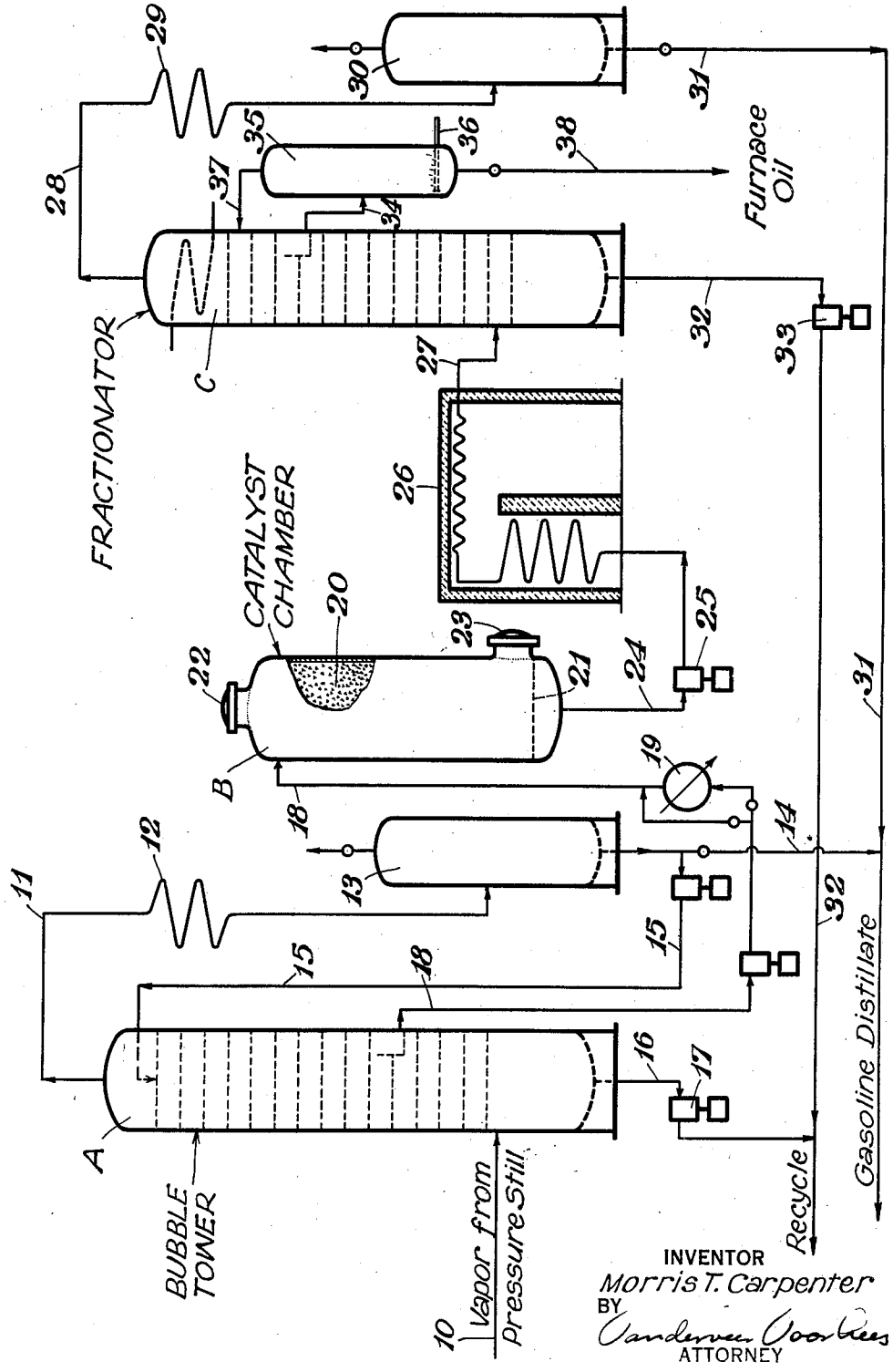
Feb. 6, 1940. M. T. CARPENTER 2,189,196

REFINING FUEL OIL

Filed Nov. 23, 1936



INVENTOR
Morris T. Carpenter
BY
Vanderveer Voorhees
ATTORNEY

Patented Feb. 6, 1940 2,189,196

UNITED STATES PATENT OFFICE

2,189,196

REFINING FUEL OIL

Morris T. Carpenter, Chicago, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application November 23, 1936, Serial No. 112,261

