

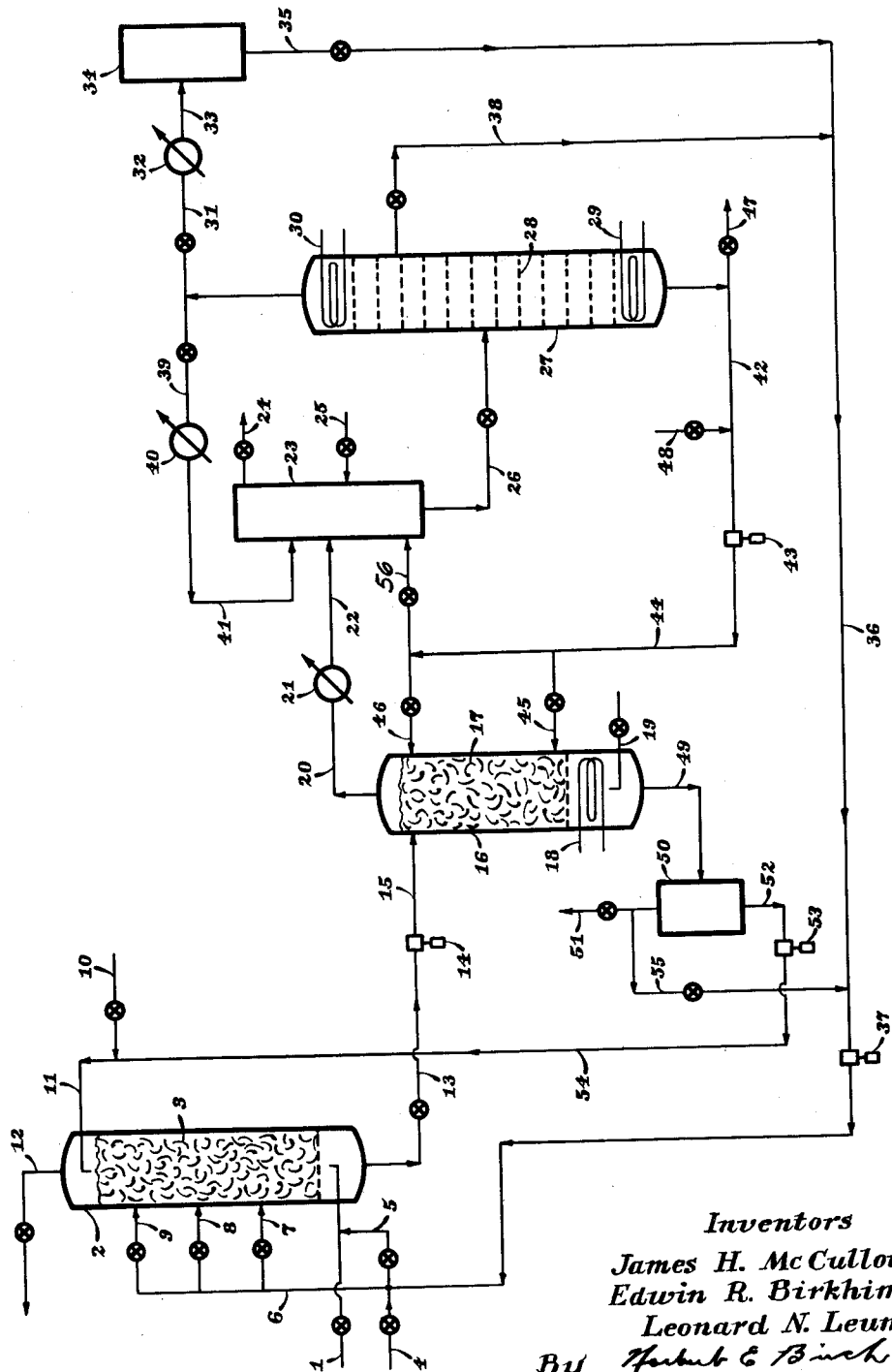
Feb. 2, 1943.

J. H. McCULLOUGH ET AL

2,309,651

TREATMENT OF HYDROCARBON OIL

Filed Feb. 13, 1941



Inventors

James H. McCullough

Edwin R. Birkhimer

Leonard N. Leum

By *Herbert C. Birch*
Their Attorney

Their Attorney

UNITED STATES PATENT OFFICE

2,309,651 -

TREATMENT OF HYDROCARBON OIL

James H. McCullough and Edwin R. Birkhimer,
Philadelphia, and Leonard N. Leum, Upper
Darby, Pa., assignors to The Atlantic Refining
Company, Philadelphia, Pa., a corporation of
Pennsylvania

Application February 13, 1941, Serial No. 378,830

5 Claims. (Cl. 196—32)

The present invention relates to a method for removing acidic organic compounds from hydrocarbon oil, and more particularly to the removal of mercaptans and phenolic compounds from petroleum distillates.

