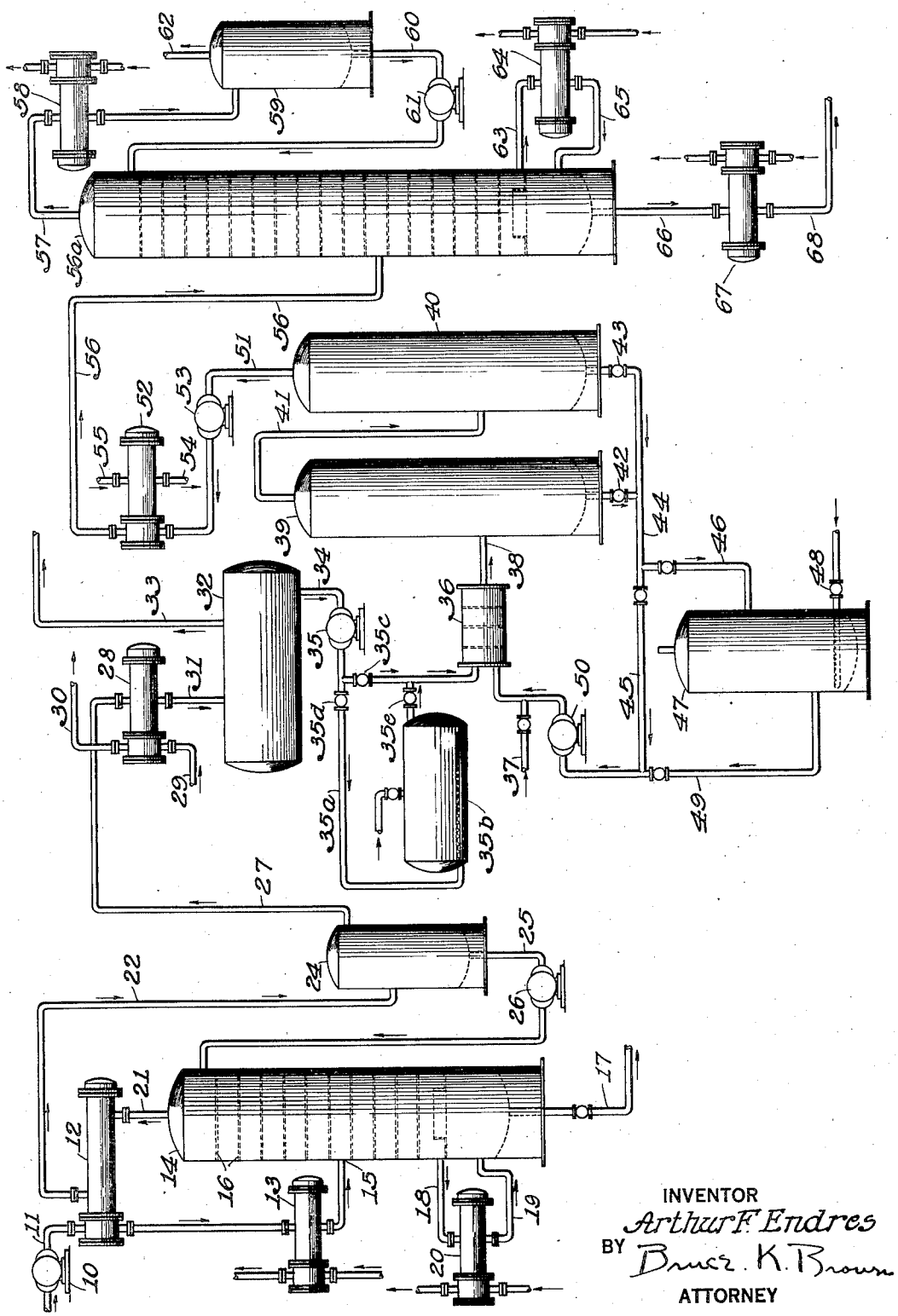
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PROCESS OF SWEETENING LIGHT NAPHTHAS

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## PROCESS OF SWEETENING LIGHT NAPHTHAS

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This invention relates to a process for sweetening hydrocarbon naphthas and it pertains more particularly to a process for sweetening light hydrocarbon naphthas.

In the process for preparing hydrocarbon motor fuels by cracking and/or the distillation of mineral oils, the low boiling distillates or fractions contain the hydrocarbons suitable for use as gasoline and motor fuels. Usually the end boiling point of the fraction is below 450° F. and in most cases the end boiling point falls within the range of 395 and 435° F. This fraction of hydrocarbons will be referred to hereinafter as raw naphtha or raw cracked naphtha. Generally, these raw naphthas comprise the chain, or aliphatic and olefinic hydrocarbons. Also some low boiling cyclic hydrocarbons are usually present.

