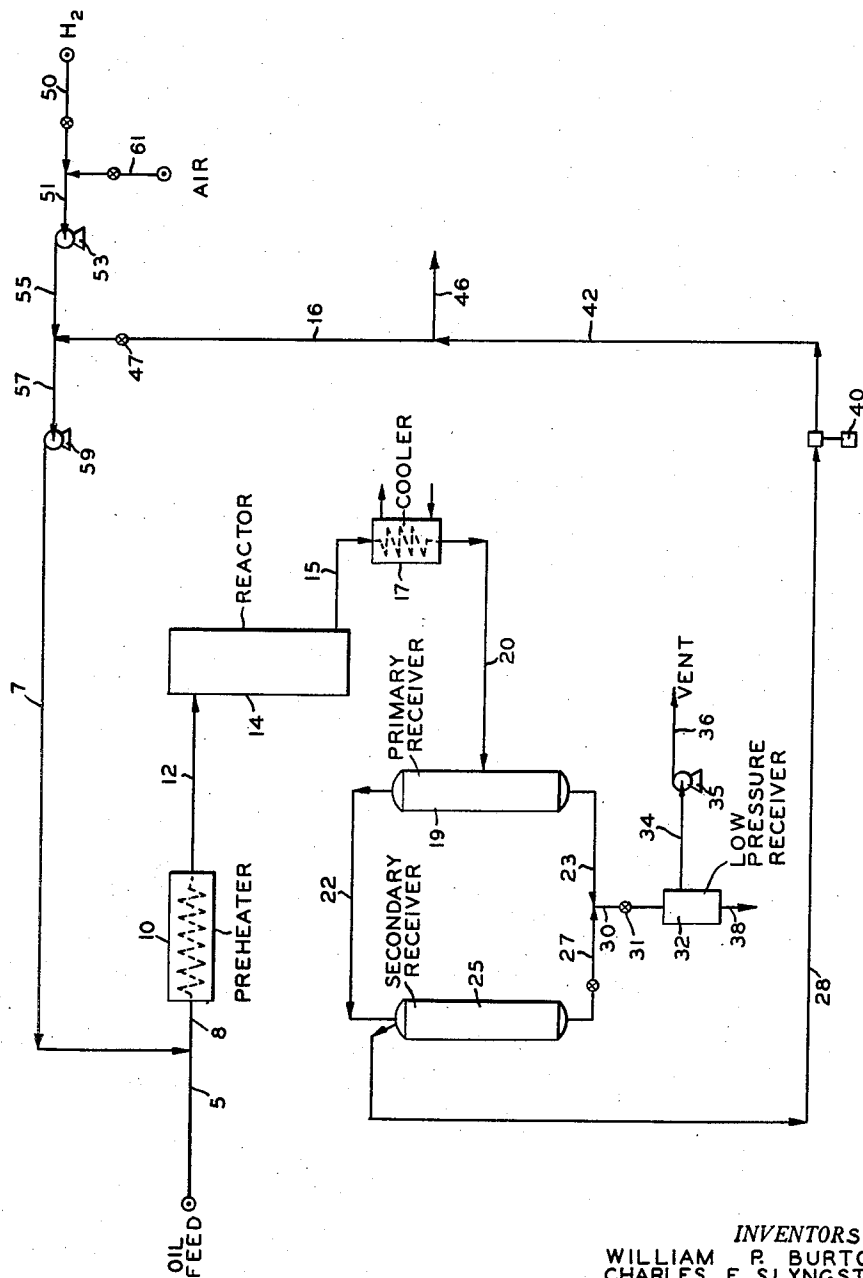


June 24, 1958

W. P. BURTON ET AL
STABILIZATION OF FURNACE OIL BY HYDROTREATING
TO REMOVE SULFUR AND GUM
Filed Sept. 29, 1955

2,840,512



INVENTORS
WILLIAM P. BURTON
CHARLES E. SLYNGSTAD
BY

H. H. Palmer
ATTORNEYS

1

2,840,512

STABILIZATION OF FURNACE OIL BY HYDRO-TREATING TO REMOVE SULFUR AND GUM

William P. Burton, Little Silver, and Charles E. Slynstad, Rutherford, N. J., assignors to The M. W. Kellogg Company, Jersey City, N. J., a corporation of Delaware

Application September 29, 1955, Serial No. 537,414

4 Claims. (Cl. 196—24)

This invention relates to a method of stabilizing a furnace oil without effecting a change in color.

