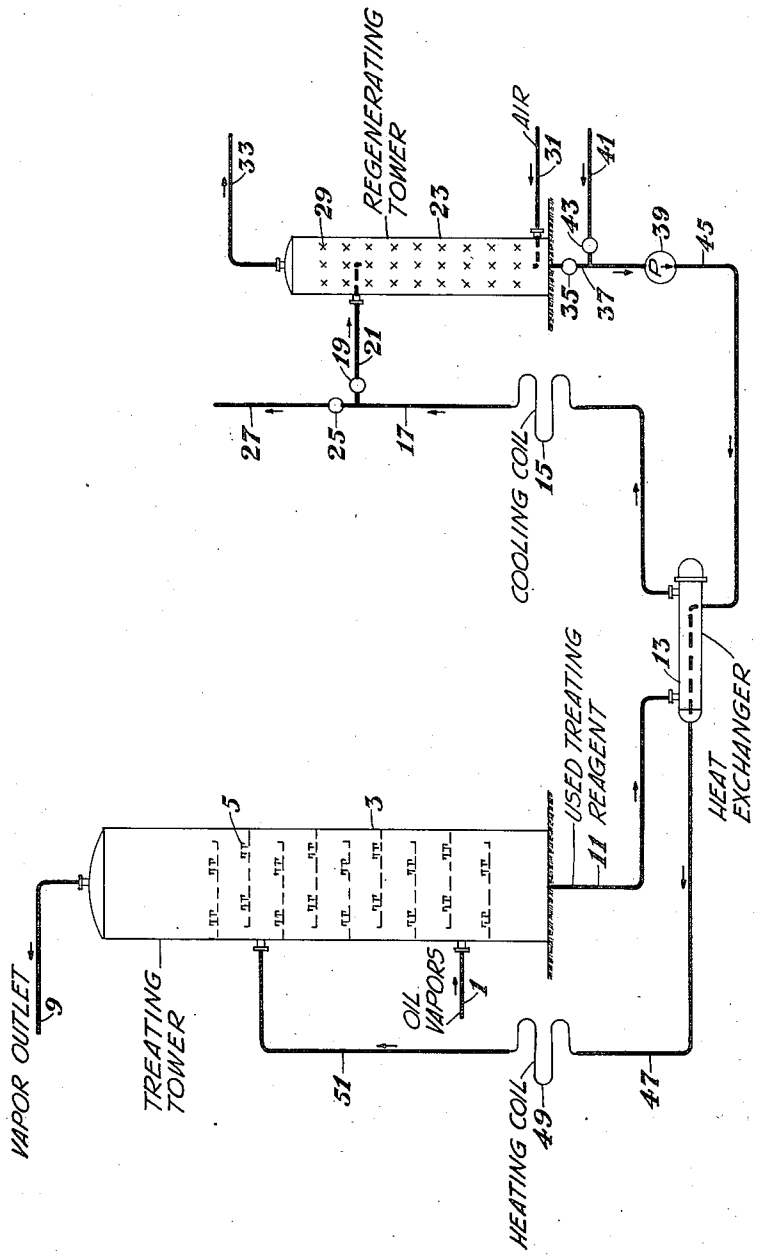
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HYDROCARBON OIL TREATING

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HYDROCARBON OIL TREATING

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This invention relates to an improved method of treating hydrocarbon oils and more particularly to a process of sweetening petroleum distillates such as are obtained by the distillation and/or cracking of petroleum oils in which the treating agent can be continuously and easily reactivated, thereby enabling the treating agent to be recycled or reused indefinitely.

More specifically, this invention relates to a novel method of sweetening gasoline and naphthas containing undesirable malodorous sulfur compounds such as mercaptans, and to the recovery of the treating reagent wherein the untreated distillate is first freed of hydrogen sulfide by any of a number of well known methods, and is then contacted at suitable temperature in the vapor state with a salt of an organic acid and a polyvalent metal, preferably copper naphthenate, which is dissolved or suspended in a suitable medium such as a high boiling mineral oil. The salt solution or suspension is then regenerated by oxidation at elevated temperature and recycled.

Various methods have been developed for the sweetening of sour petroleum distillates and a large number of materials have been used as sweetening agents. Sweetening with sodium plumbite is probably the best known and most commonly used. Other methods include the use of sodium or calcium hypochlorite and copper chloride.