Attempts have been made to sweeten the entire charge of raw naphtha before it is fractionated, but these processes have proven to be uneconomical and very troublesome.

The object of my invention is to provide a method for sweetening certain fractions of light naphtha after a debutanized fraction has been removed therefrom and before stabilization, in order to overcome the troubles heretofore encountered in sweetening light naphthas.

Before these raw naphthas can be used as a satisfactory motor fuel, they must be cut into fractions of hydrocarbons suitable for use as motor fuels. The first step usually comprises separating substantially all of the hydrocarbons boiling above and including a small amount of the hexanes from the lower boiling hydrocarbons. This fraction of higher boiling hydrocarbons is referred to as the heavy fraction and is substantially free from butanes whence the process is called "debutanizing". This heavy fraction may be called debutanized naphtha. The next step usually comprises removing from the remainder of the raw naphtha a substantial proportion of the highly volatile hydrocarbons such as methane, ethane, propanes, some of the butanes and a small percentage of the pentanes. This highly volatile fraction of hydrocarbon gases is withdrawn from the system and used as a feed for gas burners or it may be used as a source for propane. The remaining portion of the crude naphtha still quite unstable, is referred to hereinafter as crude light naphtha and is composed substantially of propanes, butanes, pentanes, and a small amount of higher molecular weight hydrocarbons including the hexanes. When this crude light naphtha is sweetened, it is called sweetened light naphtha. Some of these crude light naphthas may contain a small percentage of methane and ethane. A typical example of crude light naphtha contains the following approximate percentage of hydrocarbons:

| No. of carbon atoms in the compound | Percentage |
|---|---|
| $C_1$ and $C_2$ | 3 to 7 |
| $C_3$ | 17 to 26 |
| $C_4$ | 29 to 36 |
| $C_5$ | 24 to 32 |
| $C_6$+ | 10 to 15 |

It should be understood that some crude light naphthas do not have the above general composition, for example they may contain substantially no hydrocarbons with one or two carbon atoms and a very small amount of hydrocarbons containing six or more carbon atoms depending on the condition of condensation and fractionation employed at the cracking still and the debutanizer. However, most of these crude light naphthas contain a high percentage of hydrocarbons containing 3, 4 and 5 carbon atoms. In most cases, the amount of propanes, butanes and pentanes present exceed 50% of the crude light naphtha. In other cases the amount of propanes, butanes and pentanes exceed 70 to 85% of the crude light naphtha.

This crude light naphtha fraction contains certain reactive sulfur compounds which make it unsuited for use in motor fuels, and when used in motor fuels or gasoline they impart to it an offensive odor and corrosive properties. In the U. S. Patent 1,797,145 these light hydrocarbons are blended with sweetened heavier hydrocarbons and used as a motor fuel, but unless this stock is treated for the removal of objectionable sulfur compounds so that it will pass the doctor test and other standard tests which indicate whether the fuel is sweet or suitable for satisfactory use, it is not readily marketable. Also attempts have been made to stabilize or fractionate these crude light naphthas and then sweeten the fraction to be used in the preparation of motor fuels by treating with doctor solution, but this has proven to be highly unsatisfactory because large quantities of treating agents are required to sweeten the product. Also excessive amounts of sulfur are required to effect the desired sweetening, thereby producing a corrosive gasoline. Also the color of the treated gasoline is very poor and will deteriorate upon standing. Attempts have been made to sweeten the entire charge of raw naphtha before it is introduced

into the debutanizer, but these processes have proven to be uneconomical and very troublesome.

I have discovered that the troubles encountered in the above processes for sweetening the various types and fractions of naphthas can be solved by sweetening the crude light naphtha before it is subjected to these further steps of stabilization. Further details relating to the preferred methods of performing my process, and the new and useful results obtained will be understood from the description set forth hereinafter when read in connection with the accompanying drawing, which shows a diagrammatic and elevational view of the apparatus used for effecting my process.

