

UNITED STATES PATENT OFFICE

1,938,672

DESULPHURIZING HYDROCARBON OILS

Robert F. Ruthruff, Hammond, Ind., assignor to
Standard Oil Company, Whiting, Ind., a cor-
poration of Indiana

No Drawing. Application July 5, 1929

Serial No. 376,290

9 Claims. (Cl. 196—26)

The present invention relates to improvements in desulphurizing hydrocarbon oils, and more particularly the lower boiling point distillates such as distillates in the gasoline and kerosene boiling point range. It has been found particularly suited for use in connection with cracked distillates from high sulphur oil, such as Lander and Winkler oils which distillates contain sulphur bodies of a highly refractory type and which are difficult to remove.

In accordance with the present invention, the alkali metals such as sodium and potassium are preferably employed to effect the desulphurizing. The metal used may be employed in lumps (massive) in operating in accordance with the present invention, and metals fusible at the temperature of operation are then preferred.

In carrying out the invention, the active metal is employed in a proportion equal to or substantially exceeding the atomic equivalent of the amount of sulphur present. In general, the atomic proportion of the metal to the sulphur should exceed 1 to 1, and proportions in excess of 3 to 1 are preferred. The distillate and the active metal are heated together to a temperature of at least 400° F. and preferably not exceeding 650° F. In general a temperature of at least 500° F. is preferred. The operation is conducted under pressure, generally in excess of 150 lbs. per sq. in. and preferably from 200 to 300 lbs. per sq. in. Higher pressures are employed when lower boiling constituents are present. Under these temperature and pressure conditions the distillate is of course substantially in the liquid state and the alkali metal is in the molten condition.

As an example of the operation, a gasoline derived by a vapor phase cracking operation from a high sulphur crude oil was treated with lump sodium, the atomic ratio of sodium to sulphur being 4 to 1 at a temperature of 575° F. and a pressure of 290 lbs. per sq. in. for three hours with vigorous agitation, the percentage of sulphur being reduced from an initial value of 0.182 to 0.087. The same gasoline treated with a higher proportion of sodium, the atomic proportion of sodium to sulphur being 6.3 to 1, at 575° F. under 300 lbs. per sq. in. pressure, the sulphur was reduced to 0.016%.

To further illustrate the invention, the 225° to 420° F. cut of another distillate derived by an ordinary cracking process from a sulphur-containing crude was treated in the presence of an inert substantially sulphur-free heavy oil having an initial boiling point above 600° F. with

sodium in an atomic ratio to the sulphur of 4.65 to 1 at a temperature of 560° F. and a pressure of 175 lbs., the sulphur content being reduced from 0.473% to about 0.1%. It is thus apparent that the admixture of a heavy oil which, has an initial boiling point substantially above the end point of the distillate oil and is therefore readily separable from the low boiling distillate, improves the effectiveness of the action of the active metal.

Other alkali metals, such as lithium, potassium and the like are similarly effective.

When sodium or other active alkali metal is employed in lump form, it may be screened or otherwise separated out of the treated oil and reused for the treatment of fresh sulphur-containing distillate, sufficient additional fresh metal being supplied to bring the atomic ratio of metal to sulphur to the desired figure. However, since more sodium is apparently used up in the reaction than that calculated from the amount of sulphur removed, an excess over such calculated amount should be supplied for replenishment or the amount of sodium present will be insufficient to effect the desired desulphurization. Thus, in an operation conducted with sodium in lump form in an atomic ratio relative to the sulphur of 4 to 1 on a sulphur-containing pressure distillate cut having an approximate boiling range of from 225 to 420° F., at a temperature of 575° F. and a pressure of 235 lbs. per sq. in. for three hours, in the first use of the sodium, the sulphur was reduced from an initial percentage of 0.764 to 0.067. On the second use, it was reduced from 0.764 to 0.092, and on third use from 0.764 to 0.186. Thus the sodium or other active metal may be reused as long as the amount present is sufficient for effective reaction, additional metal being added as required to maintain effectiveness.

The operation may be conducted in an atmosphere of a gas inert to the oil and alkali metal under the conditions of the process, such as hydrogen or nitrogen. This serves to increase the effectiveness of sulphur removal with a given ratio of metal to sulphur.

I claim:

1. In a process of desulphurizing a low boiling hydrocarbon distillate lying substantially within the gasoline-kerosene boiling point range the step which consists in coagitating said distillate, in substantially liquid state, and an alkali metal in molten form at a temperature substantially within the range of 450° F. to 650°

- F. under a pressure of at least about 150 pounds per square inch.
2. The process as in claim 1 in which the alkali metal is metallic sodium.
- 5 3. The process as in claim 1 wherein the distillate prior to treatment with the alkali metal, is admixed with a low sulphur oil, the initial boiling point of which is substantially above the end point of said distillate.
- 10 4. The process as in claim 1 wherein the distillate and alkali metal are coagitated in an atmosphere of a gas inert to the oil and alkali metal under the conditions of the process.
- 15 5. The process as in claim 1 wherein the excess alkali metal is separated from the treated distillate, and coagitated with a fresh portion of untreated distillate and a fresh portion of alkali metal under said conditions of temperature and pressure.
- 20 6. The process as in claim 1 in which at least three atoms of alkali metal are used for every atom of sulphur in the distillate to be desulphurized.
7. In a process of desulphurizing a low boiling hydrocarbon distillate of the gasoline-kerosene boiling point range the step which consists in coagitating said distillate in substantially liquid state and an alkali metal in molten, massive form at a temperature substantially within the range of 500° F. to 650° F. under a pressure of from about 200 to 300 pounds per square inch.
8. The process as in claim 7 in which the alkali metal is metallic sodium.
9. The process as in claim 7 in which at least three atoms of alkali metal are used for every atom of sulphur in the distillate to be desulphurized.
- ROBERT F. RUTHRUFF.

25 100

30 105

35 110

40 115

45 120

50 125

55 130

60 135

65 140

70 145

75 150