Furnace oils are used extensively in home burners and commercial installations for heating, etc. At present, there is found in furnace oils gum-forming compounds or constituents which will, upon standing, produce gum-like materials. These gum-like materials are not desired, because in the type of equipment used for burning furnace oils, the gum-like materials will clog the equipment causing operating difficulties. At present, it is not clearly understood what kind of compounds produce the undesired gum-like materials. Further, furnace oils contain color bodies or compounds which impart to the oil a color other than a colorless appearance. These color bodies do not cause operating difficulties in the equipment used for the burning of furnace oils, therefore, for the purpose of this invention, it is not intended to effect any change in the color of the oil. In addition to the color bodies and the gum-forming compounds, the furnace oils do contain sulfur compounds. The combustion of sulfur compounds in the furnace oil may produce corrosion of the equipment used for such a purpose as well as to produce an undesired smell or contamination of the surrounding atmosphere. It is apparent, therefore, that there exists a need for a process whereby furnace oil can be stabilized, with or without simultaneous removal of sulfur and without a change in color.

An object of this invention is to provide a process for the stabilization of furnace oils without a change in color.

Another object of this invention is to provide a method for the desulfurization and stabilization of furnace oils without changing the color.

Other objects and advantages of this invention will become apparent from the following description and explanation thereof.

By means of the present invention, a furnace oil is stabilized without a change in color by the process which comprises contacting the furnace oil containing gum-forming constituents with a cobalt molybdate catalyst under suitable reaction conditions including a temperature not greater than 700° F. and a weight space velocity of at least about 5.

The furnace oil to be processed by means of the present invention contains gum-forming constituents. The determination of the gum-forming tendency of the furnace oil or its stability is made by a simple test in which the oil is subjected to a temperature of 210° F. for a period of 40 hours. If the oil does not change more than ½ NPA in color and not more than 5 milligrams of gum is produced per 600 grams of oil sample, it is considered stable. This test is used for the purpose of determining the stability in the present specification and the appended claims. While the gum-forming compounds or constituents in the furnace oil are not known at present, nevertheless the stability test is sufficient for the purpose of determining the nature of a particular furnace oil. In addition to stability, furnace oils usually contain color. Here again, at present, the color bodies or compounds im-

2

parting color to the furnace oil are not clearly understood, although it is speculated that nitrogen compounds usually produce color in hydrocarbon oils. For the purpose of this invention, the furnace oil can contain an NPA color ranging from about 1 to about 6 or on a Saybolt scale, the color of the furnace oil can range from about -16 to about +30. In addition to containing color and gum-forming compounds, the furnace oil may also contain sulfur compounds. The sulfur concentration of a furnace oil can vary widely such as, for example, about 0.1 to about 4% by weight of sulfur. The sulfur content of the oil will be reduced under the conditions employed for the purpose of effecting stabilization. The furnace oil employed for the purpose of this invention will have an initial boiling point of about 300° to about 420° F. and an end point of about 500° to about 850° F., more usually, the furnace oil will have an initial boiling point of about 325° to about 350° F. and an end point of about 550° to about 650° F. The furnace oil to be treated can be a mixture of virgin or straight run stock and what is usually referred to as light cycle oil, as well as heavy cycle oils.

