Patented Mar. 28, 1944 2,345,449

# UNITED STATES PATENT OFFICE

2,345,449

## TREATMENT OF HYDROCARBON OILS

Edwin R. Birkhimer, Philadelphia, Pa., assignor to The Atlantic Refining Company, Philadelphia, Pa., a corporation of Pennsylvania

No Drawing. Application March 29, 1941, Serial No. 385,849

6 Claims. (Cl. 196—32)

The present invention relates to the treatment of hydrocarbon oil, and more particularly to the removal of acidic organic compounds such as mercaptans and phenolic compounds from petroleum oils of the nature of naphtha, furnace oil, and the like.

An object of this invention is the desulfurization of hydrocarbon oils by treatment with a concentrated aqueous solution of an alkali metal hydroxide containing a small but sufficient amount of a water-soluble organic solvent to prevent solidification of the solution when intimately contacted with mercaptan-containing oils.

I have found that when hydrocarbon oil, such as petroleum naphtha containing acidic organic compounds, i. e., mercaptans, is brought into intimate contact with a concentrated aqueous solution of an alkali metal hydroxide, particularly an aqueous solution containing from 35 per cent to 50 per cent by weight of NaOH, such solution tends to solidify even at ordinary temperatures, and cannot thereafter be readily handled. For example, when treating a mercaptan-containing naphtha with a small quantity of 47 per cent NaOH solution to remove mercaptans from the oil, it was found that the treating solution increased in volume and became a semi-solid mass. The treated naphtha could not be effectively separated from the treating solution, nor could the latter be pumped or otherwise handled in a satisfactory manner.

I have found that this difficulty may be overcome by incorporating in the concentrated aqueous alkali solution a small amount of a water-soluble organic solvent. For example, lower aliphatic alcohols such as methanol, ethanol, propanol, isopropanol, ethylene glycol, propylene glycol, or glycerol may be employed. Water-soluble glycol ethers, halohydrins, and ketones unreactive with strong alkali solutions may also be utilized. Quantities of water-soluble solvents of the order of 2 per cent to 10 per cent by volume of the alkali solution have been found very effective in preventing solidification of the solution, although in some cases as little as 1 per cent has been found satisfactory. In using, for example, from 1 per cent to 4 per cent of water-soluble solvent in the concentrated alkali solution, the formation of a small amount of solids may occur when treating a mercaptan-containing naphtha, but the treating solution remains fluid and is readily separated from the naphtha. The quantity of organic solvent necessary to prevent solidification of the alkali solutions will vary with the nature of the solvent and the concentration of the alkali in the solution. In general, from 5 per cent to 10 per cent by volume of solvent is satisfactory for aqueous solutions containing from 45 per cent to 50 per cent of alkali metal hydroxide, and from 2 per cent to 5 per cent by volume of solvent will prevent solidification of solutions containing from 35 per cent to 45 per cent of alkali metal hydroxide.

In carrying out my method, I intimately admix the oil to be desulfurized with a concentrated aqueous solution of an alkali metal hydroxide to which has been added a small but sufficient quantity of a water-soluble organic solvent, preferably methanol, to prevent solidification of the alkali solution. The quantity of treating solution employed will vary, depending upon the amount of acidic sulfur compounds present in the oil, and quantities of the order of 2 per cent to 100 per cent by volume of the oil have been found satisfactory. The treatment may be carried out at ordinary temperatures, although higher or lower temperatures may be employed. After the oil has been intimately contacted with the treating solution for a period of time sufficient to effect conversion of the sulfur compounds, for example, mercaptans into sodium mercaptides soluble in the treating solution, the mixture of oil and treating agent is permitted to settle and stratify, and the treating solution is separated from the oil by decantation or other suitable method. If desired the desulfurizing treatment may be carried out by passing the oil in intimate countercurrent contact with the treating solution, and continuously separating the treated oil from the treating solution. The spent solution may then be regenerated by conventional methods and reused for treating additional quantities of oil.

The following examples will serve to illustrate the results which may be obtained in accordance with my invention.

Samples of a sour gasoline distillate containing 28 mg. sulfur as RSH per 100 cc. were agitated with 10 per cent by volume of 47 per cent aqueous NaOH solution containing varying quantities of methanol, and the gasoline-NaOH mixtures were permitted to settle and stratify into layers. The appearance of the NaOH layers is indicated below.

| Volume per cent methanol added to 47 per cent NaOH solution | Appearance of NaOH layer |
|---|---|
| 0 | Substantially solid. |
| 1 | Semi-solid. |
| 2 | Fluid (contains appreciable quantity of solids). |
| 3 | Liquid (contains about 2 per cent of solids). |
| 4 | Liquid (contains less than 1 per cent of solids) |
| 5 | Liquid (trace of solids). |
| 6 | Liquid (no solids). |
| 10 | Do. |

From the above results, it will be seen that the addition of a small quantity of a water-soluble organic solvent, such as methanol, will prevent the solidification of a concentrated alkali

solution, and thus permit its use in the desulfurization of hydrocarbon oils.

What I claim is:

1. The method of desulfurizing hydrocarbon oil, which comprises contacting said oil with an aqueous solution containing from 35 per cent to 50 per cent of an alkali metal hydroxide and from 2 per cent to 10 per cent of a water-soluble organic solvent, and separating said solution from said oil.

2. The method of desulfurizing hydrocarbon oil, which comprises contacting said oil with an aqueout solution containing from 35 per cent to 50 per cent of an alkali metal hydroxide and from 2 per cent to 10 per cent of a lower aliphatic alcohol, and separating said solution from said oil.

3. The method of desulfurizing hydrocarbon oil, which comprises contacting said oil with an aqueous solution containing from 35 per cent to 50 per cent of an alkali metal hydroxide and from 2 per cent to 10 per cent of methanol, and separating said solution from said oil.

4. The method of desulfurizing hydrocarbon oil, which comprises contacting said oil with an aqueous solution containing from 35 per cent to 50 per cent of sodium hydroxide and from 2 per cent to 10 per cent of methanol, and separating said solution from said oil.

5. In the desulfurization of hydrocarbon oil by treatment with aqueous solutions containing from 35 per cent to 50 per cent of sodium hydroxide which normally tend to solidify when contacted with sulfur-bearing hydrocarbon oil, the method of preventing solidification of said aqueous solution which comprises admixing therewith from 2 per cent to 10 per cent of a lower aliphatic alcohol.

6. In the desulfurization of hydrocarbon oil by treatment with aqueous solutions containing from 35 per cent to 50 per cent of sodium hydroxide which normally tend to solidify when contacted with sulfur-bearing hydrocarbon oil, the method of preventing solidification of said aqueous solution which comprises admixing therewith from 2 per cent to 10 per cent of methanol.

EDWIN R. BIRKHIMER.