All of the methods mentioned are subject to certain disadvantages. For example, the control of the addition of sulfur in sodium plumbite sweetening has long been a source of difficulty and the degradation of the distillates being treated, due to the use of small excesses of sulfur, is well known.

It is an object of this invention to improve the odor of petroleum distillates by removal of mercaptans by means of a treating reagent capable of being regenerated for reuse.

A further object of this invention is to effect substantially complete separation of corrosive constituents from petroleum distillates without the use of oxidizing agents on the stock being treated.

It is a further object to render sweet to the doctor test, various light petroleum distillates.

Another object is to provide a process whereby with proper temperature control hydrocarbons may be sweetened in the vapor phase and the treating agent may be recovered and regenerated, all without substantial decomposition or loss of treating reagent.

A still further object is to treat petroleum distillates in such manner as to provide a finished product which will pass the severe corrosion test frequently used in the paint and varnish industry and to recover and reactivate the treating reagent in a simple, economical manner.

Another object of the invention is to provide a treating agent which can be easily regenerated and reused in a continuous operation.

Various other objects and advantages of our invention will be apparent from the following description of a method of operation of our process and from the drawing, the single figure of which is a diagrammatic, elevational view of apparatus suitable for carrying out the process embodying the invention.

In accordance with our invention, petroleum distillates obtained by the distillation and/or cracking of petroleum hydrocarbons are first treated in a liquid or vapor state to remove hydrogen sulfide. This may be accomplished by the use of soda lime or any other of a number of methods. The hydrogen sulfide free distillate is then contacted at elevated temperature in the vapor state with the treating reagent. This reagent is preferably prepared from naphthenic acids or other suitable acids, the initial boiling points of which are higher than the temperature which it is necessary to maintain during the course of the treating process. From such naphthenic acids are prepared suitable naphthenates of polyvalent metals for use in the process. Other stable organic acids of suitable boiling range can be used, such as abietic acid and others. Among the metallic naphthenates which may be advantageously used in this process are those of iron, lead and copper. The liquid in which the salt is dissolved or suspended may be any liquid capable of dissolving or homogeneously dispersing the metallic naphthenate or other metal salts of organic acids referred to above, and which is inert and does not volatilize at temperatures required in the process. Throughout this discussion and in the claims the word "solution" is intended to include not only true solution but homogeneous dispersion as well. Similarly, the use of the word "dissolve" is intended to include passing into a homogeneous dispersion as well as into true solution. A suitable liquid for that purpose is that fraction of petroleum oil commonly known as gas oil. Uncracked gas oil is preferable to cracked material. When the hydrogen sulfide free hydrocarbon vapors are contacted with the treating reagent at suitable temperature, the metallic naphthenate apparently reacts with the mercaptans to form dialkyl disulfides and naph-

thenic acid, the metal of the metallic naphthenate undergoing a reduction in valence. The sweetening phase of the treating operation may be represented by the following equation:

$$2CuN_2+2RSH\rightarrow 2CuN+2HN+R_2S_2$$

where N represents naphthenic acid radical and R is any alkyl group.

The hydrocarbon vapors after contact with treating reagent, are fractionated in suitable equipment and in a conventional manner. The heat requirement for the process is not greatly in excess of that required for the usual fractionation operation since the temperature of the treating reagent is sufficiently high that the hydrocarbon vapors do not undergo appreciable cooling in passing through the treating reagent. The lower limit of the temperature at which the treating reaction may be carried out is largely a matter of completely vaporizing the distillate being treated, after contact with the treating reagent. In the case of butane, for example, the treating temperature might well be below 50° F. The upper limit is determined by the thermal stability of the metallic naphthenate, the vapors being treated and the liquid in which the naphthenate is dissolved or suspended. The factor which generally is the limiting one is the thermal stability of the metallic naphthenate. If the treating temperatures are too high, decomposition of the naphthenate results and regeneration by means of the air blowing method becomes impossible. This temperature is preferably within the range of approximately 350° F. to 475° F. for most gasolines and petroleum naphthas. After use, the treating reagent may be intermittently or continuously withdrawn from the treating stage of the process for regeneration.