The raw naphtha is forced by the pump 10 through the feed line 11 to the heat exchangers 12 and 13 where it is heated, and thence into the debutanizer tower 14 at an intermediate point, as shown at 15. The heat exchanger 12 is heated by the vapors leaving the debutanizer 14 and the exchanger 13 is heated by any suitable media, such as hot tar or steam. The debutanizer is provided with suitable fractionation elements 16, for example, the disc and doughnut types. The high boiling fraction of hydrocarbons, or debutanized fraction, comprising mostly the higher boiling hydrocarbons and a small proportion of hexanes, pentanes and substantially no butanes, is removed from the bottom part of the debutanizer tower by the conduit 17. This fraction will be referred to hereinafter as the heavy fraction. A portion of naphtha in the lower part of the debutanizer tower is reboiled by withdrawing some of the naphthas through the line 18 and passing it through the heat exchanger 20 and then returning it to the bottom of the debutanizer through line 19. This reboiling removes the low boiling hydrocarbons from the heavy fraction before it is withdraw through the conduit 17. Usually, the reboiler maintains a temperature from 380 to 400° F. in the lower part of the debutanizer. The debutanizer tower is preferably operated at superatmospheric pressure. In this example I used a pressure of 95 lbs. per square inch. However, other pressures may be used.

The mixture of light hydrocarbons separated from the raw naphtha, representing the remainder of the raw naphtha or raw cracked naphtha, passes from the upper part of the debutanizer through the conduit 21 and into the heat exchanger 12 where the vapors are cooled and partially condensed. The condensate and vapors are then passed through the conduit 22 to the reflux drum 24. The temperature of the products entering the reflux drum should be between 134 and 150° F., and the pressure in the drum should be maintained at about 90 lbs. per sq. in. The fraction of condensed hydrocarbons that separate in the reflux drum is withdrawn through the conduit 25 and recycled by the pump 26 to the upper trays of the debutanizer and is used as reflux. The low boiling hydrocarbon vapors are removed from the upper part of the reflux drum 24 by the conduit 27 and introduced into the heat exchanger or condenser 28, where they are further cooled. Any suitable cooling media, such as water or brine, may be passed through the exchanger by the lines 29 and 30. The hydrocarbons in the exchanger 28 are cooled to about 82 to 92° F. and then removed through the line 31 to the stabilizer feed tank 32. The uncondensed hydrocarbons entering the stabilizer feed tank are removed through the vapor line 33. These gases consist mostly of methane, ethane, propanes and a small percentage of butanes and pentanes.

The condensed hydrocarbons in the stabilizer feed tank, herein referred to as crude light naphtha and whose composition is set forth hereinabove, are removed through the line 34 and then forced by the pump 35 to the mixer 36, which may be of the orifice or baffle type, and there treated with doctor, or if desired, a portion of the crude stock may be directed through line 35a to caustic wash tank 35b by controlling valve 35c, 35d and 35e. The sweetening agent introduced into the mixer 36 through the valved line 37 may be either a sodium hypochlorite solution, a solution of 2 to 4% of litharge dissolved in a 10 to 30% sodium hydroxide solution, or any other suitable sweetening agent. The crude light naphtha and sweetening agent pass from the mixer 36 through the conduit 38 and into the treater 39 where a considerable portion of the treating agent is allowed to settle. A mixture of the sweetening agent and crude light naphtha passes from the first treater into the second treater 40 through the line 41. The remainder of the sweetening agent is permitted to settle in the second treater.

The crude light naphtha and sweetening agent are permitted to remain in contact sufficient time to provide adequate sweetening. The used sweetening agent is withdrawn from the lower part of the treaters 39 and 40 by the valve draw-off lines 42 and 43 respectively and then recycled through the lines 44 and 45 to the mixer 36 and again used to treat crude light naphtha. If doctor is used to sweeten the crude light naphtha it also may be recycled through the lines 44 and 45 and reused, but when the effectiveness of the doctor has diminished, it may be bypassed through the valved line 46 and introduced into the air treater 47 and blown with air which enters through the line 48. The aerated doctor is then passed through the conduit 49 by the aid of pump 50 and reused to sweeten crude light naphtha. The sweetened light naphtha can now be stabilized and then used in motor fuels without encountering any difficulties. As pointed out hereinbefore, the sweetening must be effected at this stage of the process in order to overcome the loss of treating materials and the elimination of the formation of emulsions and other objectionable features.

