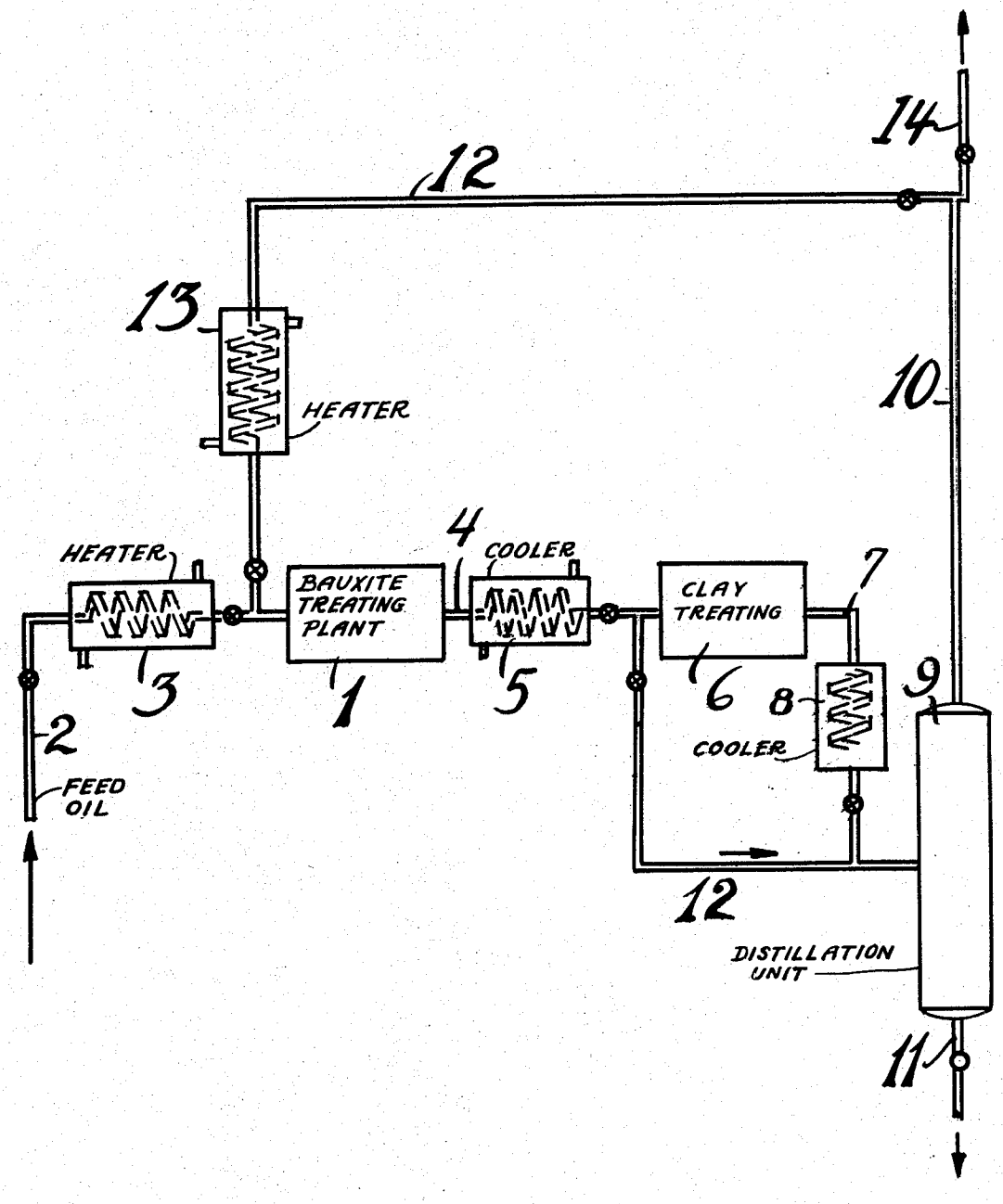
Dec. 18, 1945. A. P. HEWLETT ET AL 2,391,091

REFINING PETROLEUM OILS

Filed Dec. 20, 1939



Amiot P. Hewlett Inventors
Gerald E. Phillips
By P. L. Young Attorney

Patented Dec. 18, 1945

2,391,091

UNITED STATES PATENT OFFICE

2,391,091

REFINING PETROLEUM OILS

Amiot P. Hewlett, Summit, and Gerald E. Phillips, Cranford, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

Application December 20, 1939, Serial No. 310,094

7 Claims. (Cl. 196—28)

The present invention relates to the refining of petroleum oils. The invention is particularly concerned with the treatment of virgin petroleum oils, which oils have not been subjected to temperature and pressure conditions adapted to produce cracking, with bauxite under non-cracking conditions. In accordance with the present process, virgin petroleum oils are contacted with bauxite under non-cracking conditions at a temperature in the range of about 780° F. to about 850° F.