The furnace oil is treated by means of a cobalt molybdate catalyst. For the purpose of this specification and the appended claims, cobalt molybdate is intended to include a mixture of cobalt oxide and molybdenum oxide as well as the compound cobalt molybdate. It is believed that under the conditions employed for the purpose of treatment in accordance with this invention, it is not important whether a mixture of the oxides is used or whether cobalt molybdate is the catalyst at the start of the operation. Accordingly, the catalyst of this invention contains about 0.5 to about 10% of cobalt oxide, based on the total weight of the catalyst, and it contains about 5 to about 25% of molybdenum oxide, e. g., molybdenum trioxide, based on the total weight of the catalyst. The cobalt molybdate is supported on a suitable carrier material, such as for example, alumina, silica-alumina, halogenated alumina, activated charcoal, kieselguhr, pumice, zinc aluminate spinel, etc. When silica is employed in combination with alumina, it constitutes about 0.5 to about 5%, based on the total weight of the catalyst. Chemically combined halogen such as, for example, chlorine or fluorine, can be used in the catalyst in the amount of about 0.1 to about 8%, based on the total weight of the catalyst.

The furnace oil is treated with cobalt molybdate catalyst under carefully selected conditions. In this respect, it is essential to the present invention that the temperature of treatment is not higher than about 700° F. and the weight space velocity is at least 5. In this respect, should either the temperature or the weight space velocity fall outside of the range given above, it is noted that there is a color change, and hence, such an operation falls outside the scope of this invention. In general, the temperature of treatment can vary from about 550° F. but not greater than about 700° F. The weight space velocity, measured as the pounds of oil per hour charged to the reaction zone per pound of catalyst present therein, is at least about 5 and it can be as high as 20. It was found that the pressure of operation can be as low as about 150 p. s. i. g. and it can be as high as 1500 p. s. i. g., more usually about 300 to about 1000 p. s. i. g. The reaction is effected in the presence of hydrogen which is added to the process in the amount of at least about 300 standard cubic feet (measured at 60° F. and 760 mm. Hg) per barrel of oil feed, abbreviated as "S. C. F. B.," and the hydrogen rate can be as high as 5000 S. C. F. B. although a hydrogen rate of up to about 2000 S. C. F. B. suffices for the purpose of this invention. Consequently, it can be seen that the present invention can be operated within rather narrow ranges of conditions, for example, a high

3

hydrogen rate of about 300 to about 900 S. C. F. B., a weight space velocity of about 5 to about 15 and a reaction pressure of about 300 to about 600 p. s. i. g. Under the conditions of operation, at least part of the sulfur content in the furnace oil is removed, the oil is stabilized and the color remains unchanged.

In order to provide a better understanding of this invention, reference will be had to the accompanying drawing which contains a schematic diagram of a test unit which was employed for the purpose of evaluating this invention.

In the drawing, oil feed is supplied by means of line 5 at the desired flow rate and it is combined with hydrogen being supplied from line 7, and thence, the combined steam flows through line 8 before entering preheater 10. In the preheater, the temperature is raised to the desired temperature, for example, about 600 to about 700° F., and thereafter, it flows through line 12 before it enters the top of reactor 14. Reactor 14 is 43 inches in length and 1½ inches in diameter, and it contains about 800 grams of catalyst. The catalyst is in the form of ¾ inch pellets. Under the conditions prevailing in the reactor, the furnace oil is stabilized with removal of sulfur and without change in color. The vaporous reaction product is discharged from the bottom of the reactor by means of line 15, and hence, it enters a water cooler 17 wherein the temperature is reduced to about 80° F. The cooled reaction product contains condensed normally liquid product material, or material which is present as a liquid under reaction pressure and the temperature to which the material was cooled. The cooled reaction product flows from cooler 17 by means of line 20.

A preliminary separation of normally gaseous product material from liquid product is effected in primary receiver 19, consequently, the normally gaseous product material flows overhead therefrom by means of line 22; whereas the liquid product is discharged from the bottom by means of line 23. Any liquid product which is entrained in the normally gaseous product is separated in the secondary receiver 25 and it is discharged from the bottom thereof by means of valved line 27. The gaseous product is discharged overhead from the secondary receiver 25 by means of line 28. The liquid product in lines 23 and 27 flow into line 30 which contains a pressure reducing valve 31. By means of valve 31, the pressure is reduced to atmospheric level and the total product passes into a low pressure receiver 32. Any gaseous product which is released from the liquid product in receiver 32 is discharged therefrom by means of line 34 and it is measured by means of meter 35 before being vented from the system by means of line 36. Liquid product is discharged from receiver 32 by means of line 38.

