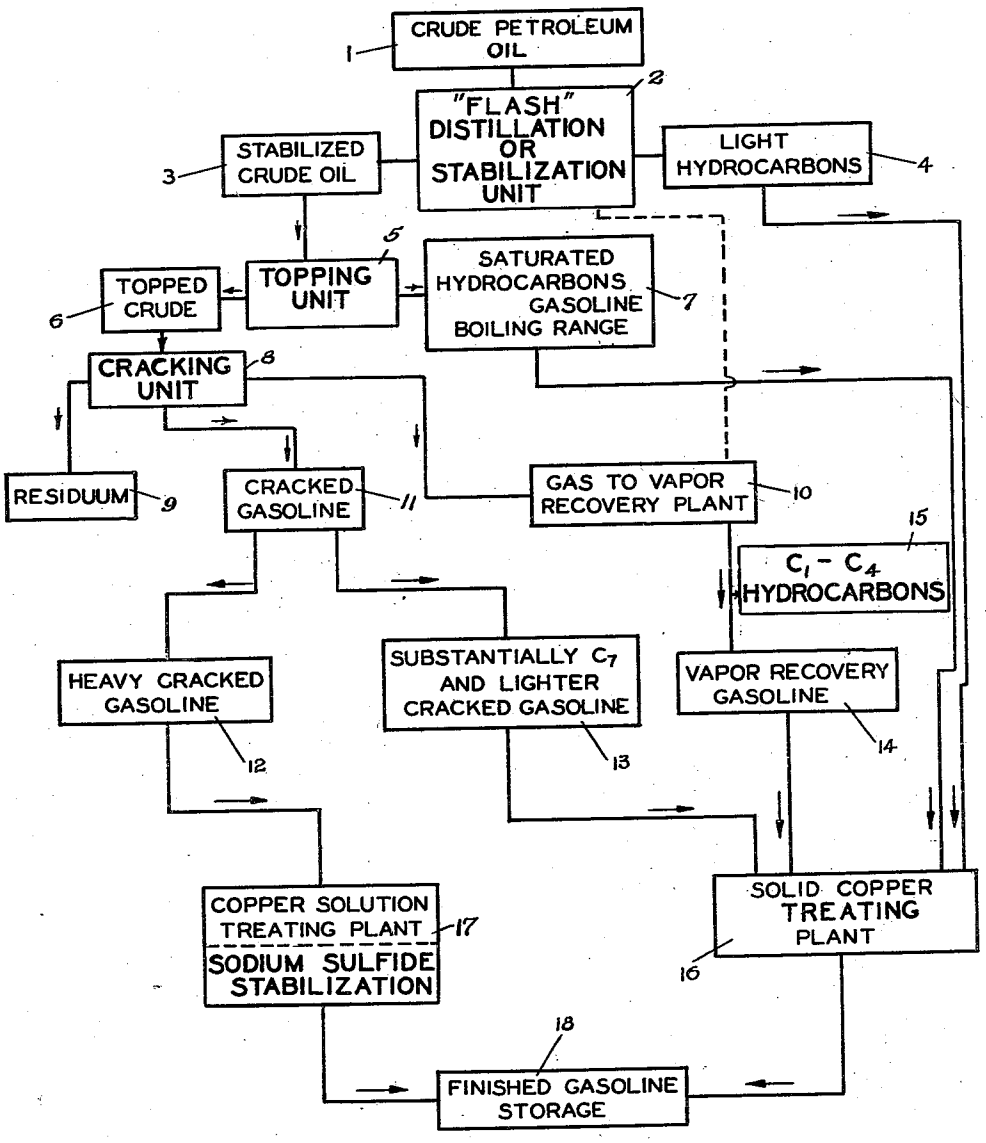
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PROCESS FOR TREATING OILS

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PROCESS FOR TREATING OILS

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This invention relates to the refining treatment of mercaptan-containing light hydrocarbon oils secured from crude petroleum and its associated products. More specifically it relates to sweetening of the mercaptan-containing light hydrocarbon oils with copper reagents.

One of the principal objects of this invention is to provide a process for refining petroleum oils whereby the mercaptan bearing oils may be sweetened in a far more efficient and inexpensive manner than heretofore practiced.

