

1

2,772,211

TREATMENT OF HYDROCARBON STOCKS WITH SODIUM

Arthur S. Hawkes, Royal Oak, and Donald O. Remter, Detroit, Mich., assignors to Ethyl Corporation, New York, N. Y., a corporation of Delaware

No Drawing. Application May 28, 1953,
Serial No. 358,171

5 Claims. (Cl. 196—26)

This invention relates to the treatment of hydrocarbon stocks and is particularly concerned with improving the storage stability, gum content, and sulfur content of these stocks.

The problem of improving the stability characteristics of hydrocarbon stocks and petroleum fractions has become increasingly important, particularly in recent years, due to the fact that the utilization of catalytic cracking has made the problem of stability, reduction of gum formation, and desulfurization of fuels more significant. Heretofore, various processes have been utilized particularly for desulfurizing petroleum distillates, but these processes have had considerable disadvantage and have been restricted in their usage. For example, treatment of hydrocarbon stocks with alkali metals has been investigated, but this process has found limited usage inasmuch as high temperatures and high pressures have been required, and the reactivity of the residues obtained is of such a nature that disposal thereof is quite hazardous. Further, in order to acquire the desirable characteristics of the fuel, it has been necessary to utilize quantities of the alkali metal in excess of the equivalent amount of sulfur present in the charge stock. This excess amount of alkali metal is therefore not considered practicable in that the economics of the process are not favorable. A further disadvantage of this process has been that the gum-reducing tendencies of the process have not been appreciable, and in addition the stability qualities of the fuel have not been obtained. High gum content is not desirable in the fuels, particularly when they are to be utilized in internal combustion engines, since they will form coatings and result in valve sticking and other undesirable features in operation. High sulfur content similarly is not considered desirable since the sulfur content contributes to wear or corrosion of the integral parts in an internal combustion engine.

It is an object, therefore, of the present invention to overcome the difficulties experienced in the prior art and to provide a process for improving the stability characteristics of hydrocarbon stocks. A further object of this invention is to provide a novel process for desulfurizing these petroleum distillates. A still further object is to treat hydrocarbon stocks in a manner which will not produce a hazardous reactive residue. These and other objects of this invention will become apparent from the discussion hereinafter.

The process of the present invention comprises treating hydrocarbon stocks with catalytic quantities of a light metal to improve the characteristics of the stock, such as gum and sulfur content, stability, and color. Surprisingly, we have found that upon treating hydrocarbon stocks with a proportion of light metal less than the stoichiometric equivalent of the amount of sulfur contained in the stock, its storage stability can be considerably improved, the gum content essentially eliminated, and the sulfur content diminished to provide a desirable product for its use in internal combustion engines or for blending with other fuels.

2

As one means of achieving this result, a dispersion of a light metal in heavy alkylate is introduced into a stream of a hydrocarbon stock. This mixed stream is then passed to a preheater, where it is heated to a designated temperature; from the preheater the stream is passed to a reactor at a higher designated temperature. The stream is then passed to a second heat exchange wherein the liquids are vaporized at a reduced pressure, and sufficient heat is maintained to pass the stream in the vapor state, entraining the non-volatile components, to the flashing chamber. Upon entry into the flash chamber the vapors and non-volatile residues are impelled against a baffle, and the vapors pass out of the flash chamber, whereby the non-volatile sulfur compounds, gums, and gum-forming constituents are retained in the flash chamber and discharged from the bottom. The vapors, now essentially void of these undesirable components, are then condensed for further processing or for use in blending with other fuels. Many arrangements and combinations of the foregoing and alternate embodiments will be apparent to those skilled in the art.

