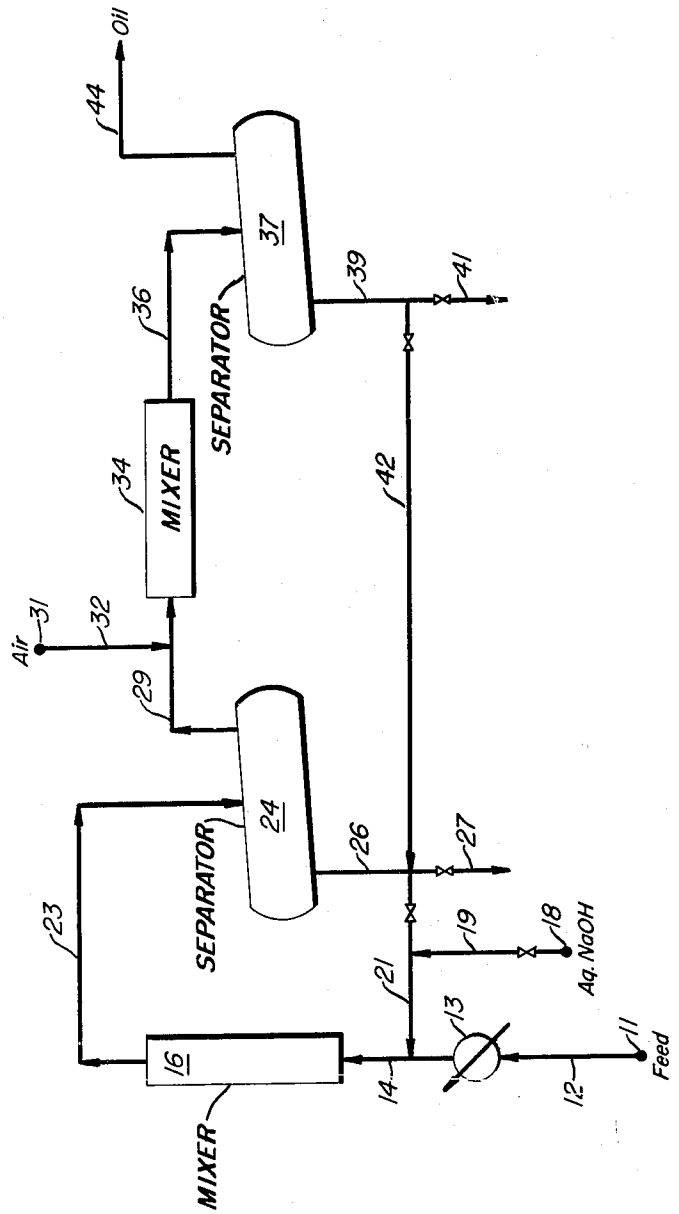
Nov. 29, 1955 M. GORDON ET AL 2,725,340

CLARIFICATION OF OILS

Filed Jan. 25, 1954



INVENTORS:
Moses Gordon
Homer M. Schauer

BY Michael Dufney
ATTORNEY

United States Patent Office

2,725,340

Patented Nov. 29, 1955

2,725,340

CLARIFICATION OF OILS

Moses Gordon, Chicago, Ill., and Homer M. Schauer, Casper, Wyo., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application January 25, 1954, Serial No. 405,803

6 Claims. (Cl. 196—41)

This invention relates to the clarification of oils containing droplets of an aqueous phase dispersed throughout said oil. More particularly the invention relates to the dehazing of petroleum distillates containing a haze formed by the presence of a dispersion of droplets of aqueous caustic.

Hydrocarbon oils are frequently treated or contacted with aqueous caustic as one step in a refining process. Even after prolonged settling, normally some of the aqueous caustic remains in the oil in the form of a dispersion of droplets. These droplets reduce the translucency of the oil and the oil is described as containing a haze or as being hazy. Even though the aqueous haze may not have any harmful effect in consumer usage, consumers' preference calls for a substantially haze-free oil. It is extremely difficult to remove these aqueous caustic dispersions by ordinary methods. The better known methods are (1) washing the oil with water; frequently this results in the substitution of a water haze for the aqueous caustic haze and (2) filtering the oil through a coalescing medium such as fibre glass, sand, or rock salt.