Another object of this invention is to provide a process whereby the mercaptans in such unrefined oils may be converted to the disulfide form without production and consequent introduction into the oil of various undesirable compounds formed as by-products in nearly all of the sweetening methods used heretofore.

A further object is to avoid instability of the product by selective treatment, under carefully controlled conditions, of stocks susceptible to gum and color formation, and to simplify treatment for stocks which are inherently stable, thus contributing to ease and economy of operation.

Unrefined petroleum products contain mercaptans, commonly called "sour" elements, which give the oil undesirable odor, and render it corrosive and unstable. Until recently these compounds have been customarily removed or altered, by the so-called "doctor" process, a laborious, cumbersome and very uneconomical chemical treatment with alkaline plumbite and sulfur. In some instances, e. g., natural gasoline, the sweetening action has been accomplished through the use of alkaline hypochlorite solutions, but this method, too, has not proved satisfactory in most cases due to the introduction into the oil of undesirable constituents as bad as those originally present.

Recently, however, sweetening of petroleum products has been accomplished with much improved results through the use of the so-called "Copper sweetening" methods. These methods have been referred to in the literature as the "Solution process" and the "Solid process" respectively. The Solution process employs the copper solutions described in U. S. Patent 1,964,219 issued to Schulze and Frey, June 26, 1934. The copper solutions are maintained active and the oxidation potential controlled as shown in U. S. Patent 2,058,720 to Reid and Schulze, dated October 27, 1936. Following treatment with the copper solutions the petroleum oils are treated with alkaline sulfide solutions as shown in U. S. Patent 1,980,555 to Schulze and Frey, dated November 13, 1934. This latter treatment is commonly referred to as the stabilizing step. Oils which are treated with copper solutions contain traces of organic copper compounds which cause instability of the treated gasoline with respect to color and gum formation; hence the traces of copper compounds must be removed by the stabilizing solution.

The so-called "Solid" copper sweetening process, as described in a patent by Buell, Patent No. 2,094,485, dated September 28, 1937, employs moist solid copper reagents for sweetening. These reagents are prepared by impregnating adsorbent carriers such as fuller's earth with aqueous solutions containing cupric and chloride ions. The petroleum products are sweetened by filtration through these reagents. With proper control, the treated product does not contain even traces of copper compounds and hence no stabilizing treatment is necessary. The process is limited, however, to those fractions of petroleum products which are relatively stable and do not readily form gum and colored compounds.

I have found that all of the light products from crude petroleum fluid may be copper sweetened in a highly satisfactory and economical manner by selective treatment, under carefully controlled conditions, of stocks susceptible to gum and color formation, and to simplify treatment for stocks which are inherently stable.

I have discovered that petroleum fractions which are substantially free of unsaturated hydrocarbons may be treated under controlled conditions by means of the Solid copper reagent without depreciation in color or gum stability of these products or of blends of these products with other less stable fractions. These sweetened fractions which are composed predominantly of paraffin and naphthenic hydrocarbons are free of copper compounds and do not require a stabilizing treatment.

I have discovered furthermore that those petroleum fractions which contain substantial quantities of unsaturated hydrocarbons containing seven or less carbon atoms may likewise be treated satisfactorily with the solid reagent with results similar to those obtained on fractions composed of saturated hydrocarbons. However, those fractions containing appreciable quantities of unsaturated hydrocarbons with eight or more carbon atoms must be treated by the solution method since such fractions are relatively unstable and tend to become discolored and to form gum during the treatment with the solid reagent. Likewise, these fractions containing the higher

unsaturated hydrocarbons contain traces of copper which accelerate color and gum formation. Thus, the solution method must be used to sweeten these fractions since there is no deterioration in the product during the "Solution" treatment and the final stabilizing step insures the removal of traces of copper so that no deterioration occurs during storage.

My invention may be best understood by referring to the drawing, wherein there is shown diagrammatically one embodiment of my invention. Crude petroleum oil 1 is separated in a "flashing" or stabilization unit 2 into light hydrocarbons 4 and stabilized crude oil 3. The light hydrocarbons 4 after removal of hydrogen sulfide, if present, may be sent directly to the "Solid copper reagent" treating plant 16 for sweetening, where they may be treated alone or in a blend with other fractions. The stabilized crude oil 3 is subjected to the usual topping operation in a topping unit 5 for the separation of gasoline constituents 7 from the higher boiling hydrocarbons termed herein topped crude 6. The fraction containing the saturated hydrocarbons boiling substantially within the gasoline range may be sent, after removal of hydrogen sulfide, to the "Solid copper reagent" treating plant 16 for sweetening.