We have found that we can treat the hydrocarbon stocks according to the process of our invention at comparatively moderate temperatures and pressures. In general, we prefer to use temperatures being between about 150 and 500° F., the contact time at this temperature being between about 0.5 and 40 minutes. The pressures utilized will vary depending upon the particular temperature used and the particular stock which is charged. However, we generally prefer to use pressures of between about 300 and 750 pounds per square inch. The flash vaporization step of our process is preferably conducted at temperatures between about 200 and 500° F. and at atmospheric pressure. It is not intended that we be restricted to the foregoing temperatures and pressures but that they may be varied from these limits. For example, the process of our invention is applicable to temperatures up to and including about 1000° F. and pressures up to and including about 2000 p. s. i. However, substantial variation beyond the limits mentioned is not desirable inasmuch as we have found that as the temperature is increased the quality of the product obtained is decreased; that is, higher temperatures produce additional cracking which will result in increased gum formation and decreased storage stability. Further, the contact time may be extended beyond the limits of 0.5 to 40 minutes; that is, the treatment may be for several hours if desired.

The light metals are intended to include both the alkali and alkaline earth metals; that is, sodium, potassium, rubidium, cesium, lithium, magnesium, calcium, strontium, and barium. Although not required, it is preferred that they be utilized in a dispersed form; that is, the metal is dispersed in an inert medium such as in the hydrocarbon stock, heavy aviation alkylate, toluene, benzene, the xylenes, and other materials which are suitable for this purpose. It is not necessary that the dispersion be pre-prepared. It may be prepared in situ using the hydrocarbon stocks as the dispersing medium. Although the particle size of the dispersed light metal is not critical, we prefer to use particle sizes of substantially below 20 microns in that these sizes are more susceptible to dispersion techniques, and also, clogging of the various stream lines will be diminished. Further, as the particle size decreases, the catalytic action of the metal increases.

A particular light metal which we have found quite suitable for utilization in the process of our invention is sodium. We prefer to use sodium because of its greater availability and susceptibility to dispersion formation. Further, the melting point of sodium (97.5° C.) is particularly advantageous in that lower temperatures can be utilized for maintaining the dispersion properties of the

stream and thus produce more advantageous contact between the particles and the stock being treated. A further consideration in the utilization of sodium is that its density (0.97 grams per cc.) is also favorable in that it approaches the density of the stock being treated, which is normally of the order of 0.70 to 0.95 grams per cc., and thus, uniformity of the stream and dissipation of the particles therein is more advantageously accomplished. By utilizing sodium, lower temperatures can surprisingly be used, and also the cost of sodium as compared with the other metals adds an additional economic feature.

As stated hereinbefore, excessive quantities of the alkali metal have been utilized prior to this invention, and therefore, the processes have had limited scope due to the fact that the residues obtained are reactive and hazardous. For example, when sodium has been used, it is known that sodium on contact with water produces hydrogen which is subject to ignition instigated by the heat of the reaction, a condition untenable in refinery operations. We have now found that catalytic quantities of the light metal can be used which result in a non-reactive residue and therefore eliminate this hazard. In general, we utilize less than the equivalent (that is, stoichiometric) amount of light metal required for complete sulfur removal.

Specifically, when the light metal is an alkali metal, we prefer to use less than two moles of the alkali metal per mole of sulfur contained in the stock. When the light metal is an alkaline earth metal, we prefer to use less than one mole of the alkaline earth metal per mole of sulfur contained in the stock. In utilizing these quantities it has been found that a considerable reduction in gum content and an increase in the stability is obtained concurrently with the reduction in the sulfur content. Further, the product obtained is colorless, which is also a desirable feature of the finished product.

The hydrocarbon stocks or petroleum distillates which we can treat according to the process of our invention are those materials commonly known to the petroleum refinery industry. We have found this process to be particularly adaptable to the so-called "catalytically cracked naphtha" fractions. This fraction is known to contain the major portion of gum-forming constituents and high sulfur content. By treatment of this fraction according to the process of our invention, the gums, gum-forming constituents, and sulfur compounds are removed to a satisfactory percent, and the product obtained is particularly suitable for use in blending with other fractions or for use in internal combustion engines. Other fractions, such as, for example, the gasoline and diesel fractions, or crudes may also be treated according to the process of the present invention. Further, these stocks may also be previously washed with caustic, and in general this is preferred inasmuch as it is known that caustic washing reduces the phenolic content and other undesirable constituents of these stocks.