The sweetened light naphtha is removed from the treater 40 through the conduit 51 and forced through the heat exchanger or heating means 52 by the pump 53. Any suitable heating media may be used in the heat exchanger 52, for example, hot oils or steam may be passed through the lines 54 and 55. The light naphtha should be heated to a temperature within the range of 205 to 230° F. and, if desired, several heat exchangers or heating elements may be used to heat the light naphtha to this desired temperature. The heated light naphtha is introduced into the stabilizer tower 56a through the line 56 at a point near or a little below the middle of the stabilizer tower. The stabilizer is operated under superatmospheric pressure, usually between 200 and 280 pounds per square inch, in this example I used 250 lbs. pressure per square inch. The pump 53 may be used to maintain the suitable pressure within the stabilizer tower. The light hydrocarbons comprising mostly ethane, propanes and some butanes, are removed from the top part of the stabilizer through conduit 57, cooled by the condenser or heat exchanger 58 to a temperature within the

range of 96 to 115° F. and then introduced into the reflux drum 59. The condensed hydrocarbons are removed from the bottom of the reflux drum 59 by the conduit 60 and recycled by the pump 61 to the top part of the stabilizer for use as reflux. The uncondensed hydrocarbons are removed from the top part of the reflux drum by the conduit 62. These uncondensed hydrocarbons comprise mostly ethane and propanes.

The liquid hydrocarbons in the lower part of the stabilizer are reboiled by withdrawing a portion of the hydrocarbons through the line 63, heating them with a suitable heating means such as the heat exchanger 64, and then returning them to the bottom of the stabilizer through the conduit 65. The liquid hydrocarbons in the bottom of the stabilizer should be maintained at a temperature within the range of 252 to 273° F. The sweetened stabilized light naphtha is withdrawn from the bottom of the stabilizer through the conduit 66, passed through the condenser or heat exchanger 67 and then passed to storage through the line 68. This stabilized light naphtha is substantially free from methane, ethane and propane, and it is comprised mostly of butanes and pentanes. A typical stabilized light naphtha will contain the following general composition:

| No. of carbon atoms in the hydrocarbon | Percentage |
|---|---|
| $C_3$ | Less than 1 |
| $C_4$ | 38 to 55 |
| $C_5$ | 28 to 50 |
| $C_6+$ | Approximately 20. |

It should be understood that some stabilized light naphthas will vary to some extent from the above general composition. In fact, the change in composition may be effected by altering the temperatures and pressures used in the respective steps of the process.

As pointed out hereinabove, attempts have been made to use crude light naphtha in motor fuel by sweetening after stabilization but such attempts have proven to be highly unsatisfactory. The doctor forms emulsions or suspensions in the stabilized light naphtha and also develops undesirable colorations and large quantities of doctor are required for sweetening. By my process of sweetening the crude light naphtha before it is stabilized, these troubles are not encountered and, after the light naphtha has been stabilized, it is ready to be blended with heavier naphthas and used as motor fuels. I have found that a very satisfactory motor fuel, free from tendencies to develop sourness and colorations, can be prepared by blending the stabilized light naphtha with the heavy fraction of naphtha removed from the debutanizer tower 14 by the line 17. However, the heavy fraction should be sweetened somewhat before it is blended with the stabilized light naphthas. Preferably the heavy fraction should be treated with sulfuric acid, then treated with doctor and washed before blending.

I will describe my process with reference to an actual operation. About 38,240 barrels per day of raw naphtha are passed through the heat exchangers 12 and 13 and introduced into debutanizer 14. The temperature at the bottom of the debutanizer is maintained at about 380° F. and about 200° F. at the top. A pressure of about 95 pounds per square inch is also maintained in the debutanizer. About 29,900 barrels of the heavy fraction are removed from the bottom of the debutanizer 14. The composition of the heavy fraction is substantially 0.4% of $C_3$, 2.4% of $C_4$, 3.5% of $C_5$ and 93.7% of $C_6$ and heavier hydrocarbons.

The overhead from the debutanizer is passed into the reflux drum 24 and then to the stabilizer feed tank 32. The pressure in the reflux drum and feed tank is maintained at 90 pounds per square inch, and the temperature of the stock in the feed tank is maintained at about 84° F. The uncondensed hydrocarbons released from the feed tank 32 through the line 33 have the general composition:

| | Per cent |
|---|---|
| $C_1$ | 8 to 9 |
| $C_2$ | 32 to 36 |
| $C_3$ | 35 to 42 |
| $C_4$ | 10 to 18 |
| $C_5$ | 1 to 5 |

The amount of this uncondensed fraction is about six million cubic feet per day.

The crude light naphtha in the stabilizer feed tank has the following general composition.

| | Per cent |
|---|---|
| $C_1$ | Less than 1 |
| $C_2$ | 3 to 6 |
| $C_3$ | 18 to 26 |
| $C_4$ | 28 to 38 |
| $C_5$ | 24 to 30 |
| $C_6+$ | 10 to 14 |

About 5,320 barrels of this crude light naphtha per day pass from the stabilizer feed tank to the mixer 36 and treaters 39 and 40. The crude light naphtha is sweetened by any suitable method as herein described. This sweetened crude light naphtha is called sweetened light naphtha. This sweetened light naphtha is then ready to be stabilized.