During the topping operation side streams other than that of gasoline may be taken off the bubble tower, e. g., kerosene or light naphtha fractions may be obtained simultaneous with the gasoline fraction 7. In such event these fractions may be treated in a manner similar to the gasoline fraction.

The topped crude 6 is then subjected to cracking in a cracking unit 8 in the usual manner and separated into residuum 9, cracked gasoline 11 and light hydrocarbon gases 10. The gas 10 is sent to the vapor recovery plant where the fraction termed "vapor recovery" gasoline 14 is obtained. This vapor recovery gasoline, free of hydrogen sulfide, is sweetened in the "Solid copper reagent" treating plant 16. The non-condensible and normally gaseous hydrocarbons from the flashing and cracking operations may be brought together and segregated 15 as an adjunct of the vapor recovery operation.

The cracked gasoline 11 is separated into a fraction comprising the higher boiling hydrocarbons termed herein "Heavy cracked gasoline" 12 and the lower boiling hydrocarbons comprising substantially those hydrocarbons containing seven and less carbon atoms 13. This separation of the cracked gasoline into the light and heavy fractions may be made, if desired, at the same time that the gasoline is separated from the residuum and light gases.

The cracked gasoline fraction 13 comprising substantially those hydrocarbons containing seven and less carbon atoms may be sent to the "Solid copper reagent" treating plant 16 after removal of any hydrogen sulfide which may be present. The "Heavy cracked" gasoline fraction, however, must be sent to the Copper solution treating plant 17 where it is contacted with copper solution and stabilized with alkaline sulfide solution.

The various gasoline fractions, after sweetening in either the "Solid copper reagent" treating plant 16 or the Copper solution treating plant 17, are sent to finished gasoline storage 18 where they may be blended into motor fuels of the proper specifications.

By operating in the manner indicated above, it has been possible to obtain extremely satisfactory finished gasolines comprising both saturated and unsaturated hydrocarbons of both low boiling and high boiling range. The gasoline is completely sweet, good color, free of traces of copper compounds, and exceptionally stable with respect to color and gum formation during storage. On the other hand when an attempt was made to sweeten all of the fractions either as a blend, or as individual streams blended after sweetening, for example by the Solid reagent method the gasoline became colored during treatment and was extremely unstable in storage, forming large quantities of gum and colored compounds within a short storage interval. Likewise, when all of the fractions were treated by the Solution method it was found that the plant required for treatment and for stabilization was necessarily large and expensive. Also, the stabilization step had to be performed on all the fractions or the finished blends deteriorated rapidly. Thus, in order to employ the Solution method satisfactorily to all the gasoline fractions it would have been necessary to have ample stabilizing equipment for all the gasoline and also it would have meant increased expenditure for the treating chemicals. Therefore, when operating in the manner described in this invention greatly improved results are obtained.

There are many modifications of this invention which will be apparent to those skilled in the art and the limitations are defined solely by the scope of the appended claims.

I claim:

1. In a process for producing a sweet motor fuel from crude petroleum oil by steps which comprise subjecting said crude petroleum oil to a medium-temperature flashing operation to produce stabilized crude oil and a low-boiling straight run gasoline, subjecting said stabilized crude oil to a distillation operation to produce straight run gasoline and topped crude, subjecting said topped crude to a cracking operation to produce a gaseous fraction containing some gasoline hydrocarbons and a fraction comprising cracked gasoline, processing said gaseous fraction to recover the gasoline content, and separating said cracked gasoline into a low-boiling fraction containing substantially seven and less carbon atoms per molecule and a higher-boiling fraction containing more than seven carbon atoms per molecule, the improvement comprising sweetening the cracked gasoline fraction containing more than seven carbon atoms per molecule by treatment with a cupric chloride solution of controlled chloride ion content followed by sodium sulfide stabilization, and sweetening the remaining said gasoline fractions by passage along with dissolved air over a solid adsorbent reagent impregnated with a solution of cupric chloride prior to blending at least a portion of the gasoline fractions to provide a sweet motor fuel.