An object of this invention is the provision of a simple and economic method embodying the desulfurization of petroleum hydrocarbons by chemical agents and the regeneration of the chemical agents employed in the desulfurizing treatment.

A further object of this invention is the desulfurization of petroleum hydrocarbons, particularly naphtha and gasoline, by treatment thereof with relatively small quantities of an aqueous solution of an alkaline reagent, and with an organic solvent.

A further object of this invention is a particular method of applying the treating agents to the hydrocarbons to be desulfurized, and the regeneration of the agents employed in such treatment.

It has been proposed heretofore to desulfurize gasoline by treatment with dry sodium hydroxide and anhydrous methyl alcohol, or with anhydrous alcoholic solutions of sodium hydroxide, or alcoholic solutions of alkali agents containing various percentages of water. These prior art methods have been found impractical and uneconomic due to the cost and difficulty of regenerating the spent treating agents, and to the necessity for recovering, at considerable cost, the alcohol retained in the treated gasoline.

However, these difficulties are overcome to substantial extent by operating in accordance with the present invention, wherein relatively small quantities of treating agent are employed, regeneration of the spent agent is simple and efficient, and a desulfurized oil is produced which is substantially free of treating agent.

Our invention comprises essentially counter-currently contacting an aqueous solution of an alkaline reagent with hydrocarbon oil and a solvent more soluble in the aqueous solution than in the oil, forming a phase comprising oil having a reduced content of acidic organic compounds and substantially free of solvent, and a second phase comprising an aqueous alkaline solution containing the solvent and acidic organic compounds extracted from the oil, separating the phases, and subjecting the second mentioned phase to a regeneration treatment to separate and recover the alkaline reagent, the solvent, and the acidic organic compounds removed from the oil.

Our invention may be further understood with reference to the accompanying drawing, which illustrates diagrammatically a system suitable for carrying out our process.

Hydrocarbon oil, for example, gasoline, preferably free of hydrogen sulfide, and having a content of 35 mg. sulfur as RSH per 100 cc., is continuously introduced through valve-controlled pipe 1 into the lower portion of extraction tower 2 provided with packing material 3 such as broken pumice, tile, or the like. An organic solvent, such as methanol, in a quantity of, for example, 0.5% by volume of the gasoline, is introduced into the lower portion of extraction tower 2 through valve-controlled pipes 4 and 5, along with the gasoline flowing through valve-controlled pipe 1. Or, alternatively, the methanol may be introduced at a higher elevation in tower 2 by means of pipe 6 and one or more of valve-controlled pipes 7, 8, and 9. An aqueous solution of an alkaline reagent, for example, sodium hydroxide of 47% concentration, in a quantity of, for example, 2% by volume of the gasoline, is introduced into the upper portion of tower 2 by means of valve-controlled pipe 10 and pipe 11. The temperature in the tower is maintained above the freezing point of the sodium hydroxide solution, and temperatures of the order of 90° F.—100° F. have been found satisfactory. The gasoline and methanol, in flowing upwardly through the tower packing is brought into intimate contact with the counter flowing aqueous alkaline solution, and as a result, the acidic organic compounds such as mercaptans (RSH) and phenols contained in the gasoline are converted into sodium mercaptides and phenolates. At the same time, the methanol is dissolved by the aqueous alkaline solution, and the resulting aqueous alcoholic alkaline solution dissolves the mercaptides and phenolates produced by the reaction of the sodium hydroxide with the mercaptans and phenols originally contained in the gasoline. The rate of flow of the gasoline and the treating agent, and the point of introduction of the methanol is so adjusted that the treated gasoline withdrawn from the top of tower 2 by means of valve-controlled pipe 12 is substantially free of methanol and contains substantially less acidic organic compounds than the gasoline charged to the tower. The treated gasoline withdrawn from the tower by means of valve-controlled pipe 12 may be passed through a filter containing sand, pebbles, or clay to remove traces of entrained alkaline reagent, or such gasoline may be subjected to water washing, if desired. By employ-

ing the quantities of alkaline solution and methanol above specified, the treated gasoline was found to contain 0.3 mg. sulfur as RSH per 100 cc., and was sweet to the doctor test. However, by varying the quantities and concentrations of the treating agents, either sweet or sour gasoline may be produced, such gasoline containing a reduced or controlled amount of sulfur compounds. We have found that by introducing the methanol at an elevation in the tower, but below the point of introduction of the aqueous alkaline solution, we are able to obtain better desulfurization than could be obtained if the methanol was introduced into the lower portion of the tower, along with the gasoline. In any event, the methanol must be introduced at such an elevation in the tower that complete solution of the methanol in the aqueous alkaline solution is obtained before the gasoline reaches the top of the tower, otherwise a considerable quantity of methanol would pass from the tower in solution in the treated gasoline.