3 Claims. (Cl. 196—39)

This invention relates to a process of refining petroleum oils and in particular to the refining of cracked distillate fuel oils. Heretofore, it has been the practice to refine these oils with sulfuric acid and many attempts have been made to avoid the expensive treatment with sulfuric acid by employing substitute methods of refining or omitting the chemical refining altogether. However, these attempts have met with failure for various reasons. One of the principal reasons for the necessity of chemical refining of cracked distillate fuel oil is the formation of a non-volatile residue in the oil on storage and in handling and burning, which results in fouling the oil burners. This difficulty occurs principally with the oil known as "furnace oil" which is a distillate having an initial boiling point about 400° F. and a maximum boiling point of about 600° F. The formation of any non-volatile residue or sediment in this grade of oil is especially objectionable because of the effect of this material in stopping up the small oil passages in domestic oil burners resulting from the accretion of sediment and non-volatile materials. Even very minute amounts of sediment or non-volatile residue, sometimes referred to as carbon residue, will cause this difficulty. A residue of as little as 0.2% determined on the heaviest 10% fraction of the furnace oil is definitely undesirable. The residue content of the oil is determined by the A. S. T. M. carbon residue test, and by my process I reduce the residue to less than 0.1% and even as low as 0.02%.

As a result of the difficulty of refining cracked domestic furnace oils, it has been common practice among petroleum refiners to supply the market for these products with oils derived entirely from direct non-cracking distillation of the crude petroleum. Treatment of the cracked furnace oils with sulfuric acid previously referred to has been only partially successful due apparently to the oxidizing effect of the acid on the unsaturated constituents of the oil. Attempts to refine cracked fuel oil distillates with fuller's earth in the liquid phase or the vapor phase have also met with only partial success in view of the necessity of using large proportions of fuller's earth if the desired degree of freedom from non-volatile residue formation is obtained.

It is the object of this invention to provide a process for the refining of cracked distillate fuel oils boiling within the range of 350 and 600° F. and more particularly cracked domestic furnace oil distillates to render them stable against the formation of objectionable residues and deposits in oil burning equipment. It is also the object of this invention to provide a process of chemically refining cracked distillate fuel oils which is sufficiently economical to permit of its commercial use on a product which commands a very low price.

I have discovered that cracked distillate fuel oils can be refined by treatment with phosphoric acid if the temperature of the operation is carefully controlled within certain limits. In order to obtain maximum surface of contact between the acid and the oil, I prefer to employ the acid distributed on a supporting material such as silica, kieselguhr, etc. The catalyst may be prepared by mixing the phosphoric acid with kieselguhr and calcining the mixture. For example, a mixture of about 80 parts of 90% phosphoric acid and 20 parts of kieselguhr may be heated at a temperature of about 200° C. and the solid mass which is obtained may be broken up and screened to a uniform size, such as 4 to 60 mesh. Heating of the mixture may be carried out at higher temperatures also, for example 250 to 300° C.

After conducting the treatment of a large quantity of oil the catalyst efficiency may be largely restored by blasting the catalyst bed with a current of preheated air or an air-inert gas mixture to burn off the contaminating carbonaceous material. The catalyst is then steamed to restore its activity.

The temperature range which I employ for treating oil is preferably from 450 to 500° F., although I may also use temperatures as low as 400° F. and as high as 600° F. with satisfactory results. If higher temperatures are employed, the phosphoric acid catalyst is rendered ineffective after a short period of operation and also at higher temperatures the catalyst exerts an undesirable polymerizing effect upon the unsaturated constituents of the oil, causing an excessive loss thereby. At lower temperatures the effect of the catalyst is insufficient to accomplish the desired stabilization against the formation of residues and resulting deposits in the oil burners.

