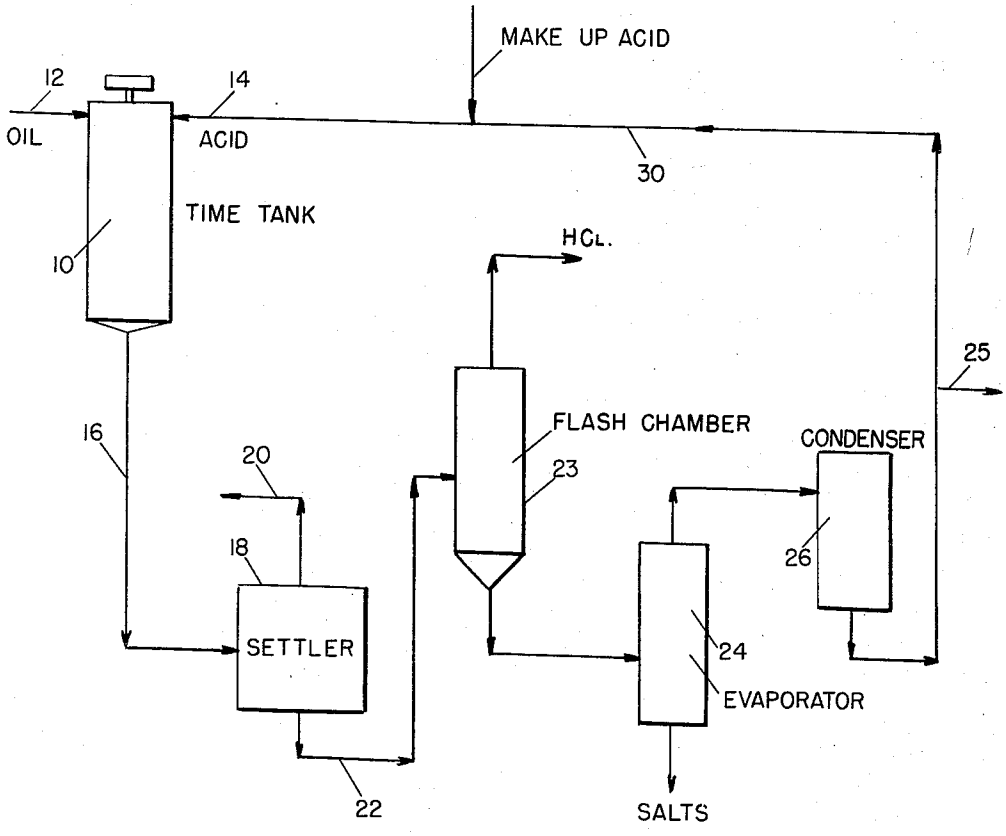
Sept. 23, 1952 E. A. COONS 2,611,735

PROCESS FOR REMOVING METALS FROM CRUDE PETROLEUM OILS

Filed June 21, 1947



INVENTOR
EDWARD ADAMSON COONS
BY
Pennie, Edmonds, Morton & Barrows
ATTORNEYS

Patented Sept. 23, 1952

2,611,735

UNITED STATES PATENT OFFICE

2,611,735

PROCESS FOR REMOVING METALS FROM CRUDE PETROLEUM OILS

Edward Adamson Coons, Chicago, Ill., assignor to Sinclair Refining Company, New York, N. Y., a corporation of Maine

Application June 21, 1947, Serial No. 756,283

3 Claims. (Cl. 196—39)

1

This invention relates to improvements in the production of motor fuels from crude petroleum oil by catalytic cracking. In catalytic cracking operations, as heretofore carried out, it has in most cases been necessary to use gas oil or other distillate as the charging stock. One important factor which has prevented the use of reduced or top crude oils, with or without deasphalting, is that with the use of such feed stocks the catalyst rapidly deteriorates. Most topped or reduced crude oils contain substantial amounts of inorganic salts, in particular sodium, calcium, and magnesium chloride, and in many cases other metallic compounds such as compounds of vanadium and nickel, the nature of which have not been fully established, and compounds of other metals. These metallic compounds are corrosive and probably responsible for the catalyst deterioration which is experienced when reduced or topped crudes are used as charging stocks to catalytic cracking operations. The economic difference between the use of such materials as gas oil and reduced crude oil as charging stocks for cracking operations is substantial; and the present invention provides improvements which permit the use of the reduced crude oil as charging stock for catalytic cracking operations.

In accordance with the present invention, the crude oil, before or after topping or deasphalting, is treated with fluorosulfonic acid under appropriate conditions of temperature and pressure, with conversion of the metals present into the corresponding fluorosulfonates substantially quantitatively. The resulting fluorosulfonates are readily separated from the oil by filtration, settling, centrifuging or the like, and the resulting crude oil, substantially free from metal contaminants, is useful as such as the charging stock for catalytic cracking operations. The use of this as charging stock as compared with gas oil or the like results in substantial economic benefits.

