United States Patent Office 2,723,221
Patented Nov. 8, 1955

2,723,221

USE OF CHELATING AGENTS TO IMPROVE ACID TREATMENT OF HYDROCARBON STREAMS

Christopher P. Stark, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

No Drawing. Application December 6, 1954, Serial No. 473,441

12 Claims. (Cl. 196—24)

This invention relates to treatment of a hydrocarbon stream. In one of its aspects this invention relates to a process for preventing the formation of an insoluble acid sludge in a process wherein a hydrocarbon stream is treated with an acid. In another aspect, this invention relates to a process for removing acid insoluble sludge from a hydrocarbon stream. In a more specific aspect this invention relates to a process for the transformation of a water insoluble acid sludge into a form which is completely soluble in water by the use of chelating agents.

The acid treatment of hydrocarbon mineral oils is a well established practice carried out primarily for the purpose of removing undesirable constituents and stabilizing the produce chemically. For example, gasolines and naphthas are acid treated to chemically stabilize unsaturated easily oxidizable gum-forming compounds and to remove sulfur and color-forming material; kerosenes are acid treated to remove gum-forming aromatic and unsaturated hydrocarbons, sulfur, and color-forming material; and lubricating oils are acid treated to remove sulfur and materials which are easily oxidizable. In this treatment, the acid or acid refining agent is intimately admixed with the hydrocarbon fraction and an insoluble precipitate of a viscous nature is formed. This precipitate is commonly termed "acid sludge" or, more briefly, "sludge." This sludge coagulates and, after agitation of the admixture has been suspended, tends to concentrate at the interface between the hydrocarbon and aqueous phase. After a sufficient period of time, the sludge settles to the bottom of the vessel and adheres rather strongly to the metal surfaces of the mixing apparatus and the vessel, necessitating a difficult and expensive cleaning operation. Sometimes a rather small amount of finely divided sludge remains suspended in the treated hydrocarbon fraction and does not settle in a reasonable period of time. The separation of the acid sludge should be complete since the accumulation of sludge in subsequent refining steps causes difficulty in these steps.

An object of this invention is to provide an improved process for treating hydrocarbon streams with an acid refining agent without the formation of an aqueous insoluble acid sludge.

Another object of this invention is to provide a process for removing acid sludge from an acid-hydrocarbon reaction mixture.

Still other objects and advantages of this invention will be apparent to those skilled in the art upon reading this disclosure.

The present invention provides a process for treating a hydrocarbon stream with an acid refining agent whereby an acid treated hydrocarbon, essentially completely free of insoluble acid sludge, is produced. In one aspect, the present invention provides a process for preventing the formation of insoluble acid sludge in a reaction mixture formed by treating a hydrocarbon stream with an acid treating agent. In another aspect, the present invention provides a process for effectively removing essentially all the acid sludge from a hydrocarbon stream

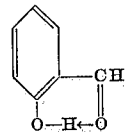
which has been treated with an acid refining agent in the conventional manner. A wide variety of hydrocarbon streams, which have been treated with acid refining agents, can be produced essentially free of insoluble acid sludge by the process of this invention. Some of these hydrocarbon streams include crude residuums or bottoms from the distillation of crude petroleum, lubricating oil distillate stocks, paraffinic or naphthenic oil fractions produced by the selective solvent extraction of lubricating oil distillates or reduced crudes, viscous hydrocarbon oils resulting from the destructive or non-destructive hydrogenation of crude oil or fractions thereof, and tar or tar distillates obtained in the cracking of petroleum for the production of motor fuel. The acid refining agent ordinarily employed in treating the hydrocarbon stream is sulfuric acid, either as a dilute acid of a concentration as low as 50 per cent or as fuming acid or oleum; however, other acids such as phosphoric acid or hydrochloric acid, are sometimes used to treat a hydrocarbon stream.

This invention is based on the discovery that the insoluble acid sludge formed when a hydrocarbon stream is treated with an acid refining agent is transformed by the use of a chelating agent to a form which is soluble in water. The chelating agent is ordinarily employed as an aqueous solution; however, a chelating agent in a solid form can also be used provided sufficient entrained water is present in the hydrocarbon stream or in the acid refining agent. In addition, water can also be injected into the hydrocarbon stream to be treated. Usually the amount of water present in the aqueous solution of the chelating agent is a sufficient volume of solvent for dissolving the water-soluble form of the acid sludge. The chelating agent can be admixed either with the hydrocarbon stream before treatment with the acid refining agent or with an acid refining agent so that the chelating agent is immediately available for converting the acid sludge as it is formed into a water-soluble form. In this manner of operation, insoluble acid sludge does not appear in the reaction mixture but the material is present in solution in the aqueous acidic phase. The chelating agent can also be used to transform the insoluble sludge formed, when a hydrocarbon stream is treated with an acid refining agent in the absence of a chelating agent, into a form which is soluble in water and can be readily removed from the hydrocarbon stream by water washing. An aqueous solution of a chelating agent is also useful in removing acid sludge from reaction vessels and other process apparatus.