Spent treating solution comprising an aqueous alcoholic solution containing unreacted sodium hydroxide, sodium mercaptides and phenolates, methanol and traces of gasoline, is withdrawn from the bottom of extraction tower 2 by means of valve-controlled pipe 13 and delivered by pump 14 through pipe 15 into the upper portion of stripping tower 16 provided with packing 17, closed heating coil 18, and valve-controlled steam jet 19. Heat is applied to the spent solution in tower 16 by circulating steam through coil 18, or by injecting open steam into the solution through valve-controlled jet 19. The temperature at the bottom of the tower may be of the order of 280° F., while that at the top of the tower is about 215° F.-220° F. As a result of the heating, the mercaptides are decomposed to mercaptans, with the liberation of an equivalent amount of sodium hydroxide, and the mercaptans, methanol, gasoline, and a portion of the water content of the spent solution are vaporized, withdrawn from the top of the tower through pipe 20, condensed in condenser 21, and the condensate delivered by pipe 22 to separator 23. This condensate may comprise an aqueous solution containing 15%-30% by weight of methanol and 10-40 mg. sulfur as RSH per 100 cc., admixed with insoluble mercaptans and traces of gasoline. The condensate is permitted to settle and stratify in separator 23, whereby there is formed an upper layer of insoluble mercaptans and traces of gasoline, and a lower aqueous layer containing 15%-30% methanol and 10-40 mg. mercaptan sulfur. The upper layer of insoluble mercaptans and traces of gasoline is removed from separator 23 by means of valve-controlled pipe 24, and may be disposed of as desired. By this separation, 95% or more of the mercaptans entering the separator with the condensate are removed from the aqueous methanol solution, only the lower molecular weight mercaptans remaining, to a small extent, in solution in the aqueous methanol. To assist in the removal of the mercaptans soluble in the aqueous methanol, a small amount of a solvent such as hydrocarbon oil or gasoline may be introduced into the separator by means of valve-controlled pipe 25. This oil, while immiscible with the aqueous methanol, is capable of extracting therefrom a considerable portion of the mercaptans normally soluble in the aqueous methanol. The added oil containing the extracted mercaptans may be removed from the separator, together with the upper layer of normally insoluble higher molecular weight mercaptans.

The aqueous methanol solution containing traces of lower molecular weight mercaptans is withdrawn from the bottom of separator 23 and passed by means of valve-controlled pipe 26 into fractionating tower 27 provided with bubble trays 28, heating coil 29, and dephlegmating coil 30. In the fractionating tower, the methanol and mercaptans are vaporized and fractionally distilled from the aqueous methanol solution, the temperature at the top of the tower being of the order of 150° F., and at the bottom about 212° F. During the fractionation a small amount of water is distilled over with the methanol and mercaptans, and the composite vapor is withdrawn from the top of tower 27 by means of valve-controlled pipe 31, condensed in condenser 32, and the condensate delivered through pipe 33 to receiving tank 34. This condensate may comprise methanol containing up to about 10% of water and up to about 70 mg. mercaptan sulfur, substantially all of which is in the form of low molecular weight mercaptans. The recovered methanol is withdrawn from tank 34 and recycled by means of valve-controlled pipe 35, pipe 36, pump 37, and pipe 6 to the extraction tower 2 for treatment of additional quantities of gasoline.

As an alternative method of operating the fractionating tower 27, the fractionation may be carried out to produce a liquid side stream of methanol which may be passed from tower 27 by means of valve-controlled pipe 38 into pipe 36 for recycling to extraction tower 2. In this event, a constant boiling azeotrope of mercaptans and methanol is withdrawn from the top of fractionating tower 27 through valve-controlled pipe 39, condensed in condenser 40 and returned by pipe 41 to separator 23, wherein the mercaptans and methanol may be separated to substantial extent. This method of operating is particularly useful in the event that the aqueous methanol supplied to tower 27 for fractionation contains excessive amounts of low molecular weight mercaptans.

