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TANK CLEANING OPERATIONS

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ABSTRACT OF THE DISCLOSURE

Hydrocarbon residues are removed from metallic surfaces by contacting the hydrocarbon residue with water containing a minor amount of a cleaning formulation composed of from 75 to 95 wt. percent of a predominantly aromatic solvent having a flash point of at least 150° F. and a boiling point at atmospheric pressure of about 350 to 550° F. and 5 to 25 wt. percent of a nonionic surfactant having a cloud point between 100 and 150° F. The nonionic surfactant is formed by the reaction of a higher primary alcohol, such as tridecyl alcohol, with ethylene oxide. Preferably, the nonionic surfactant contains an average of from 8 to 12 moles of ethylene oxide per mole of primary alcohol. After contact with the cleaning formulation, the treated hydrocarbon residue is contacted with water for a time sufficient to substantially remove the hydrocarbon residue.

The present invention relates to cleaning compositions and to a method for the removal of hydrocarbon residues from tank walls. More particularly, the invention is directed to cleaning compositions particularly adapted for the removal of oil clingage from tank walls and a two-step process employing said compositions.

With the rising popularity of high capacity oceangoing tankers and the rising throughput capacity of oil refineries, it has become increasingly important to diminish tanker turn-around time and to maximize the use of available refinery tank storage capacity. One of the principal problems encountered in attempts to reduce tanker turnaround time or to maximize refinery tank storage space is the difficulty experienced in removing hydrocarbon residues, especially heavy petroleum residues or clingage, from metallic tank walls, which removal is necessary to make the storage space available for other products without danger of contamination. Numerous methods have been devised for the cleaning of tank walls. However, even the newest techniques involving hot water cleaning with sophisticated spraying devices are not completely satisfactory because of the protracted periods of times necessary to complete the cleaning operation.

Now, in accordance with this invention, it has been discovered that hydrocarbon residues can be removed from metallic surfaces with a minimum of washing time utilizing a two-step washing process employing a cleaning formulation made up of a minor amount of a primary alcohol ethoxylate nonionic surfactant and a major amount of a high boiling, high flash point, predominantly aromatic hydrocarbon solvent. According to the present process, a minor amount of the nonionic surfactant-aromatic solvent mixture is emulsified with a major quantity of water and then sprayed onto the wall to be cleaned. This initial cleaning solution is permitted to contact the hydrocarbon residues on the wall for a time sufficient to permit the aromatic solvent and the surfactant to dissolve into the hydrocarbon residues. Following a brief holding time, the pretreated wall is sprayed with water for a time sufficient to remove the hydrocarbon residues from the wall.

As stated previously, the initial precleaning formulation is made up of a mixture of a heavy aromatic solvent and a nonionic surfactant. The solvent used should have a high aromatic content and a good solvency for the hydrocarbon residues to be removed from the wall. Preferably, the solvent consists of a heavy hydrocarbon material containing from 75 to 98 wt. percent aromatic constituents. Because of safety considerations, the solvent should have a boiling point varying from 350 to 550° F. preferably 375 to 525° F. and a flash point of at least about 150° F. Examples of useful materials include heavy aromatic naphtha (HAN) or aromatic quench oils (AQO).

The surfactant constituent of the precleaning formulation is preferably a nonionic surfactant formed by the base catalyzed reaction of a higher primary alcohol, preferably having from 12 to 14 carbon atoms, e.g. tridecyl alcohol, with ethylene oxide. The preferred ethoxylate surfactant species contains an average of 8 to 12 moles, more preferably 9 to 10 moles of ethylene oxide per mole of alcohol and exhibit a cloud point between 100 to 150° F., preferably between 120 to 130° F.

The cloud point is a convenient mode for characterizing the relative solubility of nonionic surfactants in aqueous and hydrocarbon phases. Contrary to normal solubility rules, nonionic surfactants generally become less soluble in water at increasing temperatures. The temperature at which an aqueous solution of the surfactant becomes cloudy, due to the decreased solubility of the surfactant, is called the cloud point. For the purposes of this invention, it was found that a cloud point of approximately 125° F. represented the most desirable balance of aqueous and hydrocarbon solubility.