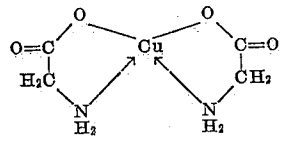
Chelating agents are well known in the art and are compounds which form a chelate compound having the same molecule attached to a central atom at two different points, whereby a ring structure is formed with at least one such attachment being a coordinate linkage. The preferred type of chelating agent to be employed in this invention is a polycarboxylic amino acid or an alkali metal salt of such an acid; however, this invention is not limited to this particular type of chelating agent. Specific examples of the polycarboxylic amino acids include ethylene diamine N,N'-tetra-acetic acid; propylene 1,2-diamine N,N'-tetra-acetic acid; 1,3-diamino propanol-2 N,N'-tetra-acetic acid; diethylene triamine N,N'-tetra-acetic acid; hexamethylenediamine N,N'-tetraacetic acid; cyclohexylamine N-diacetic acid; ethylene diamine N,N'-diacetic acid; and the like. A preferred chelating agent is the sodium salt of ethylene diamine N,N'-tetra-acetic acid. Preferably, the chelating agent is employed as an aqueous solution containing 10–75 weight per cent of the solid chelating material. Weaker or stronger concentrations of chelating agent can also be used and, if desired, a solid form can be used. The chelating agent can also be admixed with the acid refining agent in a liquid volume ratio of chelating agent to sulfuric acid of 1:5 to 5:1.

The proportion of chelating agent and acid in such an admixture varies considerably depending upon the concentration of the two materials and cannot be definitely stated.

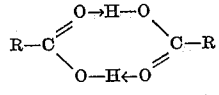
The term "chelate ring" describes a cyclic structure that arises through intermolecular coordination in systems containing a doner and acceptor center (such as occurs in salicylaldehyde



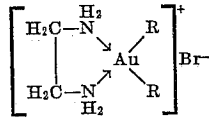
and the covalent copper salt of glycine) or a ring that is



formed by intermolecular coordination in systems that are capable of forming two or more coordinate links, other forms of which are illustrated by the dimers of carboxylic acid

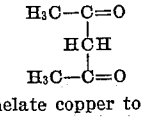


and a variety of metal complexes derived from ethylenediamine or anions of dicarboxylic acids

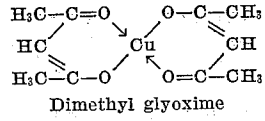


Many unsaturated radicals function as chelate groups partly because of their principle valencies and/or residual affinity, i. e., acetylacetone and oxylate groups and the univalent groups in dimethyl glyoxime.

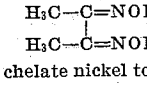
Acetylacetone



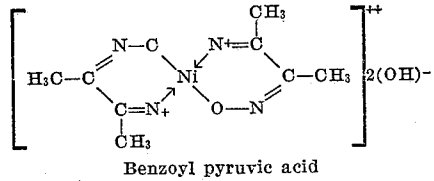
will chelate copper to form:



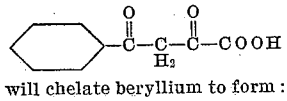
Dimethyl glyoxime



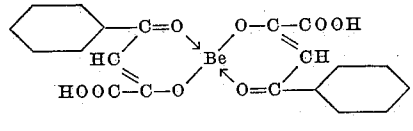
will chelate nickel to form:



Benzoyl pyruvic acid

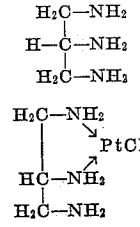


will chelate beryllium to form:

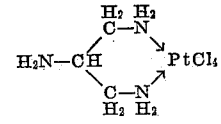


and benzilmonoxime in the alpha form is often used to chelate metals in analytical procedures.