The regeneration or reactivation phase of the process may be illustrated by the following equation:

$$4CuN+4HN+O_2\rightarrow 4CuN_2+2H_2O$$

The treating reagent may be regenerated within a rather wide range of temperature, satisfactory results being possible from 100° F. to 350° F. although the preferred range is 150° F. to 350° F. Temperatures near or above the boiling point of water are preferable in order to eliminate the water formed in the oxidation reaction of the regeneration. The upper limit of temperature for regeneration is determined by the stability of the naphthenate salt and the liquid medium in which it is dissolved or dispersed. Temperatures appreciably over 375° F. cause undesirable deterioration or decomposition of the salt and thus defeat the very purpose of the regeneration step which is to convert the used treating reagent to an active state suitable for sweetening further hydrocarbon vapors. Oxygen or a suitable oxygen-containing gas such as air, provides a very satisfactory means of converting the free naphthenic acid and the metal naphthenate in the lower valence form, to a higher valence metal naphthenate and water. As previously indicated, the water may be readily removed as water vapor by the gas required in the reactivation step. The regenerating step may be carried out at atmospheric or superatmospheric pressure, as for example, at 50 lbs. per square inch. The regenerated treating agent is preheated to the desired temperature and returned to the treating step of the process. Hydrocarbon distillate treated by this method will be found to be doctor sweet and will pass a very severe copper strip corrosion test such as the test required in the paint and varnish industry. This corrosion test is described in H. A. Gardner's book on "Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors," page 801 and is hereinafter referred to as the varnish thinner corrosion test. In this test a polished copper strip is maintained in an Engler flask throughout the usual Engler distillation. To be satisfactory the strip must show not more than a slight discoloration after the liquid has completely distilled.

If the concentration of high boiling disulfides in the regenerated treating reagent does become sufficiently high to eventually impair the efficacy of the treating solution, the reagent may be contacted with hydrochloric acid, copper being recoverable from the aqueous layer in the form of copper chloride. After water washing, the oil layer containing naphthenic acid may be treated with an alkali solution containing 50% water and 50% methanol which will extract the naphthenic acid as the alkali salt. The hydrocarbon oil containing the disulfides may be utilized as cracking stock, fuel oil or other suitable disposition made.

It will be seen that our process is readily adaptable to the usual distillation and/or cracking processes in use in the petroleum industry. Since the hydrocarbon is already brought to a vapor state in the aforementioned processes, very little additional heat is required to pass the vapors through such a liquid treating reagent when that reagent is maintained at approximately the temperature of the vapors.

Referring more particularly to the drawing, the numeral 1 represents a pipe for conveying suitable hydrocarbon vapors to be treated, as for example, gasoline or naphtha, from a source of supply to the lower portion of treating tower 3. This tower contains suitable fractionating equipment, for example, bubble plates 5, to facilitate contact of the hydrocarbon vapors with the treating reagent and to separate, by means of fractionation, the material being treated, from the treating reagent. The treating reagent enters the upper portion of tower 3 through pipe 51 and flows down through the tower in intimate contact with the ascending hydrocarbon vapors. The treated vapors pass on through the treating tower and are withdrawn at the top through pipe 9 from whence they may pass to a condenser and be recovered as finished distillate or they may pass directly to subsequent processing operations, whichever may be desired.

The partially spent treating reagent is withdrawn from the bottom of tower 3 through pipe 11, cooled in heat exchanger 13 by means of heat interchange with treating reagent being charged to the treating tower, further cooled in cooling coil 15 and passed through pipe 17, valve 19 and pipe 21 to the upper portion of regenerating tower 23. Spent treating reagent may be withdrawn from the system as desired through valve 25 and pipe 27. The regenerating tower is preferably operated under superatmospheric pressure and is partially filled with suitable packing 29 to improve the efficiency of contact between the treating reagent and the oxygen-containing gases necessary for regeneration which enter the tower at the lower portion through pipe 31 from a suitable source of supply. The gas used for regeneration is withdrawn from the top of tower 23 through pipe 33. The regenerated treating reagent is withdrawn from the bottom of tower 23 through valve 35 and pipe 37 which leads to pump 39. Fresh reagent may be added to the system from a suitable source as required, by

means of pipe 41, valve 43 and pipe 37 which passes to pump 39. Pump 39 charges treating reagent through pipe 45, heat exchanger 13, where heat is absorbed from the hot, partially spent treating reagent being discharged from the treating tower, pipe 47, heating coil 49 and pipe 51 to treating tower 3 where the treating is accomplished, as previously described.