Typical examples for carrying out the process of our invention are as follows, wherein all parts and percentages are by weight.

Example I

To a stream of a caustic washed hydrocarbon stock, feed rate 0.25 to 0.5 part per minute, having a boiling range of between 200 and 500° F., a dissolved gum content of 54.2 mgs. per 100 mls., copper dish gum content of 427 mgs. per 100 mls., and a sulfur content of 0.44 percent, was added 0.5 weight percent sodium (based on the charge weight) dispersed in heavy alkylate. Thus, 77 percent of the theoretical amount of sodium necessary to react with the sulfur was utilized. The stream was passed through a preheater maintained at a temperature of about 300° F. and then transmitted to a reactor which was at a temperature of about 400° F. The total contact time was about 0.5 minute. The stream was then passed through a flash vaporizer which was maintained at a tem-

perature of about 425° F. The vapors were flashed off in a flash chamber, and the gums, gum-forming constituents, and sulfur compounds remained as residues. These residues showed no activity when mixed with water. The pressure maintained in the system was about 400 pounds per square inch with the exception of the flash vaporizer, which was maintained at atmospheric pressure. The product vapors had a dissolved gum content of 0.9 mgs. per 100 mls., a copper dish gum content of 3.2 mgs. per 100 mls., and the sulfur content was found to be 0.306 percent. The dissolved gum content was determined by ASTM procedure D381-50, and the copper dish gum content was determined by ASTM procedure D910-50T. The sulfur content was determined by ASTM procedure D90-50T.

Other examples of the efficiency of the process of this invention are shown in the following table, wherein the equipment utilized was essentially the same as in the preceding example, but the contact time, reactor temperature, and amount of sodium utilized were varied.

| Percent Na (Based on Charged Stock) | Reaction | | Gum Content | | Sulfur, Percent By Weight |
|-------------------------------------|-------------|-------------|----------------------------|------------------------------|---------------------------|
| | Time, Mins. | Temp., ° F. | Dissolved Gum, mg./100 ml. | Copper Dish Gum, mg./100 ml. | |
| 0.5 | 0.5 | 400 | 0.9 | 3.2 | 0.306 |
| 0.5 | 40 | 400 | 0.0 | 2.4 | 0.287 |
| 0.5 | 0.5 | 200 | 1.6 | 8.0 | 0.307 |
| 0.5 | 40 | 200 | 0.6 | 5.0 | 0.339 |
| 0.25 | 1.0 | 400 | 1.2 | 427 | 0.44 |
| Charge Stock | | | 54.2 | | |

Similarly other alkali or alkaline earth metals can be utilized according to the process of our invention. For example, the hydrocarbon stocks can be treated with potassium either in a dispersed form or in a finely divided state. Likewise, we can use calcium, lithium, rubidium, cesium, magnesium, barium, or strontium for treating the hydrocarbon stocks to reduce gum and sulfur content. In general, we prefer to use the alkali metals or mixtures or alloys thereof.

Similarly, other methods for separating the gums, gum-forming compounds, and sulfur compounds from the stock may be used, as, for example, filtration, centrifugation, fractional distillation, and similar processes; however, we prefer to use the flash vaporization step. It is also understood that the streams may be preheated before entrance into either the reactor or the flash vaporizer; that is, the mixed stream of hydrocarbon stock and light metal may be preheated if desired to a temperature of between about 150 and 400° F. before entry into the reactor. Likewise, the streams leaving the reactor may be reheated to temperatures between about 300 and 500° F., or they may be maintained at the temperature the stream has obtained in the reactor by appropriate insulation of feed lines. Further, our process is equally adaptable to batch or continuous operations.