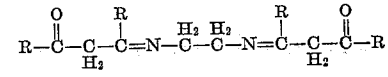
Five- and six-membered chelate rings are found in the complex amines containing ethylenediamine; triethylenediamine; 1,2,3, triaminopropane, 2,2, bipyridyl; 2 aminomethyl quinoline; β,β, diaminodiethylamine; ammonia diacetic acid; tripyridyl; etc. For example 1,2,3, triaminopropane will chelate platinum chloride as follows:



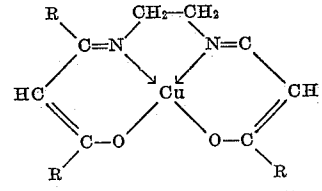
or



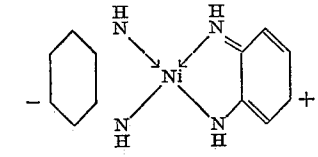
Polydentate chelate rings may be formed from molecules containing two or more coordinate centers giving rise to di- and tri-cyclic systems of the spirane type such as diethylene triamine $NH_2CH_2CH_2NHCH_2CH_2NH_2$ and compounds of the general formula



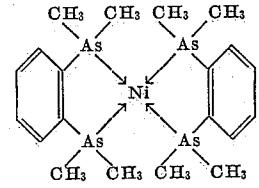
which will chelate copper to form:



and ortho-phenylenediamine which will chelate nickel to form:



also 1,2-bis-dimethylarsinobenzene which will chelate nickel to form the following nickel complex:



In all of the above examples R may represent alkyl, aryl, cycloalkyl etc. groups. These groups will generally contain from 1 to 6 carbon atoms since such compounds are generally economically available, however the invention is not limited to such a number.

The above mentioned chelating agents are not intended to be exhaustive but are typical of the chelating agents useful in the practice of this invention. As has been said, chelating agents are known in the art, a preferred type of chelating agent for the practice of this invention has been indicated.

The process of this invention is ordinarily carried out at atmospheric temperature and pressure. Slightly elevated temperature, usually not above 300 or 400 F., can be employed. Elevated pressure is not required but it is desirable to maintain the distillate in liquid phase and

pressures as high as 200 p. s. i. or higher can be used. The amount of acid refining agent used to treat a hydrocarbon stream varies and depends on the particular refining agent used, the concentration of such refining agent, the particular hydrocarbon stream being treated, and the degree of treatment desired. For example, concentrated sulfuric acid in an amount of from 1–50 per cent of the hydrocarbon stream by volume is usually used. The amount of chelating agent employed also varies over a wide range and is determined by such factors as the concentration of the aqueous solution of the chelating agent, the quantity of acid sludge formed, and the degree of sludge removal desired. Ordinarily, a volume of 10–75 per cent aqueous solution of chelating agent and more generally a 30–40 per cent solution in the range of 1–10 volume solution per 100 volumes of the hydrocarbon stream is sufficient but greater or smaller amounts of chelating agent can be used in the practice of this invention.

The advantage of this invention is illustrated by the following examples. The chelating agent used in these examples was an aqueous solution of ethylene diamine tetra-acetic acid tetra-sodium salt, which is identified as Versene Fe–3, available from the Bersworth Chemical Company, Framingham, Mass. Versene Fe–3 has a total solids content of 34 per cent, specific gravity of 1.2 and a pH of 11.8 in a 1 per cent solution, and is of a light straw color. The color of a hydrocarbon is defined by the Saybolt color scale wherein the color of +30 is water white. In order to best show the advantage of this invention I have used a particular chelating agent to treat a particular hydrocarbon. Those skilled in the art will understand that any of the chelating agents disclosed can be used for similar treatment of this hydrocarbon or other hydrocarbon streams.

Example I

In this run 200 cc. of Borger [1] kerosene of +2 Saybolt color was thoroughly admixed at room temperature with 10 cc. of 34 per cent Versene Fe–3 chelating agent in a separatory funnel and the decanted kerosene, without water washing, was treated at room temperature with 10 cc. of 84 per cent sulfuric acid (run 27). No insoluble sludge was formed in this Versene-treated hydrocarbon fraction with the addition of this acid. The treated kerosene was also washed with water without the appearance of any insoluble acid sludge. The color of this product was +30 Saybolt color and the kerosene retained this color after three months and 19 days of dark storage in the absence of air.

Example II

In this run 200 cc. of Borger kerosene (run 9) was treated at room temperature with a volume of 84 per cent sulfuric acid amounting to 20 pounds of acid per barrel of hydrocarbon. A heavy, reddish acid sludge was found in the reaction admixture. A volume of 34 per cent Versene Fe–3 amounting to 50 cc. was added to this admixture and, after thorough shaking, the insoluble acid sludge disappeared by solution in the aqueous phase. Washing the treated kerosene did not precipitate any acid sludge. The color of this kerosene was improved from +2 Saybolt color to +28 and the kerosene retained this color after five months and 15 days of dark storage in the absence of air.