In a specific example of our process gasoline vapors which contain hydrogen sulfide and which under normal methods were recovered as a doctor sour and corrosive distillate, were treated in the vapor state first with soda lime and then with copper naphthenate dissolved in topped kerosene. The thruput of gasoline was 2.75 to 3.0 gal./hour. The treating reagent was prepared from naphthenic acids of high boiling range, the initial boiling point being 504° F. The topped kerosene was an ordinary kerosene distillate from which the lower boiling materials had been removed. This kerosene had an initial boiling point of 420° F. and an end point of 521° F. The naphthenic acids were dissolved in the topped kerosene and heated to approximately 310° F. To this solution cupric carbonate was added and the temperature maintained at approximately 310° F. for about two hours. To the copper naphthenate thus formed was added additional kerosene. The gasoline vapors at approximately 350° F. were contacted in a suitable treating tower with the liquid treating reagent which had been heated to approximately 365° F. This temperature was found to be sufficiently high to completely vaporize the gasoline and was sufficiently low to avoid decomposition of the copper naphthenate. The treating reagent was circulated at a rate of 4.5 gal./hour. The gasoline vapors passed on through the tower to a fractionator and condenser where gasoline of suitable end point was obtained as a distillate. Proper fractionating conditions keep substantially all of the liquid of the treating agent in the treating tower and even though small amounts of this liquid may initially vaporize, an equilibrium is soon reached and negligible contamination of the distillate being treated, occurs. The copper naphthenate reagent was continuously withdrawn from the treating tower, cooled to approximately 110° F., regenerated by air blowing at a rate of 20 to 30 cubic feet per hour, reheated and returned to the treating tower for further use in sweetening. A total of 117 gallons of gasoline were treated. Approximately 35 pounds of treating reagent containing 0.18 lb. of copper in the form of copper naphthenate (weight of copper naphthenate 2.12 pounds) was circulated during the treating operation. The pressure on the entire system was only 1 or 2 pounds per square inch above atmospheric pressure. The gasoline distillate after treating was of good odor, good color, doctor sweet, and passed the severe copper strip corrosion test previously described. The treating reagent functioned just as efficiently at the end of the run as at the beginning, although the amount of mercaptan sulfur which was altered in form or removed, exceeded the theoretical amount which could be accounted for by the amount of treating agent used if no regeneration of treating reagent had been effected.

While we have given a specific manner in which our novel process may be carried out, it is not intended that we shall be limited thereby as there are many variations which will occur to those skilled in the art.

Tests on the gasoline before and after treating are tabulated in the following table:

Table

	Average tests of raw gasoline	Average tests of treated gasoline
Gravity, A. P. I.	60.2	59.9
I. B. P.	98	98
5%	135	138
10%	157	159
20%	190	191
30%	215	215
40%	237	237
50%	258	258
60%	280	280
70%	310	307
80%	336	335
90%	367	369
95%	395	399
E. P.	430	422
Recovery, per cent	97.0	97.0
Residue, do	1.1	1.1
Color	24	24
Doctor	Positive	Negative
Sulfur, per cent	0.025	0.019
Varnish thinner corrosion	Positive	Negative

It will thus be seen that we have devised a treating process which permits fractionating and treating operations to be carried out in what is practically a single operation. This eliminates the necessity of additional costly special treating equipment. Freedom from the necessity of adding compounds, corrosive in themselves, in order to complete the sweetening reaction, is also accomplished. While a specific example of carrying out our process has been described, it is not intended that the process shall be limited thereby, but that the process may be as broadly interpreted as is permitted in view of the prior art and of the following claims.

We claim:

1. In the process of repeatedly utilizing stable polyvalent heavy metal salts of organic acid selected from the group consisting of naphthenic and abietic acids, dissolved in an oil miscible liquid for sweetening petroleum hydrocarbon vapor, the step which comprises treating said vapors with the solution but below the decomposition temperature of said salt, reactivating the solution by passing an oxygen-containing gas therethrough at a temperature sufficiently high to effect regeneration but below the temperature of decomposition of said salts and utilizing the regenerated solution for treatment of additional vapors.

2. In the process of regenerating a solution in an oil-miscible liquid of a stable polyvalent metal salt of a stable organic acid whose boiling point is above the temperature to which said salt is subjected in the sulfur compound removal step hereinafter set forth, which solution has been employed at elevated temperatures below the decomposition temperature of said salt for removing sulfur compounds from hydrocarbon fluids, the step which comprises passing oxygen-containing gas through the solution at a temperature sufficiently high to effect regeneration but below the temperature of decomposition of said salt.