The water, comprising the bottoms or residue from the fractional distillation, is withdrawn from the bottom of tower 27 through pipe 42 and may be recycled by means of pump 43, pipe 44, and either of valve-controlled pipes 45 and 46 to the stripping tower 16. This water is substantially free of methanol but may contain small amounts of mercaptan, i. e., of the order of 0.2 mg. mercaptan sulfur per 100 cc. If desired, a portion of the water may be diverted and introduced into separator 23 to assist in the separation of mercaptans from the stripper overhead condensate, provided such condensate is deficient in water. In the event that open steam is utilized in stripping tower 16, excessive water may be removed from the system by means of valve-controlled pipe 47 associated with fractionating tower 27. In the absence of open steam stripping, it will be obvious that a certain amount of fresh water will be required to reach equilibrium operating conditions, and this may be supplied by means of valve-controlled pipe 48.

The regenerated sodium hydroxide solution comprising, for example, a 47% concentration of sodium hydroxide in water and containing sodium phenolates and from about 50 to 250 mg. mercaptan sulfur per 100 cc., is passed from the bottom of stripping tower 16 through pipe 49 into separator 50, wherein the insoluble phenolates are permitted to settle and stratify as an upper layer above the lower layer of concentrated sodium hydroxide solution. The phenolates may be withdrawn from the top of sep-

arator 50 by means of valve-controlled pipe 51 and disposed of as desired, while the regenerated sodium hydroxide solution may be drawn from the bottom of the separator through pipe 52 and delivered by pump 53 and pipes 54 and 11 to the upper portion of extraction tower 2 for use in the treatment of additional quantities of gasoline. However, we have found that more complete desulfurization of the gasoline may be accomplished by carrying out the treatment in extraction tower 2 in the presence of recycled sodium phenolates. To accomplish this end, at least a portion of the phenolates separated in separator 50 are withdrawn therefrom by means of valve-controlled pipe 55 and passed, together with recycle methanol, through pipe 36 to pump 37, and delivered thereby through pipe 6 to the extraction tower 2.

While in the operation of our system as above described, we have shown the use of a single extraction tower 2 in which removal of acidic organic compounds from gasoline may be accomplished, we may employ in lieu thereof, two extraction towers in series since two short towers are more convenient to build and operate than a single tall tower. In such case, the aqueous solution of sodium hydroxide is introduced into the upper portion of the first tower, flowed downwardly through the first tower and drawn from the bottom thereof, mixed with methanol, and the aqueous methanol solution of sodium hydroxide then introduced into the upper portion of the second tower. This solution is then flowed downwardly through the second tower and is withdrawn from the bottom thereof. Simultaneously, the gasoline to be treated is introduced into the lower portion of the second tower, flowed upwardly in intimate countercurrent contact with the descending aqueous methanol solution of sodium hydroxide whereby acidic organic compounds are extracted, and the treated gasoline containing some dissolved methanol is drawn from the top of the second tower. This treated gasoline is then introduced into the lower portion of the first tower, flowed upwardly therethrough in intimate countercurrent contact with the descending aqueous solution of sodium hydroxide and is then withdrawn from the top of the first tower. The gasoline so withdrawn is substantially free of methanol and has a substantially reduced content of acidic organic compounds. The spent treating solution from the bottom of the second tower may be regenerated in accordance with the method hereinbefore described, and the recovered sodium hydroxide solution and methanol recycled for the treatment of additional quantities of gasoline. Thus, the two towers in series function in the same manner as the single extraction tower 2, the first tower corresponding to the upper portion of tower 2 and the second tower corresponding to the lower portion of tower 2. A continuous countercurrent flow is maintained through the two towers, in exactly the same manner as in tower 2.

In the description of our process given hereinbefore, we have indicated that gasoline may be substantially desulfurized by treatment with 2% by volume of 47% sodium hydroxide and 0.5% by volume of methanol. It is to be understood, however, that we may treat hydrocarbons other than gasoline, for example, gaseous hydrocarbons, liquefied normally gaseous hydrocarbons, naphtha, kerosine, furnace oil, gas oil, and other higher boiling hydrocarbons. Furthermore, the quantity and concentration of the aqueous solu-

tion of alkaline reagent may be varied considerably. For example, the quantity of aqueous alkaline solution employed may range from 1% or 2% by volume to as much as 100% by volume, based on the hydrocarbons to be treated, while the concentration of alkaline reagent in the aqueous solution may be of the order of 10% to 50% by weight. We prefer to use relatively strong aqueous solutions containing from about 35% to about 47% by weight of alkaline reagent. While sodium hydroxide is preferred because of its availability and cheapness, other alkaline reagents may be used, including sodium carbonate, sodium phenolates, sodium alcoholates, potassium hydroxide, carbonate, or phenolate, potassium alcoholates, potassium isobutyrate, ammonia, ammonium hydroxide, strong organic bases such as amines, hydroxyamines, guanidine, quaternary ammonium bases, and the like, or mixtures of two or more of these alkaline reagents.