An object of this invention is the clarification of oils containing a dispersion of droplets of aqueous caustic. Another object is the dehazing of petroleum distillates containing an aqueous caustic haze. Still another object is a process for refining a petroleum distillate with aqueous caustic under conditions to substantially eliminate the presence of an aqueous caustic haze in the refined oil.

The objects of the invention are attained by adding air to the liquid hydrocarbon oil which contains a dispersion of aqueous caustic, in an amount between about 1 and about 6 standard cubic feet per barrel (42 gal.) of hazy oil. The hazy oil-air mixture is maintained, at a temperature above the freezing point of the aqueous caustic and/or the pour point of the hazy oil and below about 150° F., for a time sufficient to form a separate layer of aqueous caustic, that is, a body of aqueous caustic distinctly separate from the main body of hydrocarbon oil which is formed by agglomeration of the haze droplets. The separate layer of aqueous phase is separated from the hydrocarbon oil that is substantially free of haze forming dispersed aqueous phase, i. e., is substantially haze-free.

The invention is described in connection with the annexed figure which forms a part of this specification. It is to be understood that this illustrative embodiment is merely one example of a process wherein the invention may be used.

The illustrative embodiment concerns the removal of hydrogen sulfide from a hydrocarbon oil by treatment with aqueous caustic solution. The feed may be any hydrocarbon oil which is fluid at the temperature of treating. For example, petroleum distillates which boil from about 100° to about 700° F., such as naphtha, heavy naphtha, kerosene, diesel oil and heater oil. The heavier-than-gasoline distillates are particularly suitable feeds. In this embodiment, kerosene from source **11** is passed by way of line **12** into heat exchanger **13**. Heat exchanger **13** brings the temperature of the feed to 110° F. The heated feed is passed from exchanger **13** by way of line **14** into mixer **16**.

An aqueous caustic solution containing about 10 weight percent of sodium hydroxide is passed from source **18** by way of valved line **19** into valved line **21**. In addition to the aqueous caustic solution from line **19**, valved line **21** contains recycled aqueous caustic solution. The total aqueous caustic stream is passed by way of lines **21** and **14** into mixer **16**. In this embodiment, 15 volume percent of aqueous caustic solution is used, based on feed in line **14**.

The feed and aqueous caustic solution are thoroughly intermingled in mixer **16** in order to remove the H_2S by reaction with the sodium hydroxide. From mixer **16** the oil and aqueous caustic stream is passed by way of line **23** into separator **24**.

The temperature of contacting in mixer **16** may be that temperature suitable for the particular oil and aqueous caustic concentration. This temperature is not necessarily the same as that used for the air dehazing procedure of the invention. However, normally it will be convenient to operate in mixer **16** at about the temperature desired for the subsequent air dehazing step.

Separator **24** is a vessel designed for the separation of two immiscible liquids by gravity settling. A lower aqueous caustic layer is removed from separator **24** by way of line **26**. This aqueous caustic layer is recycled to mixer **16** by way of valved line **21** and line **14** until the sodium hydroxide content has been lowered to a level wherein the solution is no longer effective. The spent aqueous caustic solution is then withdrawn from the system by way of valved line **27**. Herein an aliquot amount of caustic solution from line **26** is continuously withdrawn by way of valved line **27** and make-up caustic solution is added from source **18** by way of line **19**.

An upper oil phase which is substantially free of hydrogen sulfide is removed from separator **24** by way of line **29**. Commercially practicable settling times do not remove sufficient aqueous caustic phase from the oil to render it substantially haze free. And the oil layer in line **29** is hazy owing to the presence of a dispersion of drops of aqueous caustic solution throughout the body of the oil.

Air from source **31** is added by way of line 32 into line **29**; 4.5 standard cubic feet—SCF—of air per barrel (42 gal.) of hazy oil are added to line **29**. The air-oil stream is passed through mixer **34** and line **36** into separator **37**.

In general, the amount of air introduced into the hazy oil will be dependent on the temperature of agitation, the type of oil and the amount of aqueous caustic dispersed in the oil. Usually between about 1 and about 6 standard cubic feet of air per barrel (42 gal.) of hazy oil will result in the production of an acceptable product oil. It is preferred to use between about 3 and about 5 s. c. f. of air per barrel (42 gal.) of petroleum distillate.