Example III

An acid solution containing a chelating agent was prepared in a third run by admixing 10 cc. of 84 per cent sulfuric acid with 20 cc. of 34 per cent aqueous solution of Versene Fe–3. This acid-chelate admixture was used to treat 150 cc. of Borger kerosene in a separatory funnel without the precipitation of any insoluble acid sludge. The color of the untreated kerosene was +2 Saybolt color and the color of the product, which was not water washed, was +17. The color of this product was found to be +14 after 5 months and 25 days of dark storage in the absence of air.

Example IV

As a comparison for the above examples, 200 cc. of Borger kerosene of +2 Saybolt color was treated with 84 per cent sulfuric acid in an amount corresponding to 20 pounds of acid per barrel of hydrocarbon in a separatory funnel (run 10). A heavy precipitate of insoluble acid sludge was formed and the kerosene was separated by decantation, water washed, and filtered through filter paper. The color of this product was +28 Saybolt color and after five months and 15 days of dark storage in absence of air a color of +16 was obtained.

The above examples illustrate the advantages of the chelating agent treatment of the hydrocarbon stream. The treatment not only removes the acid sludge, but also stabilizes the color.

I have illustrated this invention in one of its preferred embodiments. Those skilled in the art will see many modifications which can be made and still obtain the advantage of this invention.

I claim:

1. In the process of treating a hydrocarbon stream with an acid, the improvement comprising incorporating in said stream an aqueous solution of a chelating agent to convert acid sludge to an aqueous soluble form.

2. A process for acid treating a hydrocarbon stream which comprises adding a chelating agent to a hydrocarbon stream in the presence of water, contacting the hydrocarbon stream with an acid, and separating the resulting hydrocarbon phase from the resulting aqueous phase.

3. A process for acid treating a hydrocarbon stream which comprises contacting said stream with an acid thereby forming an aqueous insoluble sludge, contacting the resulting stream containing said sludge with a chelating agent in the presence of water thereby converting said sludge to an aqueous soluble form, and separating the hydrocarbon from the resulting aqueous solution.

4. A process for acid treating a hydrocarbon stream which comprises preparing an aqueous solution of a chelating agent having the chelating agent in a concentration range of 10 to 75 weight per cent, admixing 100 volumes of a hydrocarbon stream with 1 to 10 volumes of the resulting chelating agent solution, contacting the resulting admixture with an acid in an amount sufficient to treat said hydrocarbon stream, and separating the treated hydrocarbon stream from the resulting aqueous solution.

5. A process for acid treating a hydrocarbon stream which comprises contacting said hydrocarbon stream with 1 to 50 volumes of a concentrated acid per 100 volumes of the hydrocarbon stream in the presence of an aqueous solution of a chelating agent having a concentration in the range of 30 to 40 weight per cent, the said solution of a chelating agent being present in an amount in the range of 1 to 10 volumes solution per 100 volumes of said hydrocarbon stream, and separating the treated hydrocarbon stream from the resulting aqueous solution.

6. A process for stabilizing the color of a hydrocarbon stream which comprises contacting said hydrocarbon stream with concentrated sulfuric acid in a volume ratio in the range of 1 to 50 volumes acid per 100 volumes hydrocarbon, contacting said hydrocarbon stream with an aqueous solution of a chelating agent in a concentration range of 10 to 75 weight per cent and in an amount in the range of 1 to 10 volumes of chelating agent solution per 100 volumes of hydrocarbon stream, and separating the treated hydrocarbon from the resulting aqueous solution.

7. The process of claim 6 wherein the chelating agent is selected from the group consisting of polycarboxylic amine acids and alkali metal salts thereof.

[1] From the Borger, Texas, Refinery of Phillips Petroleum Co.

8. The process of claim 7 wherein the chelating agent is the sodium salt of ethylene diamine N, N'-tetra-acetic acid.

9. The process of claim 7 wherein the chelating agent is propylene-1,2-diamine N,N'-tetra-acetic acid.

10. The process of claim 7 wherein the chelating agent is the sodium salt of 1,3-diamine propanol-2,N,N'-tetra-acetic acid.

11. The process of claim 7 wherein the chelating agent is diethylene triamine N,N'-tetra-acetic acid.

12. The process of claim 7 wherein the chelating agent is hexamethylene diamine N,N'-tetra-acetic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,463,015	Bersworth	Mar. 1, 1949
2,523,549	Axe	Sept. 26, 1950
2,651,595	Moulthrop	Sept. 8, 1953
2,659,691	Gilson	Nov. 17, 1953