The sweetened light naphtha is then reheated by the exchanger 52 to about 218° F. and passed into the stabilizer tower 56*a* which is maintained under a pressure of about 250 pounds per square inch. The gas removed from the reflux drum 59, by the conduit 62, amounts to about 3,040,000 cu. ft. per day and comprises mostly ethane, propane and a small percent of butane.

The finished light naphtha removed from the bottom of the stabilizer tower amounts to about 3,720 barrels per day and has the following general composition.

| | Per cent |
|---|---|
| $C_3$ | Less than 0.2 |
| $C_4$ | 44 to 46 |
| $C_5$ | 32 to 34 |
| $C_6+$ | 19 to 22 |

In view of the foregoing example of operation, it is apparent that it would be very economical to sweeten only the light naphtha removed from the bottom of the stabilizer tower 56*a*, but when attempts are made to sweeten this fraction, the treating agents form troublesome emulsions and suspensions and large quantities of the treating agent are required to effect satisfactory sweetening. However, by sweetening the light naphtha before it is stabilized, the troublesome emulsions are not formed and a small amount of the treating agent is very effective for sweetening the light naphtha.

My invention is not limited to the herein specific embodiment except insofar as it is limited by the appended claims.

I claim:

1. The method of preparing sweetened light naphthas, which comprises debutanizing raw

naphtha and separating the debutanized naphtha from the remainder of the raw naphtha, removing a substantial proportion of the normally gaseous hydrocarbons from the remainder of said raw naphtha, sweetening the resulting portion of said raw naphtha with an alkaline solution of sodium plumbite and then stabilizing this sweetened naphtha.

2. The method of preparing sweetened light naphtha, which comprises debutanizing raw cracked naphtha and separating the debutanized naphtha from the remainder of the raw cracked naphtha, removing a substantial proportion of the normally gaseous hydrocarbons from the remainder of said raw cracked naphtha, sweetening the resulting portion of said raw cracked naphtha and then stabilizing this sweetened naphtha.

3. The method of preparing sweetened light naphtha, which comprises debutanizing raw cracked naphtha and separating the debutanized naphtha from the remainder of the raw cracked naphtha, removing a substantial proportion of the normally gaseous hydrocarbons from the remainder of said raw cracked naphtha, sweetening the resulting portion of said raw cracked naphtha, then stabilizing this sweetened naphtha and recovering a fraction of the sweetened naphtha containing more than 50% of butanes and pentanes.

4. The process of preparing a sweetened naphtha comprising at least 60% of butanes and pentanes, which comprises debutanizing raw cracked naphtha and removing the debutanized naphtha from the remainder of the cracked raw naphtha, removing a substantial proportion of the normally gaseous hydrocarbon from the remainder of said raw cracked naphtha, sweetening the resulting raw cracked naphtha with doctor solution, and then stabilizing this sweetened naphtha.

5. The process of preparing a sweetened naphtha comprising at least 60% of butanes and pentanes which comprises, passing raw cracked naphtha into a debutanizer and separating the naphtha into a high boiling fraction of hydrocarbons substantially free from butanes and a low boiling fraction of hydrocarbon, removing substantially all of the methane, ethane and propanes from the low boiling fraction of hydrocarbons, sweetening the remainder of said low boiling fraction of hydrocarbons with an alkaline solution of sodium plumbite, stabilizing this sweetened fraction of hydrocarbons and separating therefrom a sweetened naphtha comprising at least 60% of butanes and pentanes.

6. In the process of preparing light naphthas comprising mostly butanes and pentanes from crude light naphtha, the step of sweetening the crude light naphtha with an alkaline solution of sodium plumbite before said crude light naphtha is stabilized.

7. In the process for preparing sweetened light naphtha containing at least 50% of butanes and pentanes from crude light naphtha, the step of sweetening the crude light naphtha with doctor before it is stabilized but after a debutanized fraction of hydrocarbons has been removed from the crude light naphtha.

8. In the process of preparing sweetened light naphthas containing at least 38% of butanes and at least 28% of pentanes from crude light naphtha, the step of sweetening the crude light naphtha with doctor solution before it is stabilized but after a debutanized fraction of hydrocarbons has been removed from the crude light naphtha

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