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METHOD OF SWEETENING PETROLEUM DISTILLATES

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1 Claim. (Cl. 196—30)

This invention relates to the art of petroleum refining, and pertains particularly to the "sweetening" of co-called "sour" petroleum distillates.

5 The process of the present invention involves the conversion of corrosive sulphur compounds, mainly mercaptan substances, into soluble and insoluble metallic mercaptide substances and the subsequent removal of such metallic mercaptides from the distillate in the production of a stable "Doctor-sweet" product. The present invention is directed primarily to the step of removing dissolved metallic mercaptides from the distillate through a novel step involving the use of active reagents which have not hitherto been recognized as having the property of removing such compounds, but in its broad aspect the invention also contemplates the practice of the above-mentioned step in connection with the step of converting corrosive mercaptan substances in a distillate into the aforesaid soluble and insoluble metallic mercaptides by treatment of such a distillate with a suitable metallic reagent.

20 One of the important objects of the invention is to provide for the substantially complete removal of dissolved metallic mercaptide substances from a petroleum distillate, in the formation of a stable "Doctor-sweet" product.

25 A further object of the invention is to provide a process for sweetening a petroleum distillate which may be practiced at a low cost and which is dependable from the standpoint of consistency in performance.

30 A further object of the invention is to provide a sweetening process which may be carried out as a liquid phase procedure at ordinary temperature and pressure.

35 A further object of the invention is to provide a process for the removal of dissolved metallic mercaptides from a distillate which has been subjected to a chemical treatment to cause conversion of the contained mercaptan substances into metallic mercaptides.

40 A further object of the invention is to provide a process of the character described which involves a two-stage treatment of a sour petroleum distillate, in which the first stage results in a complete chemical conversion of mercaptan substances into metallic mercaptides which are in part soluble in the distillate, and in which the second stage effects a complete removal from such distillate of the residual metallic mercaptides resulting from the first stage, whereby such distillate is rendered stable to the "Doctor" test.

55 The method of the present invention comprises,

essentially, the step of contacting a distillate which has been subjected to a chemical treatment for the conversion of contained mercaptan substances into soluble and insoluble metallic mercaptides, with a solid adsorptive material which possesses a strong affinity for dissolved metallic mercaptides, to effect a removal of such mercaptides in the production of a permanently stable "Doctor-sweet" distillate.

5 Numerous processes have been heretofore suggested for the conversion of mercaptan substances in a sour distillate into relatively insoluble metallic mercaptides which may be separated from the distillate by decantation, filtration, or the like, but it has been found that some of the metallic mercaptides produced by such chemical conversion treatments, with the use of commercially economic reagents, remain dissolved in the distillate, and it has also been found that these residual soluble mercaptides are unstable and may revert to corrosive sulphur compounds on standing or on redistillation.

10 Under some circumstances treatment of a sour petroleum distillate with caustic sodium plumbite will result in a conversion of mercaptan substances into metallic mercaptides which are relatively insoluble, but in view of the fact that the so-called Doctor treatment ordinarily relies upon the presence of elemental sulphur to react with dissolved mercaptides in the formation of non-corrosive disulphides and lead sulphide, the total sulphur content of such distillate is not changed in any great degree unless the elemental sulphur was present in the distillate as dissolved sulphur before the contact with the sodium plumbite. In the case of the lower mercaptans such as ethyl mercaptan, the lead alkyl mercaptide formed with the caustic sodium plumbite is relatively insoluble and is readily separable from the distillate by filtration or the like. However, very few sour distillates will contain only the lower mercaptans, and the higher lead mercaptides are considerably more soluble and treatment with sulphur is required for alteration thereof into non-corrosive disulphides. Other processes have been suggested for the conversion of mercaptan substances in a sour distillate into relatively insoluble metallic mercaptides, but the only reagents which are effective in formation of sufficiently insoluble mercaptides from an extended range of mercaptans are silver compounds such as silver nitrate, and the high cost of silver compounds prevents the economic commercial practice of methods of this type.

According to the present invention, a distillate containing dissolved metallic mercaptides resulting from a chemical conversion treatment is subjected to contact with an advantageous type of reagent which effects a removal of such compounds from the distillate to a very complete degree. Any undissolved mercaptides produced by the chemical conversion treatment are readily separated by filtration or the like as in the prior practice, and the dissolved metallic mercaptides are separated from the distillate by a process which is believed to be based primarily upon "adsorption" phenomena, the hereinafter designated active materials employed in this step being found to all possess adsorption characteristics with respect to such metallic mercaptides. While the present process is adaptable to the removal of substantially all known soluble metallic mercaptides, it is found to be particularly useful in the removal of cadmium and mercury mercaptides, due to the fact that cadmium and mercury compounds will react with substantially all of the known mercaptan substances from the relatively low "ethyl" through the higher "nonyl" mercaptans in the formation of metallic mercaptides, which property provides a highly efficient sweetening process where the mercaptide removal process to which the present invention is particularly directed is practiced in connection with the formation of metallic mercaptides through the agency of cadmium or mercury compounds.

The present process is also particularly useful in the removal of dissolved lead mercaptides formed by treatment of a sour distillate with caustic sodium plumbite preferably in the substantial absence of added sulphur whereby the present process, when combined with a so-modified "Doctor" treatment provides a substantially complete sweetening together with a reduction in total sulphur content of the distillate, which is not ordinarily effected by the conventional "Doctor" treatment.