The temperature of the dehazing operation is in part determined by the character of the oil itself, i. e., boiling point and particularly flash point. In general, the maximum temperature is about 150° F. The minimum temperature is imposed by physical characteristics of the oil such as viscosity or pour point and the aqueous caustic phase. It is preferred to operate at temperatures between about 80° and about 110° F., that is, the usual range of refining operations wherein aqueous caustic is used.

Since the process requires the agglomeration of minute individual droplets into large droplets which are not suspendable in the oil, sufficient time must be allowed for the agglomeration process to proceed to completion. The amount of time allowed is dependent upon the operating

conditions, particularly the temperature, and also on the amount of air used. The appearance of the body of hydrocarbon oil is the best guide for determining whether or not sufficient time has been allowed. As the agglomeration process progresses, a separate body of aqueous caustic, described herein as a separate layer, appears below the main body of oil. That is, in the vessel there will appear a lower layer of aqueous caustic and an upper layer of dehazed oil.

The body of air and oil is maintained in a state such that the air does not separate appreciably to form a distinct gas phase. The settling zone may be operated at super-atmospheric pressure to increase the solubility of the air in the oil. In general the body of air and oil is maintained for a time between about 2 hours and about 25 hours. More usually the time is between about 5 and 10 hours.

In separator 37, 8 hours are allowed to permit the formation of a distinct separate layer of aqueous caustic solution and an oil layer. The lower separate aqueous caustic solution layer is withdrawn, either periodically or continuously, from separator **37** by way of line **39** and is discharged from the system by way of valved line **41**; or it may be recycled to mixer **16** by way of lines **42, 21** and **14**.

A hydrogen sulfide-free product oil is continuously withdrawn from separator **37** by way of line **44**. This product oil is substantially free of haze forming aqueous caustic solution dispersion. That is, the oil is substantially haze free.

The process of this invention is applicable to the treatment of hazy oils derived from any process wherein aqueous caustic has been used to intimately contact hydrocarbon oil. Examples of some of these processes are: treatment with aqueous caustic to remove hydrogen sulfide or to neutralize acid treated oils; and oil sweetened by contacting with caustic-cresylate solution.

The results obtainable by the process of the invention are illustrated by the following tests carried out on commercial size equipment wherein dilute aqueous sodium hydroxide was used to remove hydrogen sulfide from diesel oil. In these tests the aqueous agent contained 6 weight percent of sodium hydroxide and 20 volume percent of agent was used based on raw diesel oil charged.

The raw oil was heated to 110° F. and was then passed into vessel A–1. Vessel A–1 operates as a gravity separator to remove occluded water from the oil. The dewatered oil from A–1 was intimately contacted with 8% aqueous NaOH, 20 volume percent based on oil, by vane mixers and loopbend mixers before passing into vessel A–2. In A–2 the oil was gravity separated by the aqueous NaOH. The hazy oil from A–2 was passed into vessel A–3 where some gravity separation takes place; the oil from A–3 was passed to vessel A–4 for further gravity separation of oil and aqueous caustic.

Normally the oil from A–4 was contacted in a vane mixer with water which was supposed to remove the aqueous caustic haze. The oil-water mixture was passed to vessel A–5 for gravity separation of oil and water. The oil from A–5 was passed to vessel A–6 for further gravity separation of water from the oil. The effluent from A–6 was passed to storage as product oil. (Vessels A–1 to A–6 were horizontally positioned and were 10 feet in diameter and 30 feet long.)

The feed to the test runs consisted of a diesel oil having the following characteristics:

Degrees, API	38
Flash (PM)	170° F.
Pour	−10° F.
Sulfur, weight percent	0.20
Viscosity, SSU, 100° F	36

In all the tests the temperature of the liquid in vessels A–1 through A–6 was maintained at about 100° F.