The gaseous product material which is discharged from receiver 25 and is flowing through line 28 is recompressed by means of compressor 40. The compressed hydrogen containing gas or recycle gas flows from compressor 40 to line 42. The recycle gas passes through a valve 47 in line 42 when recycle is employed for the stabilization treatment. Alternatively, a once-through hydrogen treatment can be employed and in such event, valve 47 is maintained in a closed position. Hydrogen can be purged from the system via line 46. Fresh hydrogen is supplied from a valved line 50, and it flows to line 51 before being measured by means of meter 53. The measured hydrogen flows from meter 53 to line 55 where, in the case of the recycle gas operation, it combines with recycle gas flowing through line 42 and the combined stream flows through line 57. The total hydrogen stream is measured by means of meter 59, and thence, it flows into line 7 before combining with feed which is flowing to the preheater 10. For the purpose of regeneration, air can be supplied from a valved line 61 and valved line 50 can be employed for the purpose of supplying nitrogen for ad-

4

mixture with the air in case a diluted air stream is desired for the regeneration.

The feed stocks evaluated for the purpose of this invention are given in Table I below.

Table I

Feed.....	A	B	C	D
° API Gravity.....	24.0	23.8	29.9	33.4
ASTM Distillation, ° F.:				
IBP.....	386	433	466	326
10.....	472	481	504	408
50.....	539	536	536	518
90.....	605	608	600	586
E. P.....	649	644	642	639
Sulfur, Wt. percent.....	1.02	2.13	0.21	0.18
Color, NPA.....	2	3½	2	1½

The catalyst employed for this evaluation consisted of cobalt molybdate supported on alumina. The catalyst contained 4.1% by weight of cobalt oxide, 12.0% by weight of molybdenum trioxide and the remainder was alumina.

The data reported in Table II below serves to illustrate the critical feature of temperature when it is desired to stabilize furnace oils without changing color.

Table II

Run No.....	1	2
Feed.....	B	A
Temperature, ° F.....	750	780
Pressure, p. s. i. g.....	350	400
Space Vel., W ₀ /hr./W.....	5.0	10.0
H ₂ rate, S. C. F. B.....	520	480
Results	Feed	Product
Sulfur, Wt. percent.....	2.13	0.77
Color, NPA.....	3½	1.02
Stability *.....	No	Yes

* 80% hydrogen.

b 100% hydrogen.

* Stable oil is defined herein as changing not more than ¼ NPA color and producing no more than 5 mg. gum/600 gm. oil during the stability test of 40 hours in a 210° F. oven.

It is apparent from the data given above in Table II that as long as the temperature was above 700° F., notwithstanding that all other conditions fall within the range to be used for the treatment of furnace oil in accordance with this invention, the oil product was stabilized with a change in color.

Additional experiments were performed and reported in Table III below.

Table III

Run No.....	1	2	3	4
Feed.....	A	A	A	A
Pressure, p. s. i. g.....	400	400	400	400
Space Vel., W ₀ /hr./W.....	1	5	10	10
Temperature, ° F.....	700	700	700	780
H ₂ rate, S. C. F. B.....	500	520	520	480
Results	Feed	Products		
Sulfur, Wt. percent.....	1.02	0.05	0.24	0.38
Color, NPA.....	2	2	2	2
Stability.....	No	Yes	Yes	Yes

It is apparent from the data contained in Table III above that where the temperature was 700° F. and the weight space velocity was at least 5, the furnace oil was stabilized without a change in color. However, where the temperature of treatment was 700° F. and the weight space velocity was below 5, the oil was stabilized with a change in color. Further, when effecting the treatment above 700° F. with a weight space velocity of 10, it is noted that the oil was stabilized with a change in color.

5

Further evaluation of the present invention was made and the results are reported in Table IV below.

