroxide or sodium hydroxide. The products are neutralized by mixing a suitable base (e.g. a 50 percent solution of KOH) therewith and heating to a temperature in the range of from about 200° to about 400° F. After the base and phosphorus sulfide-hydrocarbon reaction product are mixed they are preferably steamed at a temperature of about 400° F. to about a half hour. The steaming may take place during neutralization.

The most useful detergents appear to be characterized in composition and structure by the presence of a metal, e.g. potassium, calcium, barium, magnesium, zinc, aluminum etc., coupled to an oil solubilizing group by the polar phosphorus and sulfur containing group.

The polyamine constituents, which are employed in a preferred but more specific aspect of the invention, are amines such as N-n-cetylpropylene diamine, the various "Duomeens" (products of Armour Chemical Division) which have the general formula $RNHCH_2CH_2CH_2NH_2$ wherein R may be derived from coconut fatty acid ("Duomeen C"), from tallow fatty acid ("Duomeen T"), from lauric acid ("Duomeen 12"), or from soya fatty acid ("Duomeen S"), etc. The "Duomeens" are industrial or technical grade chemicals with an amine content of approximately 80% calculated as di-amine. The approximate melting ranges for each of the aforementioned "Duomeens" are "Duomeen C"—20° to 24° C., "Duomeen 12"—28° to 32° C., "Duomeen S"—38° to 42° C., and "Duomeen T"—44° to 48° C.

The salts of the polyamines may be employed as antirusts in accordance herewith and may be prepared by reacting, under carefully controlled, non-dehydrating conditions, i.e. below about 200° F. and preferably below about 195° F., a carboxylic acid containing from about 6 to about 20 carbon atoms, and preferably at least about 12 carbon atoms, e.g. hexanoic, nonanoic, lauric, stearic, oleic, linoleic, linolenic, palmitic, etc., with any of the

described amines to obtain either the mono-or di-substituted acid salts of the amines. Care must be taken in the preparation of such salts inasmuch as prolonged exposure to temperatures higher than about 200° F. results in the formation of amides or even glyoxalidines (if 1,2-substituted polyamines are employed) upon splitting out water. Among the very economical, commercially available salts of this type are the oleic acid mono- and/or di-salts of the Duomeens (above described), particularly of Duomeen T.

Other oil soluble anti-rusts including organic acid, sulfonate, amine and amine salt types may be used. For example, a salt formed by reaction of a polymerized higher carboxylic acid with a 1,2-disubstituted imidazoline, e.g. a dilinoleic or trilinoleic acid salt of 1-heptadecenyl-2-hydroxyethyl imidazoline, may be used with particular advantage. The additives may be used in variable proportions but it is preferred to use about 0.5 to 1.5% of the detergent-dispersant in the finished composition, together with about 0.4 to 1.0% of the alkylene polyamine, and a small amount, say about 0.001% to 0.1% of the oil soluble anti-rust. For convenience in handling, the additive combination may be prepared in the form of a solution of the desired components in a hydrocarbon solvent such as a xylenes fraction, toluene, or a light cycle oil for example, in a concentration of say 10 to 50% or more by weight. The hydrocarbon oil used as the base oil for the cleaning composition obviously may comprise any inexpensive distillate petroleum or aromatics fraction. The use of a light catalytic cycle oil, boiling in the range of about 450° to 750° F. is especially advantageous because of its low price, relative high aromatics content, and ready availability. Kerosene, naphtha or gas oil fractions however are also suitable.

What is claimed is:

1. In a process for cleaning metal surfaces of equipment such as tank cars, storage vessels, transfer lines, and the like, which have been contaminated by tarry or

resinous products such as crude oil, fuel oil, asphalt and other petroleum residual products, the step of washing the metal surface at elevated temperature with a distillate non-viscous hydrocarbon fraction which contains an additive combination essentially consisting of about 0.2 to 2.0 weight percent of a detergent-dispersant consisting of a non-gaseous hydrocarbon which has been reacted with a phosphorus sulfide and thereafter has been neutralized with a basic reagent selected from the class consisting of basic compounds of alkali and alkaline earth metals and about 0.4 to 1.0 weight percent of an N-alkyl propylene diamine having the formula $RNHCH_2CH_2CH_2NH_2$ wherein the alkyl radical R is selected from the group consisting of n-cetyl and fatty acid residue derived from lauric acid, coconut fatty acids, soya fatty acids and tallow fatty acids.

2. The process of claim 1 in which the detergent-dispersant is a potassium neutralized phosphorus pentasulfide-butylenes polymer reaction product.

3. The process of claim 1 in which the concentration of the additive combination is about 1.0 to 2.0 percent by weight.

4. The process of claim 1 in which the hydrocarbon fraction comprises a light catalytic cycle oil boiling in the range of about 450° to 750° F.

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