Test 1.—The feed to the plant was varied from about 60 to about 200 barrels (42 gal.) per hour and samples of effluent oil from vessel A–4 and A–6 were taken. A nephelometer measured the haze on an arbitrary scale. The nephelometer readings and the amount of sodium hydroxide present in the oil have the following relationship:

Nephelometer Reading:	NaOH parts per million
5	>1
10	11
15	23
20	35
25	47

Numerous samples taken periodically over several days showed that in the normal method of operation of this unit, the average nephelometer readings for the effluents were:

Vessel:	Reading
A–4	29
A–6	29

Thus, insofar as haze was concerned, the water washing step had no beneficial effect on the treated oil.

Test 2.—In this test the unit was operated in a manner as that for test No. 1 except that air was injected into the line which carries the oil phase from vessel A–2 to vessel A–3 and the stream was passed through a vane mixer and a loop mixer prior to entering vessel A–3. Operation at varying feed rates from 60 to 200 B. P. H. indicated that feed rate had no bearing on haze at constant injection of air per barrel of hazy oil. The average of several nephelometer readings of the effluent oil from vessel A–4 at various air injection rates are given below. The air rates are given as standard cubic feet per barrel (42 gal.) of hazy oil:

Air, S. C. F./B.:	Reading
2.7	13
3.6	9
3.9	7
5.0	11
6.3	14

These data show that the poorest results with air injection represent more than a 50% decrease in the amount of haze present in the effluent from vessel A–4. The best results show that 75% of the haze can be removed by the use of about 4 s. c. f. of air per barrel of hazy oil.

Test 3.—In view of the ineffectiveness of the water washing to improve the haziness of the oil from vessel A–4, a test was carried out to determine the influence of additional settling time on the hazy oil with the use of air injection and no water washing. In this test the water washing was eliminated and vessels A–5 and A–6 were used as ordinary aqueous caustic solution settling vessels in the same manner as vessels A–3 and A–4. The results of these tests at various air injection rates are given below:

Air, S. C. F./B.	Reading	
	A–4 Effluent	A–6 Effluent
None	36	25
1.8	23	16
2.6	16	8
3.0	13	7

These data show that increased settling time did have some beneficial effect on the haziness of the product oil from the operation. Furthermore, the effluent oil from vessel A–6 was as good as that obtained in test No. 2 when water washing was employed. This test shows that

by the use of the process of this invention, water washing can be eliminated in the aqueous caustic treating of a hydrocarbon oil. Elimination of the water wash on this plant has resulted in the elimination of 26,000 gallons of water from the refinery sewage system with a corresponding decrease in stream contamination.

Thus having described the invention, what is claimed is:

1. A continuous refining process which comprises (1) treating a petroleum distillate boiling between about 100° and 700° F. with aqueous caustic, (2) continuously separating a distinct aqueous caustic phase from an oil phase, which oil phase consists of treated oil and dispersed droplets of aqueous caustic and is hazy in appearance, (3) adding to a flowing stream of said hazy oil between about 1 and about 6 standard cubic feet of air per barrel (42 gal.) of hazy oil, (4) maintaining, at a temperature between about 30° and about 150° F., the air-oil stream in a settling zone for a time between about 2 hours and about 25 hours and (5) continuously withdrawing from said zone a distinct aqueous phase formed by agglomeration of haze droplets and a substantially haze-free oil.

2. The process of claim 1 wherein said oil is a heavy naphtha.

3. The process of claim 1 wherein said oil is a diesel oil.

4. The process of claim 1 wherein the air usage is between about 3 and about 5 standard cubic feet.

5. The process of claim 1 wherein said temperature is between about 80° and about 110° F.

6. A refining process which comprises (1) treating a petroleum distillate boiling in the heavier-than-gasoline range with aqueous caustic, (2) separating an aqueous caustic phase from an oil phase consisting of treated oil and a haze-forming dispersion of aqueous caustic droplets, (3) adding air, in an amount between about 3 and about 5 standard cubic feet per barrel of hazy oil, to a flowing stream of hazy oil, (4) passing the air-oil stream into an enlarged settling zone, maintained at a temperature between about 80° and 110° F., (5) maintaining the air-oil stream in said zone for a time between about 5 and about 10 hours and (6) withdrawing from said zone a separate aqueous phase formed by agglomeration of haze droplets and withdrawing continuously a substantially haze-free treated oil.

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