2. In a process for producing a sweet motor fuel from crude petroleum oil by steps comprising subjecting said oil to a medium-temperature flashing operation to produce stabilized crude oil and a low-boiling straight run gasoline, subjecting said stabilized crude oil to a distillation operation to produce straight run gasoline and topped crude, subjecting said topped crude to a cracking operation to produce straight run gasoline and topped crude, subjecting said topped crude to a cracking operation to produce a gaseous fraction containing some cracked gasoline hydro-

carbons which are recovered by suitable means and a fraction comprising cracked gasoline, the improvement comprising fractionating said total cracked gasoline and vapor recovery gasoline into a portion containing substantially seven and less carbon atoms per molecule and a portion containing substantially more than seven carbon atoms per molecule, sweetening the last-named portion by treatment with a solution of cupric chloride of controlled chloride ion content followed by sodium sulfide stabilization and sweetening the other said gasoline fractions by passage along with dissolved air over a solid adsorbent reagent impregnated with a solution of cupric chloride prior to blending at least a portion of the gasoline fractions to produce a sweet motor fuel.

3. In the process of producing motor fuel from crude petroleum oil, in which saturated hydrocarbons boiling within the gasoline range are separated from the petroleum oil and at least a portion of the remaining petroleum oil is cracked to produce hydrocarbons boiling within the gasoline range and containing quantities of unsaturated hydrocarbons, the method of sweetening said hydrocarbons boiling in the gasoline range which comprises separating the cracked hydrocarbons boiling in the gasoline range into a fraction containing seven and less carbon atoms per molecule and a fraction containing seven and more carbon atoms per molecule, sweetening said saturated hydrocarbons boiling in the gasoline range and said unsaturated hydrocarbon fraction containing seven and less carbon atoms per molecule by treatment with a solid adsorbent reagent impregnated with a solution of cupric chloride and sweetening said unsaturated hydrocarbon fraction containing seven and more carbon atoms per molecule by treatment with a solution of cupric chloride followed by stabilization of the sweetened fraction with respect to minute amounts of copper remaining in the sweetened oil, and blending the sweetened fractions into motor fuel.

4. In the process of producing motor fuel from crude petroleum oil, in which low boiling saturated hydrocarbons are separated from the petroleum oil and at least a portion of the remaining petroleum oil is cracked to produce low boiling hydrocarbons containing quantities of unsaturated hydrocarbons, the method of sweetening said low boiling hydrocarbons which comprises separating the cracked hydrocarbons into a fraction containing seven and less carbon atoms per molecule and a fraction containing seven and more carbon atoms per molecule, sweetening said low boiling saturated hydrocarbons and said unsaturated hydrocarbon fraction containing seven and less carbon atoms per molecule by treatment with a solid adsorbent reagent impregnated with a solution of cupric chloride and sweetening said unsaturated hydrocarbon fraction containing seven and more carbon atoms per molecule by treatment with a solution of cupric chloride followed by stabilization of the sweetened fraction with respect to minute amounts of copper remaining in the sweetened oil, and blending the sweetened fractions into motor fuel.

5. In the process of producing gasoline, kerosene and naphtha from crude petroleum oil in which a saturated hydrocarbon fraction boiling in the gasoline range, kerosene and naphtha are separated from petroleum oil and at least a portion of the remaining petroleum oil is cracked to produce hydrocarbons boiling within the gasoline range and containing quantities of unsaturated hydrocarbons, the method of sweetening said fractions which comprises separating the cracked hydrocarbon fraction boiling within the gasoline range into a fraction containing seven and less carbon atoms per molecule and a fraction containing seven and more carbon atoms per molecule, sweetening said saturated hydrocarbons boiling in the gasoline range, kerosene and naphtha and said unsaturated fraction containing seven and less carbon atoms per molecule by treatment with a solid adsorbent reagent impregnated with a solution of cupric chloride and sweetening said unsaturated hydrocarbon fraction containing seven and more carbon atoms per molecule by treatment with a solution of cupric chloride followed by stabilization of the sweet fraction with respect to minute amounts of copper remaining in the sweetened oil.

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