I have now determined that the dissolved metallic mercaptides may be effectively removed by treating a distillate containing the same with any one of a number of readily available and inexpensive reagents, whereby a stable and permanently sweet distillate may be readily produced. As above pointed out, the active material which I employ to extract the dissolved mercaptides preferably possesses adsorptive properties, although some of the active materials hereinafter described are not now recognized in the petroleum art as "adsorbents." It is well known that certain materials will have marked adsorptive properties with respect to certain substances in solution and little or no adsorptive properties with respect to another group of substances, and it is believed entirely proper to designate such materials as adsorptive, at least with respect to dissolved metallic mercaptides in a petroleum distillate, inasmuch as little or no chemical reaction has been observed to take place in the extraction step.

The several active adsorptive materials useful according to the present invention appear to fall within three rather narrow categories, namely, heat-activated metallic oxides, activated adsorbent agencies, and natural or artificial base-exchange silicates. In the first group I have found heat-activated Fe_2O_3 , Al_2O_3 , Cr_2O_3 , Ni_2O_3 , Co_2O_3 to be effective. In the second group I have found chemically activated Fuller's earth and comparable bleaching clays, bone charcoal,

and silica-gel to be effective. In the third group I have found natural and synthetic zeolites to be effective. The metallic oxides of the first group mentioned are found to be worthless as active materials in the present process when employed in their natural state. A heat activation, which effects no presently recognizable chemical change in the oxide, has been found necessary to impart the desired active properties to these oxides, and such activation may be carried out by calcining any one of the above designated oxides in pulverized or subdivided condition, at or below a dull red heat, and allowing the same to cool. Of the metallic oxides enumerated, activated ferric oxide (hematite) is believed to be the most advantageous in the present process from the standpoint of availability and low cost, and will in general be preferred over the other designated active materials.

As above set forth, the chemical agent employed to convert the mercaptan substances in a sour distillate into metallic mercaptides may advantageously be a compound of the metals cadmium or mercury, and while substantially all compounds of these metals are effective in such chemical conversion, the oxides of these metals are somewhat to be preferred in view of the relative inactivity thereof with respect to constituents of an unsaturated nature in such distillate, although salts such as the acetates and chlorides of mercury and cadmium are entirely operative in this chemical treatment. Of the several oxides of cadmium and mercury, yellow mercuric oxide has been found to be most rapid in its action upon the mercaptan substances.

Caustic sodium plumbite solution is also effective to convert the mercaptan substances in such a distillate into lead mercaptides, as above set forth, and may, under some circumstances, be preferred to a cadmium or mercury compound.

Any one of a number of procedures may be followed in the chemical conversion step, dependent somewhat upon the physical condition of the chemical reagent employed. For example, a sour distillate in liquid state, and at atmospheric or somewhat higher temperature, may be agitated with an aqueous solution of a water-soluble salt of cadmium or mercury such as, for example, mercuric acetate, and the distillate then recovered by decantation. Similarly, a water solution of caustic sodium plumbite may be employed, as by agitating the same with a sour distillate according to the conventional "Doctor" treatment, preferably in the substantial absence, however, of added sulphur. Where a water-insoluble compound such as mercuric oxide is employed, the chemical contact may be carried out by dispersing a suspension of such oxide in the distillate or by percolating a sour distillate through a bed of such oxide in divided condition. In any of the above-described procedures, such undissolved metallic mercaptides as are present after such contact may be separated from the distillate by filtration, but in the last-described procedure it has been found that the entire proportion of such undissolved mercaptides can be retained in the bed of the divided oxide.

In carrying out the second stage of the process, a distillate containing dissolved metallic mercaptides may be agitated with an active adsorptive material selected from the above-designated groups and subsequently filtered, or may be percolated through a column or bed of such material in divided condition, and it has been found unnecessary to provide a separate step for the removal

of the undissolved mercaptides from the distillate prior to the dissolved mercaptide removal step inasmuch as the necessary filtration or percolation of the distillate through the active adsorptive material in the latter step has been found effective in obtaining a complete removal of such undissolved compounds.

- As a specific example of the practice of the present invention, I have agitated a sour distillate containing 0.216% total sulphur and 0.01082% mercaptan sulphur with divided mercuric oxide at room temperature, in which treatment the distillate was reduced to a "Doctor-sweet" condition but was found to contain 0.00798% mercaptan sulphur. This sulphur was found to be principally present as metallic mercaptides in solution, and the distillate was found sour to the "Doctor" test on standing sixteen hours, indicating the relatively low stability of the dissolved metallic mercaptides. According to the present invention, the contacted distillate containing the dissolved mercury mercaptides was percolated at room temperature through a bed of divided hematite which had been activated as above set forth, and was found "Doctor-sweet" and gave no test for mercaptan sulphur to a test which is sensitive to one part in five million. This product was found to remain "sweet" to the "Doctor" test even on prolonged standing.
- It will be appreciated that the above set forth procedural details for effecting the desired chem-

ical and physical treatment of a distillate are not essential to my invention, and that other equivalent procedures may be followed advantageously. Similarly, I do not choose to be limited to the specific active adsorptive materials enumerated in the three groups above set forth. For the above reasons I do not choose to be limited to the specific details and features outlined in this specification, but rather to the scope of the appended claims. For example, superatmospheric temperatures and pressures have been found useful, but not required in the contact of a distillate with either the chemically active metallic compound or the adsorptive material.

I claim:

The method of treating "Doctor-sour" petroleum distillates to render the same "Doctor-sweet" which comprises: contacting such a distillate with a reactive material selected from the group consisting of mercuric and cadmium oxides to cause a chemical conversion of "sour" mercaptan substances into mercaptides at least partially dissolved in said distillate; removing such distillate from contact with said reactive material; subsequently contacting said distillate with a divided solid adsorptive base-exchange zeolite to cause removal of dissolved mercaptides from said distillate; and separating said distillate from said zeolite and the removed mercaptides.

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