The process of the present invention will find particular usage in the petroleum refinery industry for the production of gasoline range fuels, diesel fuels, and the like. Similarly, the process of increasing the storage stability, reducing gum formation and sulfur content will be applicable to treatment of crude hydrocarbon stocks. In addition, the novel process of our invention will provide a method of treating hydrocarbon stocks with an active metal in which the hazard of obtaining a reactive residue has been eliminated. These and other uses will become apparent to those skilled in the art.

Having thus described the process of our invention, it is not intended that we be limited except as noted in the appended claims.

We claim:

1. A process for treating an essentially anhydrous hy-

5

drocarbon stock having gum-forming components and a low sulphur content with a finely-divided metal selected from the group consisting of alkali and alkaline earth metals comprising treating said stock with from 0.25 to 0.5% by weight of said metal based upon the weight of said stock for a period of between about 0.5 to 40 minutes at a temperature from 200 to 500° F.

2. The process of claim 1 wherein said finely-divided metal is sodium of particle size less than 20 microns dispersed in a hydrocarbon liquid which is essentially inert to said sodium, said hydrocarbon stock is catalytically cracked naphtha having less than about 0.44% by weight of sulphur and said sodium is employed in amount between 40 to 80% by weight of the stoichiometric amount required to react with the sulphur content of said stock.

3. The process of treating an essentially anhydrous gasoline range hydrocarbon feed stock having gum-forming components and a low sulphur content whereby the gum-forming tendencies are virtually eliminated and appreciable reduction in sulphur contaminant is accomplished comprising blending a preformed dispersion of an alkali metal in a hydrocarbon liquid essentially inert to said metal with said feed stock in proportions providing from 0.25 to 0.5 percent by weight of said metal based on the weight of said stock, heating said blend under continuous flow conditions at a temperature from 200 to 500° F. for a period from 0.5 to 40 minutes while maintaining under supra-atmospheric pressure sufficient to prevent appreciable vaporization of the gasoline range hydrocarbon, then flash vaporizing the gasoline range hydrocarbon at substantially atmospheric pressure and separating the so formed vapors and non-volatile residues.

4. The process of treating an essentially anhydrous gasoline range hydrocarbon feed stock containing gum-forming components and a low sulphur content whereby the gum-forming tendencies are virtually eliminated and

6

appreciable reduction in sulphur contaminant is accomplished, comprising (a) forming a dispersion of sodium metal substantially below about 20 microns in size in a portion of said gasoline range hydrocarbon under conditions at which substantially no reaction occurs, (b) blending said preformed dispersion with the gasoline range hydrocarbon in proportions providing between 40 to 80 percent by weight of the stoichiometric amount of sodium required to completely convert the sulphur to sodium sulphite, (c) heating said blend under continuous flow conditions for a period between 0.5 to 40 minutes at a temperature from 200 to 500° F. while maintaining sufficient pressure to maintain substantially all the feed stock in the liquid phase, (d) flash vaporizing the gasoline range hydrocarbon at substantially atmospheric pressure and separating the so formed vapors and non-volatile residues.

5. The process of claim 4 wherein said gasoline range hydrocarbon is catalytically cracked naphtha treated for a period of 0.5 minute.

References Cited in the file of this patent

UNITED STATES PATENTS

| | | |
|-----------|-------------------|---------------|
| 534,295 | Suckert | Feb. 19, 1895 |
| 1,801,412 | Carlisle | Apr. 21, 1931 |
| 1,864,687 | Fields | June 28, 1932 |
| 1,865,235 | Cross | June 28, 1932 |
| 1,938,670 | Sullivan et al. | Dec. 12, 1933 |
| 1,938,671 | Sullivan et al. | Dec. 12, 1933 |
| 1,938,672 | Ruthruff | Dec. 12, 1933 |
| 1,952,616 | Vose | Mar. 27, 1934 |
| 1,962,698 | Vose | June 12, 1934 |
| 2,058,131 | Carlisle | Oct. 20, 1936 |
| 2,078,468 | Stratford | Apr. 27, 1937 |
| 2,614,967 | Vanderbilt et al. | Oct. 12, 1952 |