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PROCESS OF PRODUCING A COLORLESS DOCTOR SWEET GASOLINE

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9 Claims. (Cl. 196—32)

This invention relates to sweetening of petroleum products, especially gasolines, naphthas and kerosenes which have been refined by treatment with adsorbents rather than by chemical reagents.

The invention is particularly applicable to cracked gasoline obtained from naphthenic base crudes or from a charging stock composed of a mixture of naphthenic and paraffinic base crudes which has been purified by passage in vapor phase through fuller's earth in accordance with the well-known Gray vapor phase process. Such purification or any similar treatment with adsorbents yields a gasoline or other hydrocarbon product having the requisite gum content and color, but unless the fuller's earth or other adsorbent is treated or mixed with a sweetening agent, the treated hydrocarbon product will ordinarily be sour to the so-called doctor test. Such condition is usually undesirable and the refined hydrocarbon product is treated further in order to make it sweet. The usual methods of sweetening involve the use of an alkaline solution, such as caustic soda, sodium plumbite, sodium or calcium hypochlorite and the like. When such a sweetening step is applied to gasoline from naphthenic base crudes and especially to cracked gasoline from such crudes which has been refined by treatment with adsorbents, the gasoline so sweetened darkens in color during the sweetening operation. This characteristic is more particularly noticeable in products from Gulf Coast crudes (such as Refugio, Mirando, Babers Hill, etc.) and California oils which are commonly known as naphthenic base crudes. The naphthenic base crudes have the above described undesirable characteristic even if they are present only as a constituent of the charging stock.

An example is the behavior of cracked gasoline obtained by cracking Babers Hill crude and refined by passage in vapor phase through fuller's earth in Gray towers. The gasoline, after passing through the fuller's earth and being condensed and stabilized was of 30+ Saybolt color. This color was maintained throughout the treatment of more than 3,000 barrels of gasoline per ton of fuller's earth in the tower. However, the condensed product was sour to the doctor test. When treated with sodium plumbite or other alkaline sweetening agent, the gasoline treated while the fuller's earth was fresh, that is before 250 barrels of gasoline per ton of fuller's earth had been treated, remained 30+ color, but after that time the sweetened product gradually darkened. Such darkening is undesirable since gasoline is often stored for long periods before use and has a gradual tendency to darken in color on storage. The color depreciation was found to be about as rapid in the samples darkened by sweetening as in those not so darkened so that at the end of a given storage period, gasoline which had been darkened during sweetening was from 2 to 5 Saybolt color darker than gasoline which had not darkened during sweetening. As a result, the storage period of gasoline darkened during sweetening was reduced by several months, since there is a limit of approximately 23 Saybolt color below which a gasoline is considered unsatisfactory as not being water white.

An object of this invention is a process for obtaining a sweet petroleum product from and of equal color with a sour petroleum product resulting from cracking naphthenic base crudes followed by vapor phase treatment with adsorbents.

According to this invention, the darkening in color above described is prevented by thorough washing of the gasoline or naphtha with water before contacting it with an alkaline agent. By thus water-washing the gasoline or naphtha, the color in the sweet gasoline or naphtha is maintained equal to the color in the sour gasoline or naphtha. The washing operation is effected by thoroughly commingling the petroleum product with from 10% to 100% of its volume of water, the quantity of water required depending on the age of the adsorbent, conditions of cracking, etc.

Under certain circumstances, it may be desirable to remove low boiling hydrocarbons and hydrogen sulphide from the petroleum product prior to treatment with alkaline solution for sweetening. In such event, the petroleum product, after treatment with an adsorbent, is condensed and then heat treated to vaporize the low boiling constituents and drive off the hydrogen sulphide. However, such removal of low boiling compounds and hydrogen sulphide is not an essential step as the process is equally efficacious for preventing darkening of the sweetened product whether or not such product contains low boiling hydrocarbons or hydrogen sulphide.

Water-washing has previously been suggested as a step in the chemical refining of petroleum products, but the function of such step has, however, been the removal of chemical reaction products or in some cases, the removal of hydrogen sulphide. In the present invention, the step

of water-washing is not concerned with the removal of reaction products from chemical treatment nor with the removal of hydrogen sulphide.

This is evident from the fact that the darkening above referred to is also experienced with gasoline which has been stabilized, that is heat-treated after condensation for the removal of low boiling hydrocarbons during which treatment the hydrogen sulphide contained therein was also removed. Such stabilized gasoline requires water-washing prior to sweetening in order to prevent color depreciation.