The fluorosulfonic acid may be brought into contact with the metal-contaminated oil in any suitable way. Advantageously, the fluorosulfonic acid is used as the anhydrous liquid material, although it may be in the vapor phase or in aqueous form. The temperature used in the treatment may vary from about atmospheric temperature to around 400° F., advantageously above 200° F., and the pressure used should advantageously be such as to keep the anhydrous fluorosulfonic acid liquid at the temperature selected. What is required is adequate intimate contact of the fluorosulfonic acid with the oil, because the reaction forming the metal fluorosulfonates proceeds rapidly and substantially quantitatively if adequate contact is provided.

2

The amount of fluorosulfonic acid required for the removal of metal contaminants from the oil is slightly in excess of one equivalent of fluorosulfonic acid for each equivalent of metal; and with most reduced or topped crude oils, this corresponds to a fraction of 1% of fluorosulfonic acid based on the oil. Because difficulties may be encountered in bringing about intimate contact of the oil with this small amount of fluorosulfonic acid, it is usually advantageous to use a somewhat larger amount, for example, 3 to 5% of fluorosulfonic acid based on the oil, recover the excess acid and recycle it until it is consumed. As the fluorosulfonic acid reacts with the metal compounds, it forms a substantially equivalent quantity of hydrogen chloride, which may be permitted to remain in the recycle stream or may be flashed off if it is desired. Retaining it in the recycle stream gives the stream an approximately constant bulb without interfering with the chemical efficiency of the reaction.

The operation may be carried out batch-wise by thoroughly mixing the oil with the fluorosulfonic acid and permitting the batch to settle, separating the oil from the acid and metal salts by decantation, flashing off the hydrogen chloride if desired, and using the recovered fluorosulfonic acid from another batch until it is exhausted.

The operation may also be carried out continuously as by passing the oil and the fluorosulfonic acid to a continuous mixer such as a time tank provided with an agitator or a contacter of the type used for cold acid treating and alkylation, consisting of a vertical vessel with an open inner cylinder with a circulating pump at its bottom such that the liquid in the vessel is circulated downwardly through the inner cylinder and upwardly through the annulus between the inner cylinder and the wall of the vessel thus affording intimate admixture of immiscible liquids or liquid and gas. The effluent mixture of oil, acid, and metal fluorosulfonates is passed to suitable separators such as settlers, centrifuges, filters or the like to separate the oil from the acid and salt.

Apparatus suitable for such an operation is illustrated diagrammatically in the appended drawing. In the drawing, 10 represents a time tank provided with agitating means. The oil to be treated is introduced through the inlet 12 and fluorosulfonic acid through the inlet 14. The fluorosulfonic acid and the oil are brought into intimate contact in the time tank, with such metal

compounds as there are in the oil being converted to the corresponding fluorosulfonates. The treated oil, in admixture with the acid and salt flows out of the outlet 16 to the settler 18, where the oil separates from the acid and the salts, and is removed by the line 20. The fluorosulfonic acid and fluorosulfonates, with the hydrogen chloride formed, are removed from the bottom of the settler 18 by the conduit 22 to the flash chamber 23, in which the hydrogen chloride is flashed off and then supplied to the evaporating chamber 24 in which the fluorosulfonic acid is taken as an overhead product, condensed in the condenser 26 and recycled. If desired, hydrogen chloride or a part of it, may be carried away with the fluorosulfonic acid and recycled, in which case a bleed 25 is provided. Make up fluorosulfonic acid is supplied to the line 30. Advantageously the operation is carried out at a temperature of about 200° F. Pressure is not required unless hydrogen chloride is recycled, in which case pressure is used to prevent its vaporization. The quantity of circulating fluorosulfonic acid or a mixture of fluorosulfonic acid and hydrogen chloride is a few per cent by volume based on the oil, for example, 3 to 5%.

I claim:

1. In a process involving pretreatment of crude petroleum oils containing metal compounds and subsequent use of the pretreated crude petroleum oils as a charging stock in a catalytic cracking operation, the improvement which comprises subjecting the crude petroleum oils in the pretreating operation and prior to bringing the oil into contact with the cracking catalyst into intimate admixture with fluorosulfonic acid whereby the metal compounds initially present in the crude petroleum oils react with the fluorosulfonic acid to form the corresponding fluorosulfonates, and separating the resulting fluorosulfonates from the oil.

2. In a process as defined in claim 1 the improvement consisting of conducting the pretreating operation by admixing anhydrous liquid fluorosulfonic acid with the crude petroleum oils under a superatmospheric pressure sufficient to maintain the fluorosulfonic acid in liquid phase.

3. In a process as defined in claim 1 the improvement consisting of admixing fluorosulfonic acid with the crude petroleum oil during the pretreating operation in an amount substantially in excess of that required to react with the metal compounds present in the oil.

EDWARD ADAMSON COONS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,833,331	Park	Nov. 24, 1931
1,984,903	Wagner	Dec. 18, 1934
2,203,470	Pier et al.	June 4, 1940
2,206,500	Fischer et al.	July 2, 1940
2,428,753	Linn	Oct. 7, 1947
2,450,588	Evering et al.	Oct. 5, 1948

FOREIGN PATENTS

Number	Country	Date
309,042	Great Britain	Sept. 3, 1930