United States Patent Office 2,778,777 Patented Jan. 22, 1957

2,778,777

REMOVAL OF METAL COMPONENTS FROM PETROLEUM OILS

Ray Powell, Darien, Conn., assignor to The Texas Company, New York, N. Y., a corporation of Delaware

No Drawing. Application February 16, 1954, Serial No. 410,727

9 Claims. (Cl. 196—40)

This invention relates to the treatment of crude petroleum and petroleum oils to effect the removal of metal contaminants.

Petroleum commonly contains small quantities of heavy metals, such as vanadium, nickel, iron, chromium and molybdenum. These heavy metals presumably occur in petroleum as compounds. The exact chemical composition of the heavy metal compounds is subject to some question. It is generally agreed that the metals are present, at least in part, in the form of oil-soluble metallo-organic compounds. In the processing of the crude oil and distillates therefrom it has been found that the presence of these metal constituents is deleterious, particularly in certain catalytic processes such as catalytic cracking due to deposits of the metal contaminants on the catalyst and also to some extent in the utilization as fuel oil of petroleum products containing these metals.

By means of distillation these heavy metal constituents may be concentrated to some extent in the distillation residues, but nevertheless the metals or their compounds are also present in the distillate products, particularly in the products of vacuum distilling. The presence of the metals in the distillates may be due either to actual vaporization of the metal compounds or to physical carryover or entrainment. These metals have also been found in such stocks as propane deasphalted oil and solvent refined distillate charging stocks. Thus, for example, in the case of gas oil charging stocks for catalytic cracking, it is common for such stocks to contain quantities of heavy metals such as vanadium, nickel, chromium, molybdenum and iron which although minute in amounts are nevertheless definitely deleterious in the catalytic cracking operation. These metals are dehydrogenating catalysts and their effect in fluid catalyst cracking operations is evidenced by an increase in the hydrogen content of the gases produced and by a decrease in the hydrogen content of both the liquid products of the process and the coke deposited on the catalyst. There is also a significant increase in coke production at a given conversion level and a corresponding decrease in yield of liquid products. The adverse economic effects of these factors may be extremely high as a result of loss in unit capacity, decrease in liquid yield and increased requirements of makeup catalyst which is required to minimize the effect of the buildup of active metal contaminants on the circulating catalyst.

In accordance with the invention it is found that by treating petroleum stocks containing heavy metal constituents with acid the original metal compounds are converted into water-soluble constituents or to constituents separable in aqueous phase from the oil phase. Accordingly, the present invention contemplates acidifying the oil containing heavy metal constituents, e. g., with acid in aqueous solution, and then subjecting the acid oil to a dehydrating or demulsification operation, such as chemical or electrical dehydration. The metal constituents are separated from the oil by removal in the aqueous phase.

Petroleum frequently contains also objectionable

amounts of water-soluble metal salts. A common method of removing the salts is to mix the oil containing the salts with water to produce an aqueous solution of the salts and then to effect desalting or demulsification as by chemical means or electrical precipitation. This method of desalting crude oil is not effective for the removal of the undesirable heavy metal contaminants. The present invention affords an improvement on such desalting operations in that oil, such as crude petroleum containing water-soluble salts, as well as heavy metal constituents, may be treated with acid and then subjected to a desalting or dehydrating operation as by chemical means or electrical precipitation to thus remove from the oil both the salts and the heavy metal constituents in the aqueous phase.

In practising the invention, the oil containing metal contaminants is intimately admixed with dilute sulfuric acid. The acid is conveniently used in amounts considerably in excess of the stoichiometric quantity required for reaction with the heavy metal constituents since these constituents normally exist in the oil in such minute proportions that some excess of acid is desirable in order to insure a satisfactory mixing of the oil and acid. The oil is then washed with water so that the acidified metal components are transferred from the oil to the aqueous phase. In cases where no difficult emulsions are produced, the mixture may be settled to effect separation of the oil and aqueous phases with the acidified metal constituents being collected in the aqueous phase. In the event that difficult emulsions are formed, the emulsion is resolved by suitable means, such as electrical precipitation. Optionally, the mixture of crude petroleum and dilute acid is neutralized with an alkaline agent, preferably to a pH value within the range of 6.5 to 7.5 prior to separation of the aqueous phase from the oil.

In an example of the invention, a West Texas crude oil containing 0.0015% iron, 0.0006% vanadium and 0.0005% nickel, was treated with 10% sulfuric acid in the proportion of 3 volumes of oil to one volume of the dilute acid. The treated oil was washed with water and settled into oil and water phases. The oil thus treated was found to contain 0.00011% iron, 0.00018% vanadium and 0.00019% nickel.

In another example, a straight run California gas oil containing 0.00017% iron, 0.00014% vanadium and 0.00015% nickel was similarly treated with dilute sulfuric acid, washed with water and settled into oil and aqueous phases. The treated gas oil was found to contain 0.00007% iron, 0.00006% vanadium and 0.00011% nickel.

In treating crude oil for the removal of both heavy metal contaminants and salts, such as sodium, calcium and magnesium salts, the oil is treated with dilute acid to convert these metal constituents into water-soluble constituents. The acidified oil is then neutralized by the addition of a suitable alkaline agent, such as sodium hydroxide. The neutralized oil is preheated to temperatures such as about 200 to 220° F. and thoroughly commingled or emulsified with hot water. An advantageous method of effecting good emulsification is to pass the oil and hot water in a stream through a pressure reducing valve. The quantity of water required varies with the proportion of salt contained in the oil and ordinarily will be in the range of from some 2 or 3 percent up to 20 percent by volume. The mixture is preferably maintained with a pH value in the range of 6.5 to 7.5. The mixture is sprayed into an electric treating tank between electrodes to effect electrical precipitation and separation into oil and water phases. The treating tank may be held under such pressure as may be necessary to prevent vaporization of the oil or water. The water containing salts and heavy metal contaminants, and the purified

crude oil are separately withdrawn. Upon distilling the crude oil, both the gas oil distillate and the crude residue will be sufficiently low in heavy metal constituents as to be satisfactory as charging stock to a catalytic cracking process.