We prefer to employ as our organic solvent, methanol, although other lower aliphatic alcohols may be employed in lieu of or admixed with methanol. Solvents which are more soluble in an aqueous solution of alkaline reagent than in hydrocarbons are particularly useful in our process, including ethanol, propanol, isopropanol, ethylene glycol and the homologous glycols, the glycol ethers, ethylene chlorhydrin, glycerol, acetone, ethylmethyl ketone, and the like. These solvents may be employed in an anhydrous condition, or in admixture with water. For example, anhydrous methanol, or methanol containing up to 90% of water may be utilized. Methanol solutions containing from about 10% to about 80% of water, when used in conjunction with concentrated solutions of an alkaline reagent, such as sodium hydroxide, have been found particularly effective.

What we claim is:

1. The method of removing acidic organic compounds from hydrocarbon oil containing the same, which comprises introducing an aliphatic alcohol containing less than 4 carbon atoms per molecule into a stream of said hydrocarbon oil, and countercurrently contacting the said oil stream with a stream of an aqueous solution of an alkaline reagent in which said alcohol is more soluble than in the hydrocarbon oil, whereby the alkaline reagent will admix with the alcohol in the oil stream and the mixture will act upon the oil stream to remove acidic organic compounds therefrom, the point of introduction of said alcohol being in advance of the point of introduction of said alkaline reagent and sufficiently removed therefrom to effect extraction of entrained alcohol from the oil stream.

2. The method of removing mercaptans from hydrocarbon oil containing same, which comprises introducing methanol into a stream of said hydrocarbon oil, and countercurrently contacting said oil stream with a stream of an aqueous solution of sodium hydroxide in which the methanol is more soluble than in the hydrocarbon oil, whereby the sodium hydroxide solution will admix with the methanol in the oil stream and the mixture will act upon the oil stream to remove mercaptans therefrom, the point of introduction of the methanol being in advance of the point of introduction of the sodium hydroxide solution and sufficiently removed therefrom to effect extraction of entrained methanol from the oil stream.

3. The method of removing acidic organic com-

pounds from hydrocarbon oil containing the same, which comprises countercurrently contacting a stream of said hydrocarbon oil with a stream of an aqueous solution of an alkaline reagent, and introducing into said streams an aliphatic alcohol containing less than 4 carbon atoms per molecule, whereby the alkaline reagent and alcohol will admix and the admixture will act upon the oil stream to remove acidic organic compounds therefrom, the point of introduction of the alcohol being in advance of the point of introduction of the alkaline reagent and sufficiently removed therefrom to effect extraction of entrained alcohol from the oil stream.

4. The method of removing mercaptans from hydrocarbon oil containing the same, which comprises countercurrently contacting a stream of said hydrocarbon oil with a stream of an aqueous solution of sodium hydroxide, and introducing methanol into said streams, whereby the sodium hydroxide solution and the methanol will admix and the admixture will act upon the oil stream to remove mercaptans therefrom, the point of introduction of the methanol being in advance of the point of introduction of the sodium hydroxide solution and sufficiently removed therefrom to effect extraction of entrained methanol from the oil stream.

5. The method of removing acidic organic compounds from hydrocarbon oil containing the same, which comprises introducing an aqueous solution of an alkaline reagent into the upper portion of an extraction zone, introducing said hydrocarbon oil into the lower portion of said zone, introducing an aliphatic alcohol containing less than 4 carbon atoms per molecule into said zone at a point in advance of the point of introduction of the alkaline reagent and sufficiently removed therefrom to effect extraction of entrained alcohol from the oil, countercurrently contacting the alkaline reagent with the oil and alcohol, whereby the alkaline reagent and alcohol will act upon the oil to extract acidic organic compounds therefrom, withdrawing from the upper portion of said zone oil having a reduced content of acidic organic compounds and substantially free of alcohol, and withdrawing from the lower portion of said zone an aqueous alkaline solution containing the alcohol and acidic compounds extracted from the oil.

JAMES H. McCULLOUGH.
EDWIN R. BIRKHIMER.
LEONARD N. LEUM.