For example, if the surfactant-solvent mixture were applied in an aqueous stream at a temperature of about 140° F., most of the surfactant would remain in the aromatic solvent phase and therefore diffuse with the solvent into the oil clingage of the wall to be cleaned. It is not desirable to use a surfactant which has a low cloud point, i.e. less than 100° F., since this limited water solubility would make the final wash less effective. At the same time, it is not desirable to use a surfactant which has a high cloud point, i.e. greater than 150° F., since most of the surfactant would remain in the water (as opposed to the solvent) and therefore not penetrate the hydrocarbon contaminant.

The pretreat cleaning formulation consists of from 5 to 25 weight percent, preferably 10 to 20 weight percent of the nonionic surfactant with the balance of the formulation being the heavy predominantly aromatic solvent. In operations wherein the cleaning formulation is admixed with water, from 0.5 to 2.0, preferably 0.75 to 1.5 wt. percent of the total mixture consists of the cleaning formulation.

According to the present process, the cleaning formulation-water mixture is applied to a hydrocarbon residue coated surface a a temperature varying from 60 to 180° F., preferably 130 to 140° F. in amounts sufficient to thoroughly wet the wall with the solvent-surfactant mixture. The cleaning formulation may be applied by injecting the material into the water spray of a conventional tank cleaning machine. Following the initial contacting, the surfactant and solvent constituents of the emulsion earlier applied is permitted to dissolve into the hydrocarbon residue on the wall of the tank prior to the final washing operation. The holding time prior to final washing may vary from about 15 minutes to 3 hours, preferably from about 45 minutes to 1.5 hours. After the solvent and surfactant have been permitted to dissolve into the hydrocarbon residue, the treated wall is then contacted with water maintained at a temperature of between 60 to 180 F., preferably 130 to 160° F. for a time sufficient to remove the residue from the wall.

This invention and its advantages will be better understood by reference to the following example:

EXAMPLE 1

A series of experiments were conducted demonstrating the efficiency of the cleaning formulations and washing techniques of the present invention. In each test, one foot square rusty carbon steel panels were dipped into various types of crude oils or residual oils and permitted to drain for one hour. After a draining period, a number of the coated panels were dipped into a precleaning emulsion made up of water containing about 1 wt. percent of the formulation of the present invention and then permited to stand for an additional one-hour period. The precleaning formulation consisted of 80 wt. percent of a predominantly aromatic solvent and 20 wt. percent of a nonionic surfactant, formed from the reaction of tridecyl alcohol with ethylene oxide, having an average of from 9 to 10 moles of ethylene oxide per mole of alcohol. After the holding period, the precleaned and an equal number of non-precleaned panels were uniformly sprayed with hot water and the times necessary for the complete removal of the hydrocarbon from the steel panels recorded. The results of the tests are set forth in Table I below:

TABLE I

Hydrocarbon coating	Cleaner	Temp. of wash water, ° F.	Washing time (seconds)	Washing time, percent of control
Kuwait:				
Crude	None (control)	100	75	100
Crude	Invention	100	27	36
Lago Bunker C	None (control)	140	282	100
Do	Invention	140	192	65
Waxy, scaly residual oil	None (control)	140	137	100
Do	Invention	140	123	90

The data presented in Table I clearly show the advantages realized in utilizing the cleaning formulations and process of the present invention. While the experiments do not precisely duplicate commercial operations, the data does demonstrate that the washing time necessary for removal of hydrocarbon materials from the steel panels was significantly reduced using the cleaning formulations and process of the present invention. In actual commercial practice, protracted holding times after the initial contacting of the tank wall with the precleaning solution and prior to the final washing operation would not be necessary as the time expended to initially contact the entire storage vessel is normally a sufficient hold-up time prior to the final washing operation. Additionally, the cleaning formulation can be applied at full strength to contaminated surfaces followed by a wash water rinse; however, economy usually requires that the precleaning formulation be diluted with substantial quantities of water.

Further advantages of this invention will be apparent to those skilled in the art. It is to be understood that this invention is not limited to the specific example set forth herein, which has been offered merely as an illustration and that modifications may be made without departing from the spirit and scope of the appended claims.

What is claimed is:

1. A cleaning formulation comprising from 75 to 95 wt. percent of a predominantly aromatic solvent having a flash point at least 150° F. and boiling point at atmospheric pressure of between about 350 to 550° F. and 5 to 25 wt. percent of a nonionic surfactant having a cloud point between 100 and 150° F. formed by the reaction of a higher primary alcohol with ethylene oxide.

2. The composition of claim 1 wherein said nonionic surfactant contains an average of from 8 to 12 moles of ethylene oxide per mole of primary alcohol.