It is well known in the art to treat petroleum oils with various metallic oxides and the like in various refining operations. For example, it is known to remove objectionable sulfur compounds from petroleum oils, particularly from petroleum oils boiling in the motor fuel boiling range, by contacting the same with bauxite at elevated temperatures which vary over a relatively wide range. However, temperatures employed in the treatment of virgin oils in commercial operations are in the range from about 600° F. to 700° F., even though broad statements have been made that temperatures as high as 800° F. may be employed in the bauxite treatment of petroleum oils. Temperatures above 750° F. are not employed in desulfurization of virgin petroleum oils when utilizing bauxite and, as a matter of fact, a practice is to employ temperatures in the range from about 775° F. to 850° F. to regenerate the bauxite. The utilization of temperatures in the range below about 750° F. in desulfurization operations employing bauxite when processing virgin oils was based upon the fact that no substantial improvement in the desulfurization operation is secured by employing temperatures above this range which we have found to be substantially correct. However, we have discovered that if virgin petroleum oils are treated by contacting the same in the vapor phase with bauxite under non-cracking conditions at temperatures above about 780° F., particularly above about 800° F., unexpected desirable benefits are secured. Although the extent of the desulfurization is not materially increased by utilizing temperatures above about 650° F. to 750° F., the bauxite at temperatures above these ranges apparently functions to rearrange the molecular structure of the molecules in a manner which improves the clear octane number of the treated product, as well as the ability of the treated product to respond to knock suppressing agents. The applicants have discovered that if in desulfurization operations employing bauxite temperatures above about 780° F. are employed, the bauxite will not only function as a desulfurization agent, but will also function as an agent to secure a desired molecular rearrangement.

The process of our invention may be readily understood by reference to the attached drawing illustrating one modification of the same. A petroleum feed oil, which for the purposes of illustration is taken to be a petroleum 400° F. end-point prime cut naphtha, is introduced into bauxite treating plant 1 by means of feed line 2. Prior to introducing the oil into bauxite treating plant 1 the temperature of the same may be raised to the desired extent by means of heating unit 3. The bauxite contacted oil is withdrawn from bauxite treating plant 1 by means of line 4, passed through cooler 5, and introduced into clay contacting plant 6. The bauxite and clay treated oil is withdrawn from clay contacting plant 6 by means of line 7, cooled in cooler 8, and introduced into distillation plant 9. Uncondensed gases are removed overhead from distillation plant 9 by means of line 10, while the bauxite and clay treated material is withdrawn by means of line 11 and handled in any manner desirable. Under certain conditions the bauxite treated oil may bypass clay contacting plant 6 by means of line 12 and be introduced directly into distillation unit 9. Portions of the gas removed overhead from distillation unit 9 in the preferred modification of the invention are recycled and introduced into the fresh feed by means of line 12. These recycled gases may be raised to the desired temperature by passing the same through heating unit 13. Gases may be withdrawn from the system by means of line 14.

The process of the present invention may vary widely. Any virgin feed oil may be employed which will not decompose into relatively higher and into relatively lower boiling fractions at these temperatures. The process, however, is particularly applicable in the treatment of prime cut petroleum oils boiling in the motor fuel boiling range. In general, the conditions are adapted in the bauxite treating plant so that substantially non-cracking conditions exist. It is essential that the temperatures employed be above about

780° F., preferably in the range of about 800° F. to 850° F. The pressures employed may vary widely and are adjusted to secure substantially non-cracking conditions. The bauxite treating plant may comprise any number of units containing bulk or powdered bauxite. The flow arrangement may be arranged in any desirable manner. It has been found that overall optimum results are secured when the temperature maintained in the bauxite treating unit is in the range from 800° F. to 820° F. Under the conditions of operation substantially no gas is formed. However, the small amount of gas removed from distillation unit 9 by means of line 10 comprises from 50% to 85% hydrogen by volume, based on dry gas. By recirculating the total quantity of this gas, we have found that the catalyst life is materially lengthened and that improved yields are secured.