No attempt is made to explain the reaction involved in the washing step. It is apparent, however, that light products such as gasoline, kerosene, naphtha and the like from naphthenic base crudes, especially such products as are obtained by a cracking reaction, contain, as impurities, substances of unknown composition which are removed by adsorbents only when the latter are fresh and which are allowed to pass by the adsorbents over a considerable period during which the adsorbents are effective to purify the gasoline otherwise sufficiently for use. These substances are deleterious in that they cause darkening of the gasoline when treated with alkaline treating agents but are soluble in or otherwise removable by water.

I claim:

1. In the sweetening of cracked gasoline obtained from a charging stock comprising naphthenic base oil and purified by treatment with an adsorbent, the step of preventing such gasoline from darkening in color during treatment with an alkaline sweetening agent which comprises washing it with water before contacting it with said alkaline solution.

2. The process of obtaining purified cracked gasoline which comprises cracking charging stock comprising naphthenic base oil, purifying cracked gasoline thus obtained by treatment with an adsorbent, washing the purified gasoline with water and sweetening the washed gasoline with an alkaline sweetening agent.

3. The process of obtaining purified cracked gasoline which comprises obtaining cracked gasoline from a charging stock comprising naphthenic base oil, purifying the cracked gasoline by contacting the same in vapor phase with an adsorbent, sweetening the purified gasoline by treatment with an alkaline sweetening agent, and preventing darkening in color of the gasoline by washing the same with water prior to the sweetening treatment.

4. The process of producing a colorless doctor sweet gasoline from a charging stock comprising naphthenic base oil, which comprises cracking said oil to obtain gasoline, refining the gasoline with an adsorbent, treating the purified gasoline with an alkaline sweetening agent to sweeten the same and preventing darkening in color during the alkaline treatment by washing the gasoline with from 10 to 100% its volume of water previous to the alkaline treatment.

5. The process of producing a colorless doctor sweet gasoline from a charging stock comprising naphthenic base oil which comprises cracking said oil to obtain gasoline, refining the gasoline with an adsorbent, heat treating the refined gasoline to remove low boiling hydrocarbons and hydrogen sulphide, treating the resulting stabilized gasoline with an alkaline sweetening agent to sweeten the same and preventing darkening in color during said alkaline treatment by water washing the gasoline previous to the alkaline treatment.

6. The process of producing a colorless doctor sweet gasoline from a charging stock comprising naphthenic base oil which comprises cracking said oil to obtain the gasoline, refining the gasoline with an adsorbent, heat treating the refined gasoline to remove low boiling hydrocarbons and hydrogen sulphide, treating the resulting stabilized gasoline with an alkaline sweetening agent to sweeten the same and preventing darkening in color during said alkaline treatment by washing the gasoline with from 10 to 100% its volume of water previous to the alkaline treatment.

7. The process of producing a colorless doctor sweet gasoline from relatively high boiling hydrocarbon oils which comprises cracking the same to obtain gasoline, refining the gasoline with an adsorbent, sweetening the purified gasoline by contact with an alkaline sweetening agent and prior to the sweetening treatment, removing from the purified gasoline bodies which on contact with an alkaline medium impart color to the gasoline by washing said gasoline with water.

8. The process of obtaining purified cracked gasoline which comprises cracking relatively high boiling hydrocarbon oils, treating the resultant distillate with an adsorbent, sweetening the purified distillate by contact with an alkaline solution and prior to the sweetening treatment, washing the distillate with water to remove therefrom bodies which on contact with an alkaline medium impart color to the distillate.

9. The process of producing a colorless doctor sweet gasoline from relatively high boiling hydrocarbon oils which comprises cracking the same, treating the resultant distillate with an adsorbent, sweetening the purified distillate by contacting the same with an alkaline solution sweetening agent and prior to the sweetening treatment, washing said distillate with water to remove therefrom bodies which on contact with an alkaline medium impart color to the distillate.

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CERTIFICATE OF CORRECTION.

Patent No. 2,013,083. September 3, 1935.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, second column, line 44, claim 8, for "solution" read sweetening agent; and line 54, claim 9, strike out the word "solution"; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 8th day of October, A. D. 1935.

(Seal)

Leslie Frazer
Acting Commissioner of Patents.