3. The composition of claim 2 wherein said primary alcohol is tridecyl alcohol.

4. The composition of claim 2 wherein said predominantly aromatic solvent contains from 75 to 98 wt. percent aromatic constituents and said surfactant has a cloud point between 120 to 130° F.

5. A method for removing hydrocarbon residues from metallic surfaces which comprises contacting the hydrocarbon residue with water containing from 0.5 to 2.0 wt. percent of a cleaning formulation, said cleaning formulation comprising from 75 to 95 wt. percent of a predominantly aromatic solvent having a flash point of at least 150° F. and a boiling point at atmospheric pressure of about 350 to 550° F. and 5 to 25 wt. percent of a nonionic surfactant having a cloud point between 100 and 150° F. formed by the reaction of a higher primary alcohol with ethylene oxide and thereafter contacting the treated hydrocarbon residue with water maintained at a temperature of about 60 to 180° F. for a time sufficient to substantially remove said hydrocarbon residue.

6. The method of claim 5 wherein said nonionic surfactant contains an average of from 8 to 12 moles of ethylene oxide per mole of primary alcohol.

7. The method of claim 6 wherein said primary alcohol is tridecyl alcohol.

8. The method of claim 6 wherein said predominantly aromatic solvent contains from 75 to 98 wt. percent aromatic constituents and said surfactant has a cloud point between 120 to 130° F.

9. The method of claim 8 wherein said cleaning formulation comprises from 80 to 90 wt. percent aromatic solvent and from 10 to 20 wt. percent nonionic surfactant.

10. The method of claim 9 wherein said treated hydrocarbon residue is contacted with water maintained at a temperature of from about 130 to 160° F. from 15 minutes to 3 hours after initial contact with said precleaning formulation.

11. A cleaning formulation comprising from 75 to 95 wt. percent of a predominantly aromatic solvent having a flash point of at least 150° F. and a boiling point at atmospheric pressure of between about 350 and 550° F. and 5 to 25 wt. percent of the nonionic surfactant having a cloud point between 100 and 150° F. formed by the reaction of a higher primary alcohol having from 12 to 14 carbon atoms with ethylene oxide, said nonionic surfactant containing an average of from 8 to 12 moles of ethylene oxide per mole of primary alcohol.

12. The composition of claim 11 wherein said alcohol is tridecyl alcohol.

13. The composition of claim 12 wherein said predominantly aromatic solvent contains from 75 to 98 wt. percent aromatic constituents and said surfactant has a cloud point between 120–130° F.

14. The composition of claim 13 wherein said nonionic surfactant contains an average of from 9 to 10 moles of ethylene oxide per mole of tridecyl alcohol.

15. A method for removing hydrocarbon residues from metallic surfaces which comprises contacting the hydrocarbon residue with water containing from 0.5 to 2.0 wt. percent of a cleaning formulation, said cleaning formulation comprising from 75 to 90 wt. percent of a predominantly aromatic solvent having a flash point of at least 150° F. and a boiling point at atmospheric pressure of about 350 to 550° F. and 5 to 25 wt. percent of a nonionic surfactant having a cloud point between 100 and 150° F. formed by the reaction of a higher primary alcohol having from 12 to 14 carbon atoms with ethylene oxide, said nonionic surfactant containing an average of from 8 to 12 moles of ethylene oxide per mole of pri-

mary alcohol, and thereafter contacting the treated hydrocarbon residue with water maintained at a temperature of about 60 to 180° F. for a time sufficient to substantially remove said hydrocarbon residue.

16. The method of claim **15** wherein said primary alcohol is tridecyl alcohol.

17. The method of claim **16** wherein said predominantly aromatic solvent contains from 75 to 98 wt. percent aromatic constituents, said surfactant has a cloud point between 120 to 130° F. and said nonionic surfactant contains an average of from 9 to 10 moles of ethylene oxide per mole of tridecyl alcohol.

18. The method of claim **15** wherein said cleaning formulation comprises from 80 to 90 wt. percent aromatic solvent and from 10 to 20 wt. percent nonionic surfactant and said cleaning formulation forms from

0.75–1.5 wt. percent of the total water-cleaning formulation mixture.

References Cited

UNITED STATES PATENTS

2,442,100	5/1948	Showalter	134—40
2,934,568	4/1960	Barker	252—89
3,057,804	10/1962	Berkeley et al.	252—89
3,078,189	2/1963	Baker	234—40
3,167,514	1/1965	Baker	252—170

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