This application is a continuation-in-part of my copending application, Serial No. 105,040, filed July 15, 1949, now abandoned.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of treating crude petroleum containing minute amounts of water-insoluble heavy metal compounds included in the group consisting of compounds of vanadium, nickel, iron, chromium and molybdenum which comprises contacting said crude petroleum containing minute amounts of heavy metal compounds included in said group with dilute sulfuric acid of the order of 10 percent strength acid in an amount substantially in excess of the stoichiometric amount required for reaction with said heavy metal compounds converting said heavy metal compounds to water-soluble metal salts, forming an aqueous phase containing said salts, and separating resulting purified oil from said aqueous phase.

2. A method as defined in claim 1 wherein the mixture of crude petroleum and dilute acid is neutralized with an alkaline agent to a pH value within the range of about 6.5 to 7.5 prior to said separation.

3. The method of treating crude petroleum containing minute amounts of water-insoluble heavy metal compounds included in the group consisting of compounds of vanadium, nickel, iron, chromium and molybdenum which comprises contacting said crude petroleum containing minute amounts of heavy metal compounds included in said group with dilute sulfuric acid of the order of 10 percent strength in an amount substantially in excess of the stoichiometric amount required for reaction with said heavy metal compounds, converting said heavy metal compounds to water-soluble metal salts, neutralizing the resulting mixture of crude petroleum and dilute acid with an alkaline agent to a pH of about 6.5 to 7.5, emulsifying the resultant neutralized mixture with added hot water while maintaining the pH value of the resulting emulsion within said range, resolving said emulsion into a purified crude oil phase and an aqueous phase containing dissolved therein said water-soluble heavy metal salts, and separating the purified crude oil phase from the aqueous phase.

4. A method as defined in claim 3 wherein said emulsion is resolved by electrical precipitation.

5. A method as defined in claim 3 wherein the acid treated and neutralized crude oil mixture is heated to about 200–220° F., and the quantity of hot water added for emulsification is about 2 to 20 percent by volume based on the crude oil.

6. The method according to claim 3 wherein the acid treatment is conducted with about one volume of dilute acid to three volumes of crude petroleum.

7. In the catalytic cracking of gas oil obtained from crude petroleum containing minute amounts of water-insoluble heavy metal compounds included in the group consisting of vanadium, nickel, iron, chromium and molybdenum, wherein the gas oil is subjected to contact under cracking conditions with a circulating solid cracking catalyst and wherein said circulating solid cracking catalyst normally becomes contaminated with deposits of said metal compounds transferred from said gas oil in the cracking operation, the method of increasing the liquid hydrocarbon yield and concomitantly decreasing the hydrogen content of the gases produces in said catalytic cracking operation, which comprises treating said crude petroleum containing minute amounts of said heavy metal compounds included in said group with dilute sulfuric acid of the order of 10 percent strength in an amount substantially in excess of the stoichiometric amount required for reaction with said heavy metal compounds thereby converting said heavy metal compounds to water-soluble metal salts, neutralizing the resulting mixture of crude petroleum and dilute acid with an alkaline agent to a pH of about 6.5 to 7.5, heating the resultant neutralized mixture to a mildly elevated temperature and emulsifying the heated mixture with added hot water while maintaining the pH value of the resulting emulsion within said range, subjecting said resulting emulsion to electrical precipitation to separate the same into a purified crude oil phase and an aqueous phase containing dissolved therein said water-soluble heavy metal salts, removing the purified crude oil phase and subjecting the same to distillation to separate therefrom a gas oil fraction of substantially reduced heavy metal content over that obtained by distillation of said crude petroleum in the absence of said pretreating steps, and then passing said gas oil fraction as charge stock to said catalytic cracking operation, whereby objectionable deposition of said heavy metal compounds on said circulating solid cracking catalyst is substantially avoided.

8. In a process wherein crude petroleum containing metal compounds is pretreated to effect removal of said compounds and the pretreated petroleum is subsequently fed to a catalytic cracking operation, the improvement which comprises effecting removal of water-insoluble heavy metal compounds from crude petroleum prior to contacting said petroleum with cracking catalyst by contacting crude petroleum containing heavy metal compounds with dilute sulfuric acid of the order of 10 percent strength in an amount substantially in excess of the stoichiometric amount required for reaction with said metal compounds forming water-soluble metal salts of said compounds, washing the resulting acid-oil mixture with water in an amount sufficient to form a separate aqueous phase containing the water-soluble reaction products, and separating said aqueous phase containing said water-soluble reaction products comprising compounds of said metals from the resulting purified oil.

9. In the treatment of a petroleum oil containing water insoluble heavy metal compounds wherein said oil is contacted with an aqueous phase and said oil and said aqueous phase are separated, the improvement which comprises contacting said oil with an aqueous phase comprising of the order of 10% sulfuric acid whereby said water insoluble heavy metal salts are rendered soluble in said aqueous phase and are dissolved therein.

References Cited in the file of this patent

UNITED STATES PATENTS

2,179,008	Campbell	Nov. 7, 1939
2,434,528	Wadley	Jan. 13, 1948
2,447,530	Perkins	Aug. 24, 1948
2,567,173	Arundale et al.	Sept. 11, 1951
2,611,735	Coons	Sept. 23, 1952
2,662,062	Sumerford	Dec. 8, 1953