In order to further illustrate the invention, the following examples are given which should not be construed as limiting the same in any manner whatsoever:

EXAMPLE 1

Prime cut light petroleum oils secured from a West Texas crude oil boiling in the motor fuel boiling range were bauxite treated at various temperatures with the following results:

Table 1

	Bauxite treating temperature	Sulfur determination of treated product	Yield of treated product	Clear octane number
	°F.			
Feed oil		.101		60.9
Operation A	650	.010	100.0	61.6
Operation B	750	.012	99.8	61.6
Operation C	800	.009	99.7	64.3
Operation D	850	.008	98.3	68.5

The volatility of the respective oils as determined by an Engler distillation was as follows:

Table 2

	Feed oil	Treated oils			
		Operation A	Operation B	Operation C	Operation D
Initial boiling point	109	99.0	95.0	95.0	102
Percent distilled at—					
158° F	10.0	11.5	11.0	11.0	11.5
212° F	39.0	40.5	39.5	40.0	41.0
257° F	72.0	72.0	73.0	72.0	72.5
302° F	89.5	90.5	91.0	91.0	90.0
Final boiling point	365	367	365	367	381
Percent recovered	98.0	98.0	99.0	98.5	98.5
Percent loss	1.0	1.5	0.3	0.5	0.7
Gravity	62.3	62.7	62.7	62.5	61.8

From the above data it is apparent that no substantial improvement in the extent of the desulfurization is secured by bauxite treating at temperatures substantially in excess of about 650° F. It is also apparent from the octane number increase above about 800° F. that a critical temperature zone exists with respect to molecular arrangement immediately before the temperature zone at which cracking or decomposition of the oil occurs.

EXAMPLE 2

Additional prime cut heavy petroleum oils secured from a West Texas crude oil boiling in the motor fuel boiling range were bauxite treated at various temperatures with the following results:

Table 3

	Bauxite treating temperature	Sulfur determination of treated product	Yield of treated product	Clear octane number
	°F.			
Feed oil		.296		45.2
Operation A	630	.051	100.0	49.9
Operation B	730	.028	100.0	49.5
Operation C	780	.022	99.8	50.9
Operation D	830	.020	99.1	54.7

The volatility of the respective oils as determined by an Engler distillation was as follows:

Table 4

	Feed oil	Treated oils			
		Operation A	Operation B	Operation C	Operation D
Initial boiling point	234	230	228	228	185
Percent distilled at—					
257° F	4.0	6.0	6.5	7.5	12.5
302° F	35.0	41.0	40.0	39.0	44.5
392° F	89.0	96.0	97.0	96.0	98.5
Final boiling point	451	406	401	408	392
Percent recovered	98.5	98.0	98.0	98.0	98.5
Percent loss	0.3	1.1	0.2	1.1	0.6
Gravity	49.0	49.9	50.3	49.9	50.0

From the above data it is apparent that a molecular arrangement occurred, particularly with respect to the fractions bauxite treated above about 780° F.

From the above data it is apparent that although the reduction in sulfur was not substantially increased by temperatures above about 650° F. to 750° F., the quality of the product was substantially improved by an apparent molecular rearrangement and that this arrangement occurs to the maximum extent under non-cracking conditions at a temperature of above about 800° F.

What we claim as new and wish to protect by Letters Patent is:

1. Process for the treatment of prime cut petroleum oils comprising contacting said petroleum oils with a catalyst consisting of bauxite in the vapor phase at a temperature in the range from about 780° F. to 850° F. whereby substantially no cracking of the oil occurs and substantially no gas is formed.

2. Process for the treatment of prime cut petroleum oils boiling in the motor fuel boiling range containing objectionable sulfur compounds, comprising contacting said petroleum oils in the vapor phase with a catalyst consisting of bauxite at a temperature in the range from about 780° F. to 850° F., whereby said objectionable sulfur compounds are removed and a molecular rearrangement of the molecules of said petroleum oil is secured with substantially no cracking of the oil occurring and with less than 1% of gas being formed.

3. Process in accordance with claim 2 in which said petroleum oil is contacted with bauxite at a temperature in the range from about 800° F. to 820° F.

4. Process for the refining of prime cut petroleum oils comprising contacting said petroleum oils with a catalyst consisting of bauxite under non-cracking conditions at a temperature in the range from about 780° F. to 850° F., whereby substantially no gas is formed, withdrawing said bauxite treated oil and introducing the same into a distillation unit in which gases comprising substantially hydrogen are removed from the bauxite

treated oil, recycling said removed gases with the fresh feed being bauxite treated.

5. Process in accordance with claim 4 in which the oil is bauxite treated at a temperature in the range from about 800° F. to 820° F.

6. Process for the treatment of prime cut petroleum oils boiling in the motor fuel range and containing objectionable sulfur compounds, comprising contacting said petroleum oils with a catalyst consisting of bauxite under substantially non-cracking conditions at a temperature in the range from about 780° F. to 850° F., whereby less than 1% of gas is formed, clay treating said bauxite treated oil and removing therefrom uncondensed gases, recycling said gases to the fresh feed being bauxite treated.

7. Process in accordance with claim 6 in which the temperature of the petroleum oils is in the range from about 800° F. to 820° F.

AMIOT P. HEWLETT.
GERALD E. PHILLIPS.