Table IV

Run No.	1	2
Feed	A	A
Pressure, p. s. i. g.	400	400
Space Vel., W ₀ /hr./W _c	1.0	1.0
Temperature, °F.	700	700
H ₂ rate, S. C. F. B.	500	2,000
Results	Feed	Products
Sulfur, Wt. Percent.	1.02	0.05
Color, NPA	2	3
Stability	No	Yes

The data in Table IV above indicate that even though a higher rate of hydrogen is employed for the treatment just so long as the weight space velocity falls below 5, the furnace oil is stabilized with a change in color.

An additional experiment was performed and reported in Table V below.

Table V

Run No.	1
Feed	C
Pressure, p. s. i. g.	600
Space Vel., W ₀ /hr./W _c	5
Temperature, °F.	700
H ₂ rate, S. C. F. B.	800
Results	Feed
Sulfur, Wt. Percent.	0.2
Color, NPA	2
Stability	No

It is noted from the run made and reported in Table V above that the critical aspects of temperature and weight space velocity are not disturbed by using a higher pressure of treatment.

Another experiment at low pressure was performed and reported in Table VI below.

Table VI

Run No.	1
Feed	D
Pressure, p. s. i. g.	150
Space Vel., W ₀ /hr./W _c	20
Temperature, °F.	700
H ₂ rate, S. C. F. B.	500
Results	Feed
Sulfur, Wt. percent.	0.18
Color, NPA	1 1/2
Stability	No

6

The data in the above Table VI indicates that when treating at the maximum temperature, namely 700° F., it is possible to operate at as low as 150 p. s. i. g. with only a very small change in color in the oil treated to provide a stable oil of substantially lower sulfur content.

Having thus provided a written description of this invention along with specific examples thereof, it should be understood that no undue restrictions or limitations are to be imposed by reason thereof, but that the scope of the present invention is defined by the appended claims.

We claim:

1. A process for stabilizing a furnace oil containing gum forming constituents without changing the color thereof which comprises contacting the furnace oil with a cobalt molybdate catalyst under suitable reaction conditions including a temperature not greater than about 700° F. and a weight space velocity of at least about 5.

2. A process for stabilizing a furnace oil containing gum forming constituents without changing the color thereof which comprises contacting the furnace oil with a cobalt molybdate catalyst under suitable conditions including a temperature not greater than about 700° F., a weight space velocity of at least about 5, a hydrogen rate in the amount of at least about 300 S. C. F. B. and a pressure of at least about 150 p. s. i. g.

3. A process for desulfurizing and stabilizing a furnace oil containing gum forming constituents and sulfur compounds without changing the color thereof which comprises contacting the furnace oil with a cobalt molybdate catalyst under suitable desulfurization conditions including a temperature not greater than about 700° F., a weight space velocity of at least about 5, a pressure of about 150 to about 1500 p. s. i. g. and in the presence of added hydrogen in the amount of about 300 to about 2000 S. C. F. B.

4. A process for desulfurizing and stabilizing a furnace oil containing gum forming constituents and sulfur compounds without changing the color thereof which comprises contacting the furnace oil with a cobalt molybdate catalyst under suitable conditions including a temperature of at least about 550° F. and not higher than about 700° F., a weight space velocity of about 5 to about 20, a pressure of about 150 to about 1500 p. s. i. g. and in the presence of added hydrogen in the amount of about 300 to about 2000 S. C. F. B.

References Cited in the file of this patent

UNITED STATES PATENTS

2,587,987	Franklin	Mar. 4, 1952
2,608,521	Hoog	Aug. 26, 1952
2,694,671	Baumgarten et al.	Nov. 16 1954
2,717,857	Bronson et al.	Sept. 13, 1955

OTHER REFERENCES

Zohnstecher et al.: Oil and Gas Journal, vol. 53, December 20, 1954, pages 78 to 81.

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,840,512

June 24, 1958

William P. Burton et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 15, for "steam" read -- stream --; line 26, for "hence" read -- thence --.

Signed and sealed this 19th day of August 1958.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents