

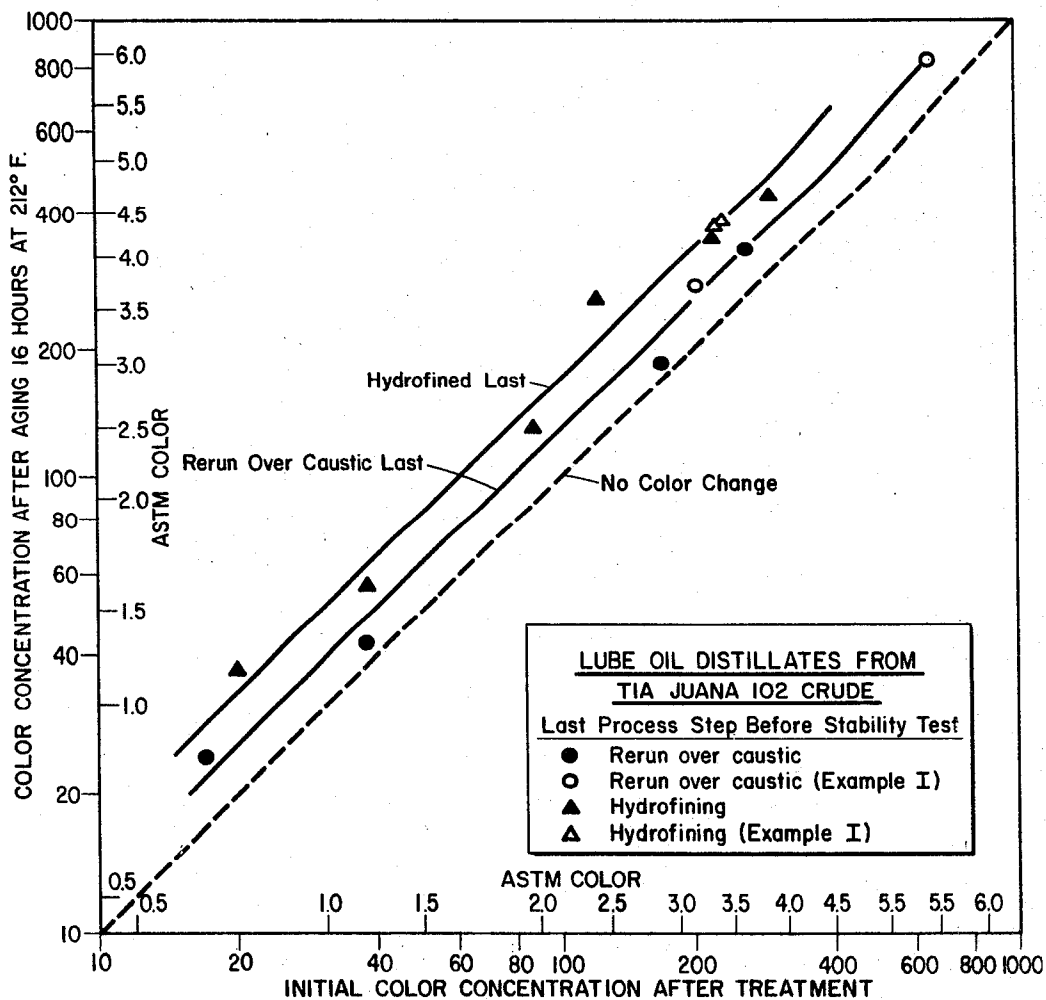
Dec. 20, 1966

P. P. McCall

3,293,173

COLOR IMPROVEMENT OF PETROLEUM LUBRICATING OILS

Filed July 31, 1964



Patrick P. McCall

INVENTOR

BY *Gary J. Gilman*

PATENT ATTORNEY

3,293,173  
COLOR IMPROVEMENT OF PETROLEUM  
LUBRICATING OILS  
Patrick P. McCall, Madison Township, Middlesex County,  
N.J., assignor to Esso Research and Engineering Com-  
pany, a corporation of Delaware  
Filed July 31, 1964, Ser. No. 386,710  
7 Claims. (Cl. 208-264)

This invention relates to upgrading and improving the color and stability of petroleum lubricating oil base stocks. More particularly, the invention relates to a process wherein unfinished or untreated lubricating oil stocks are first hydrofined and then distilled over alkali metal or alkaline earth metal hydroxides.

The treatment of petroleum lubricating oil base stocks with aqueous caustic or lime is well known in the art. The hydrofining of lubricating oils is well known in the art. It is also known to treat certain lubricating oils with excess caustic or lime and then to hydrofine the lubricating oils. Certain raw or untreated lubricating oil stocks can be given a single treatment of either hydrofining or caustic or lime treatment to achieve sufficient improvement in color, color stability, etc., to meet the specifications set down for finished lubricating oil base stocks in certain of the less demanding applications. However, there are other lubricating oil base stocks which need more than one single processing step.

It has been known that petroleum lubricating oils can be upgraded by treating them first with excess alkali metal or alkaline earth metal hydroxide, distilling the oil from the treating medium and then hydrofining the distilled oil in the presence of hydrogen and a hydrofining catalyst.

It has now been found that petroleum lubricating oils can be upgraded by first hydrofining the oil in the presence of hydrogen and a hydrofining catalyst, and then treating the hydrofined oil with solid alkali metal or alkaline earth metal hydroxide at an elevated temperature and distilling the hydrofined oil over excess alkali metal or alkaline earth metal hydroxide gives an unexpected additional benefit and results in improved oil color and in the greatest degree of color stability improvement.

The figure is a graph representing the results of various treatments and compares the color stabilities of the products obtained from these treatments.

The petroleum lubricating stocks to be treated are distillates falling within the boiling range of about 650° F. to 900° F., a viscosity in the range of about 36 to 130 S.S.U. at 210° F. The lubricating base stock is preferably one derived from naphthenic base crude oils such as Tia Juana, Coastal, Lagunillas, etc. However, the invention is not restricted to this class of crude petroleum oils since advantages are also obtained by treating base stocks derived from paraffin base crude oils. The lubricating oils which may be treated according to this invention include transformer oils, spindle oils, machine oils, base stocks for grease manufacture, and cutting oils.

The lubricating oil stock can be hydrofined under the following conditions:

TABLE I

|                                        | Broad Range | Preferred Range |
|----------------------------------------|-------------|-----------------|
| Temperature, ° F.                      | 500-700     | 550-650         |
| Pressure, p.s.i.g.                     | 100-1,500   | 400-800         |
| Feed Rate (v./hr./v.)                  | 0.3-5.0     | 0.5-2.0         |
| H <sub>2</sub> Treat (s.c.f./b.)       | 150-2,000   | 300-1,000       |
| H <sub>2</sub> Consumption (s.c.f./b.) | 75-300      | 125-200         |

The hydrofining catalysts that can be used in the hy-

drofining step include conventional hydrofining catalyst such as cobalt molybdate on alumina, molybdenum oxide on alumina, nickel sulfide, tungsten sulfide, nickel-cobalt-molybdenum on alumina, iron-cobalt-molybdenum on alumina. The cobalt molybdate catalyst comprises 2-6 wt. percent of cobalt oxide and 6-15 wt. percent of molybdenum oxide. The catalyst is preferably used in a fixed bed. Regeneration of the catalyst bed to remove carbonaceous deposits is periodically carried out with an oxygen-containing gas such as air or one in which the oxygen content may be lower or higher than in air. The regeneration is carried out at a temperature between about 750° F. and 1000° F.

In the hydrofining operation, the lubricating oil and hydrogen are contacted with a fixed bed of catalyst in a reactor vessel by continuous downward flow through the vessel. The oil feed to the reactor vessel is preheated by means of a furnace, heat exchangers or other means to a temperature between about 500° F. to 700° F. The hydrogen may or may not be preheated. After the hydrofining step has been carried out, the treated lubricating oil stock is passed to a steam stripping column to remove residual hydrogen and H<sub>2</sub>S.

The stripped lubricating oil is then reheated, vaporized and distilled under reduced pressure in a vacuum rerun tower under conditions which result in at least 90% and preferably 95% or more of the oil being taken overhead or as sidestream cuts. During the course of this distillation, a controlled amount of alkali metal or alkaline earth metal hydroxide is introduced and mixed with the oil in such a way as to provide intimate contact between the oil and a dispersion of finely divided particles of solid caustic material. The caustic material ultimately leaves the system as a finely divided solid suspension in the bottoms from the vacuum rerun tower.

The desired contact between the oil and the solid caustic material can conveniently be accomplished as follows. The stripped lubricating oil stock is mixed with an aqueous metal hydroxide. An aqueous solution of sodium hydroxide or an aqueous slurry of lime or calcium oxide is preferred as these are the cheapest. Potassium hydroxide may be used. When using aqueous sodium hydroxide, the concentration of the solution is between about 10° Bé. and 50° Bé. which is equivalent to about 7 wt. percent to 50 wt. percent of sodium hydroxide in water. A 50° Bé. aqueous sodium hydroxide is preferred. The amount of sodium hydroxide used is between about .0005 and .01 part by weight per part by weight of lubricating oil, preferably about .006 part by weight per part by weight of the lubricating oil of the preferred concentration of aqueous solution of sodium hydroxide. When using a water slurry of lime or calcium oxide, about twice as much of the lime or calcium hydroxide as sodium hydroxide is used.

The stripped lubricating oil is heated in a preheat furnace and the aqueous solution of sodium hydroxide or aqueous suspension of lime or calcium hydroxide may be introduced into the stripped lubricating oil stream before or after but preferably before the heating step in the preheat furnace. Steam is also added to the stripped lubricating oil stream, preferably ahead of the preheat furnace. The oil is at a temperature of about 100° F. to 600° F., preferably 500° F., and, after heating, it has a temperature of between about 725° F. and 775° F., preferably 750° F. The time of contact of the oil and metal hydroxide solution above about 700° F. in the preheat furnace is between about 30 and 300 seconds.

The thus treated oil is then separated from the spent metal hydroxide solution by distillation under reduced pressure in a vacuum rerun tower. The pressure in the rerun tower is between about 75 and 150 mm. Hg abso-

lute. At this temperature and pressure the water from the metal hydroxide solution is vaporized and the distillation is over solid alkali metal or alkaline earth metal hydroxide which is non-volatile and which remains behind as a fine dispersion of solid particles in the bottoms fraction in the rerun tower. The time of contacting of the bottoms oil and the solid alkaline treating agent is between about 30 and 120 seconds. The treated lubricating oil is taken off as one or more sidestreams from the rerun tower.

#### Example I

A raw Tia Juana lubricating oil distillate of high neutralization number of 0.95 mg. KOH/g. and high sulfur content (1.8 wt. percent) and having the characteristics given in Table II was hydrofined at 575° F., 800 p.s.i.g. pressure, hydrogen-containing gas (60% by volume H<sub>2</sub>) used was 500 s.c.f./b. of feed, and the space velocity was 1.0 v./hr./v. (volume of oil per hour per volume of catalyst). The hydrofined oil was steam stripped to remove H<sub>2</sub> and H<sub>2</sub>S. A portion of this hydrofined oil was distilled over 0.25 wt. percent solid NaOH in a batch vacuum distillation apparatus at a pressure of about 1 mm. Hg absolute. About 97 volume percent of the lubricating oil feed was recovered.

In Table II, results are given for caustic distillation only of the Tia Juana lubricating oil feed with recovery of 95% by volume of the feed. The treatment was by distillation over solid caustic. The concentration of the caustic and the amount used per part of oil are the same as in the caustic treatment above described in connection with the hydrofining-caustic treating combination of the present invention.

In Table II, results are also given for the reverse combination, that is, the lubricating oil is first caustic treated and then hydrofined with a recovery of 95% by volume of treated oil. The caustic treat and hydrofining were the same as given in the hydrofining-caustic treatment of the present invention.

TABLE II

|                                    | Raw<br>TJ 102<br>Distil-<br>late | Hydro-<br>fined <sup>1</sup><br>Only | 0/95%<br>OH<br>Caustic<br>Distilled<br>Only | 0/95%<br>OH<br>Caustic<br>+ Hydro <sup>1</sup> | 0/97%<br>OH<br>Hydro <sup>1</sup><br>+ Caustic |
|------------------------------------|----------------------------------|--------------------------------------|---------------------------------------------|------------------------------------------------|------------------------------------------------|
| Gravity, ° API.....                | 19.5                             | 20.4                                 | 19.7                                        | 20                                             | 20.5                                           |
| Vis/100° F., SSU.....              | 1,944                            | 1,622                                | 1,685                                       | 1,635                                          | 1,469                                          |
| Vis/210° F., SSU.....              | 95.1                             | 88.6                                 | 89.7                                        | 88.2                                           | 84.6                                           |
| Viscosity Index.....               | 34                               | 39                                   | 37                                          | 37                                             | 39                                             |
| Color, ASTM.....                   | 6.5                              | 3.4                                  | 5.4                                         | 3.3                                            | 3.2                                            |
| Colorhold, ASTM <sup>2</sup> ..... | 8                                | 4.4                                  | 5.9                                         | 4.3                                            | 3.7                                            |
| Pour Point, ° F.....               | +5                               | 0                                    | -5                                          | -15                                            | -15                                            |

<sup>1</sup> All Hydrofining done @ 575° F., 800 p.s.i.g., 500 s.c.f./b. of 60% H<sub>2</sub> treat gas, 1 v./v./hr.

<sup>2</sup> Color after accelerated aging of oil at 212° F. for 16 hours.

From the above results it will be seen that the combination of steps of first hydrofining the lubricating oil distillate stock and then treating or distilling it over solid caustic material produces the maximum improvement in color and color stability. With the present invention, a more stable lubricating oil product is obtained than when the reverse steps are used and hydrofining is the last step. If the caustic treatment comes before the hydrofining step, the improvement in stability is nullified. The effects of the two stages are beneficial only when done in the proper order.

It is essential that the caustic treatment or metal hydroxide treatment of the hydrofined lubricating oil stock be with solid metal hydroxide and at a temperature above about 400° F.

#### Example II

Lube oil distillates from Tia Juana 102 crude were subjected to a variety of treatments involving hydrofining alone, rerunning over caustic alone, rerunning over caustic followed by hydrofining, and hydrofining followed by re-

running over caustic. Some but not all of the data is included in Table II. In the figure, the color stabilities of the products obtained from these treatments are compared. On this graph are plotted the initial colors of the oils immediately after treatment vs. the color obtained on each sample after accelerated aging for 16 hours at 212° F. The data are plotted on logarithmic paper using a scale which is proportional to color-body concentration.

It can be seen that the data fall into two groups: (1) those stocks for which the final treatment was hydrofining either as one step or as the second step; and (2) those stocks for which the final treatment was rerunning over caustic either as one step or as the second step. In all cases, the caustic-rerun-last stocks showed better color stability than the hydrofined-last stocks. On the average, the caustic-rerun-last stocks increased in color concentration by a factor of 1.25 during the accelerated aging test, significantly less than the hydrofined-last stocks, which averaged a 1.65-fold increase. The data from Example I are shown on this graph also, to illustrate their consistency. It is thus apparent that rerunning over caustic leads to better color stability than does hydrofining, and that when the two steps are combined in the proper sequence, namely, hydrofining followed by rerunning over caustic, the greatest improvement in color (achieved primarily by the hydrofining step) and color stability (achieved primarily by the caustic rerunning step) results.

It is to be understood that the invention is not limited to the specific examples which are included merely as illustrations of the invention and that modifications may be made without departing from the spirit of the invention.

What is claimed is:

1. A process for improving the color and color stability of a petroleum lubricating oil base stock which comprises hydrofining the lubricating oil base stock in the presence of a hydrofining catalyst and hydrogen, introducing an aqueous alkaline metal hydroxide into the hydrofined oil, said metal hydroxide being selected from the group consisting of hydroxides of the alkali metals and alkaline earth metals and being used in an amount between .0005 and .01 part by weight per part of oil by weight, heating the resulting mixture of oil and metal hydroxide to a temperature between about 400° F. and 700° F. to vaporize and separate the water from the non-volatile solid metal hydroxide, distilling the oil under vacuum in a vacuum rerun tower in direct contact with the separated solid metal hydroxide to produce a lubricating oil stock of improved color and color stability.

2. A process for improving the color and color stability of petroleum lubricating oil base stock which comprises catalytically hydrofining the oil base stock at a temperature in the range between 500° F. and 700° F. and at a pressure in the range between 100 and 1500 p.s.i.g., steam stripping the hydrofined oil, then treating the hydrofined oil with an aqueous metal hydroxide at a temperature between about 400° F. and 700° F., said hydroxide being selected from the group consisting of hydroxides of alkali metals and alkaline earth metals, the amount of aqueous metal hydroxide used being between about .0005 and .01 part by weight per part by weight of oil and the concentration of the aqueous metal hydroxide being between about 7 and 50° Bé and the time of contact of said hydrofined oil and said metal hydroxide is between about 30 and 300 seconds, distilling the treated oil from the metal hydroxide under reduced pressure in a vacuum rerun tower, during said distillation directly contacting said hydrofined oil with solid metal hydroxide left behind in said vacuum rerun tower to produce a lubricating oil stock of improved color and color stability and recovering said lubricating oil stock of improved color and color stability as a sidestream from said vacuum rerun tower as product.

3. A process according to claim 2 wherein said hydroxide comprises sodium hydroxide.

4. A process according to claim 2 wherein said distillation step is carried out under a reduced pressure between

5

about 1 and 150 mm. Hg absolute in said vacuum rerun tower.

5. A process according to claim 2 wherein spent alkaline metal hydroxide is withdrawn in the bottoms oil fraction from the bottom of said vacuum rerun tower.

6. A process for improving color and color stability of a petroleum lubricating oil base stock which comprises hydrofining the lubricating oil base stock in the presence of a hydrofining catalyst and hydrogen, then contacting said hydrofined oil with an alkaline metal hydroxide, said metal hydroxide being selected from the group consisting of hydroxides of the alkali metals and alkaline earth metals, heating said hydrofined oil in said contacting step to a temperature between about 400° F. and 700° F., then distilling said hydrofined oil under vacuum in a vacuum rerun tower in direct contact with said alkaline metal hydroxide to produce a lubricating oil stock of improved color and color stability.

6

7. A process according to claim 6 wherein the time of contacting said hydrofined oil and alkaline metal hydroxide is between about 30 and 300 seconds at a temperature of about 700° F. and the amount of alkaline metal hydroxide is between about .0005 and .01 part by weight per part by weight of oil feed.

#### References Cited by the Examiner

##### UNITED STATES PATENTS

|    |           |         |                |         |
|----|-----------|---------|----------------|---------|
| 10 | 1,932,369 | 10/1933 | Guthke         | 208—215 |
|    | 2,944,014 | 7/1960  | Hoffman        | 208—264 |
|    | 3,121,678 | 2/1964  | Behymer et al. | 208—212 |
|    | 3,128,155 | 4/1964  | Mattox         | 208—212 |

15 DELBERT E. GANTZ, *Primary Examiner*.

S. P. JONES, *Assistant Examiner*.