The accompanying drawing, which forms a part of this specification, illustrates diagrammatically an apparatus for carrying out my process. Referring to the drawing, tower A is a fractionating tower connected to a cracking still. Tower B is a catalyst chamber containing the phosphoric acid catalyst as previously described. Tower C is a final fractionating tower for the furnace oil product.

In carrying out the process vapors from the cracking coil or other cracking equipment, which may suitably be derived from the cracking of gas oil, crude oil or residuum, are introduced into tower A by vapor line 10. The vapors are fractionated in tower A to produce a light distillate which is withdrawn by line 11 and which consists principally of gasoline and gas. The gasoline is condensed in coil 12 and the gas is largely separated in receiver 13, gasoline being withdrawn by line 14 and a portion of it being pumped back to the tower for reflux by line 15. The pressure in tower A may suitably be about 100–400 lbs. per square inch.

At the bottom of tower A the hot residue or recycle stock is withdrawn by line 16 and hot oil pump 17 which forces oil back to the heating coil of the cracking still for further cracking.

At an intermediate point of tower A a side stream is withdrawn by line 18 and this forms the stock from which the desired furnace oil is produced. This side stream will usually be of wider boiling range than the desired furnace oil. For example, it may have an A. P. I. gravity of about 37 with a boiling range as follows:

Initial boiling point	240
10	340
20	372
30	395
40	408
50	430
60	448
70	469
80	490
90	520
Maximum	586

The stock withdrawn from tower A will usually be at a temperature of 500 to 650° F. and therefore before it can be successfully treated with the catalyst it may be necessary to cool the stock by means of heat exchanger or cooler 19. The side stream now at a temperature of between 400 and 550° F. is introduced into catalyst chamber B where it is brought into intimate contact with the catalyst disposed therein, as indicated in the cut-away section by numeral 20. The catalyst chamber is suitably provided with a false bottom 21 and manways 22 and 23 for charging and discharging.

The oil leaves the catalyst chamber by line 24 and pump 25 and thence to pipe still 26 where it is substantially completely vaporized and discharged by transfer line 27 to fractionating tower C. Here the desired furnace oil fraction is freed from contaminating lighter and heavier constituents by eliminating the lighter constituents, mostly gasoline, through vapor line 28 leading to condenser 29 and receiver 30. The gasoline distillate may be conducted by line 31 connected to line 14 previously described. The heavy constituents are withdrawn at the base of fractionating colum C by line 32 and pump 33 which may suitably return this fraction to the cracking coil along with the recycle stock from the hot oil pump 17 as indicated.

The desired furnace oil fraction may be trapped out of column C by trap-out line 34 leading to side stripper 35 supplied with stripping steam from line 36. Vapors from the side stripper may be conducted back to the fractionator C by line 37 and the desired furnace oil fraction may be withdrawn at the bottom of the side stripper by line 38.

In operating the process it will usually be desirable to maintain a pressure in fractionating column A between 100 and 500 lbs. per sq. in., a suitable pressure range being about 100–300 lbs. per square inch. The same or higher pressure may be employed in the catalyst chamber B, and it is usually desirable to employ a pressure in the catalyst chamber of about 400 lbs. per sq. in.

The temperature required to vaporize the furnace oil in transfer line 27 will vary somewhat depending on the pressure but will usually lie between 400 and 500° F. In general, it is desirable to operate the fractionating column C at atmospheric pressure or slightly above, and the character of the furnace oil produced in the side stripper 35 may conveniently be regulated by controlling the reflux in column C, as well as the degree of stripping in stripper 35 by means of steam introduced through open steam coil 36.

As an example of the character of the furnace oil distillate produced in my process, an oil was obtained with the following characteristics:

Flash point °F.	154
Gravity °A. P. I.	35.5
Initial boiling point °F.	390
10% off	410
20% off	417
30% off	423
40% off	430
50% off	436
60% off	446
70% off	455
80% off	466
90% off	484
Maximum	524
Color N. P. A.	Below 1
Carbon residue of 10% bottom Percent	.02
Sediment	Nil

This oil was compared with a product produced from the same cracking still trap-out stream but without phosphoric acid catalytic refining and also with the same oil which had been treated with three-fourths pound per barrel of 75% sulfuric acid, neutralized and washed. It was found that the color of the unrefined stock was somewhat higher, specifically between 1 and 1½ N. P. A. and the carbon residue of the untreated stock was also a little more than twice as great, specifically .05%, the untreated stock having approximately the same distillation range and gravity.

Both the treated and untreated stock were subjected to a rapid aging test performed by placing a 500 cc. sample in a 2 liter flask filled with oxygen and heating at 210° F. for 8 hrs. The results obtained were as follows:

	Control—untreated	Treated with phosphoric acid catalyst	Treated with sulfuric acid
Color	2	1½	2
Carbon residue of 10% bottoms	0.36	0.07	0.37
Sediment	0.6	0.3	0.7

I have found that the failure of furnace oil burners from the deposition of gummy residues within the oil passages is closely predictable from the amount of carbon residue obtained in the analysis of the oil. It is therefore apparent that the furnace oil which has been refined with phosphoric acid catalyst is far superior to the unrefined furnace oil, as well as the oil which has been refined with sulfuric acid.

I claim:

1. The process of producing light distillate fuel oils boiling within the range of about 350 to 600° F., comprising cracking a heavy petroleum oil and producing therefrom a cracked hydrocarbon distillate, fractionating said cracked hydrocarbon distillate to separate gasoline and a heavier cracked distillate fraction boiling just above the gasoline boiling range, directly conducting said heavier cracked distillate fraction while at a temperature of about 400 to 600° F. and without further cooling to a catalytic polymerization zone, contacting said heavier cracked distillate fraction in said zone with a solid catalyst consisting essentially of a calcined mixture of phosphoric acid and kieselguhr whereby undesirable gum and sludge producing constituents of said distillate are polymerized without excessive polymerization of olefinic constituents of said distillate and said phosphoric acid is gradually rendered inactive by the deposition of carbonaceous material, redistilling said distillate after contact with said catalyst and fractionating therefrom undesirable high boiling polymerization products of said catalytic polymerization, recovering from said last-named fractionating operation said desired light distillate fuel oil having a boiling range of about 350 to 600° F. recycling said undesirable high boiling polymerization products to said cracking operation first mentioned, and intermittently restoring the activity of said catalyst by burning away carbonaceous matter accumulating thereon.

2. The process of producing from cracking still distillates, furnace oil characterized by freedom from formation of gums and non-volatile residues, comprising subjecting said distillates to polymerization by the action of a catalyst consisting essentially of a calcined mixture of phosphoric acid and kieselguhr at a temperature of 400 to 600° F. redistilling said distillate to produce a fraction suitable for domestic furnace oil, and regenerating said catalyst at intervals by burning with an oxygen containing gas, whereby substantially all organic matter is removed therefrom before reuse.

3. The process of producing from cracking still distillates, furnace oils which remain free from the formation of objectionable non-volatile residues and guns, which comprises trapping out from a cracking still fractionating tower a side stream boiling between about 240 and 586° F., subjecting said side stream to polymerization in the liquid phase with a solid catalyst consisting essentially of a calcined mixture of phosphoric acid and kieselguhr at a temperature between about 400 and 600° F., continuously revaporizing said treated oil by heating in a continuous restricted stream, fractionating said revaporized oil to produce the desired furnace oil having a boiling range of about 390 to 524° F. and a higher boiling residue, recycling said higher boiling residue to said cracking still, and regenerating said catalyst at intervals by burning with an oxygen containing gas, whereby substantially all organic matter is removed therefrom before reuse.

MORRIS T. CARPENTER.

CERTIFICATE OF CORRECTION.

Patent No. 2,189,196. February 6, 1940.

MORRIS T. CARPENTER.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 63, for "colum" read column; page 3, second column, line 16, claim 3, for "guns" read gums; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of March, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.