3. Process in accordance with claim 2 where the organic acid is naphthenic acid.

4. In a process of regenerating a hydrocarbon oil solution of a stable polyvalent metal salt of a stable organic acid whose boiling point is above the temperature to which said salt is subjected in the sulfur compound removal step hereinafter set forth, which solution has been employed at

elevated temperatures below the decomposition temperature of said salt for removing sulfur compounds from hydrocarbon vapors, the step which comprises passing oxygen-containing gas through the solution at a temperature above 100° F. and not substantially in excess of 375° F.

5. The step in accordance with claim 4 in which the solution is maintained under appreciable superatmospheric pressure while passing the oxygen-containing gas therethrough.

6. Process in accordance with claim 4 where the vapors are treated at a temperature of approximately 350° F. to 475° F. and the vapors are of such character that they remain in the vapor state at the temperatures specified.

7. Process in accordance with claim 4 where the hydrocarbon oil solvent has an initial boiling point which is appreciably higher than the temperature required to maintain the petroleum hydrocarbon vapors in the vapor state.

8. In the process of regenerating a solution of a stable polyvalent metal salt of an organic acid dissolved in hydrocarbon oil which has been employed at elevated temperatures below the decomposition temperature of said salt for removing sulfur compounds from hydrocarbon vapors, said organic acid being selected from the group consisting of naphthenic and abietic acids, the step comprising passing oxygen-containing gas through the solution at a temperature sufficiently high to effect regeneration but below the temperature of decomposition of said salt.

9. Process in accordance with claim 8 where the regeneration temperature is between approximately 100° and 375° F.

10. Process in accordance with claim 8 where the temperature at which the vapors are treated is not substantially in excess of 475° F. and the temperature of regeneration is between approximately 100° and 375° F.

11. In the process of regenerating a solution of a stable polyvalent metal salt of naphthenic acid dissolved in hydrocarbon oil which has been employed at elevated temperatures below the decomposition temperature of said salt for removing sulfur compounds from hydrocarbon vapors, the step comprising passing oxygen-containing gas through the solution at a temperature sufficiently high to effect regeneration but below the temperature of decomposition of said salt.

12. Process in accordance with claim 11 where the temperature at which the vapor is treated is not substantially in excess of 475° F.

13. Process in accordance with claim 11 in which the oxygen-containing gas is passed through the solution at a temperature of about 100° F. to 375° F.

14. In the process of regenerating a solution of copper naphthenate dissolved in an oil-miscible liquid, which solution has been employed at elevated temperatures below the decomposition temperature of said salt for removing sulfur compounds from hydrocarbon fluids, the step which comprises passing oxygen-containing gas through the solution at a temperature sufficiently high to effect regeneration but below the temperature of decomposition of said salt.

15. In the process of regenerating a solution of iron naphthenate dissolved in an oil-miscible liquid, which solution has been employed at elevated temperatures below the decomposition temperature of said salt for removing sulfur compounds from hydrocarbon fluids, the step which comprises passing oxygen-containing gas through the solution at a temperature sufficiently high to effect regeneration but below the temperature of decomposition of said salt.

16. In the process of regenerating a solution of lead naphthate dissolved in an oil-miscible liquid, which solution has been employed at elevated temperatures below the decomposition temperature of said salt for removing sulfur compounds from hydrocarbon fluids, the step which comprises passing oxygen-containing gas through the solution at a temperature sufficiently high to effect regeneration but below the temperature of decomposition of said salt.

17. In a process of regenerating a solution of copper naphthenate dissolved in hydrocarbon oil, which solution has been employed at elevated temperatures below decomposition temperature of said salt for removing sulfur compounds from hydrocarbon vapors, the step which comprises passing oxygen-containing gas through the solution at a temperature above 100° F. and not substantially in excess of 375° F.

18. In a process of regenerating a solution of lead naphthenate dissolved in hydrocarbon oil, which solution has been employed at elevated temperatures below decomposition temperature of said salt for removing sulfur compounds from hydrocarbon vapors, the step which comprises passing oxygen-containing gas through the solution at a temperature above 100° F. and not substantially in excess of 375° F.

19. In a process of regenerating a solution of iron naphthenate dissolved in hydrocarbon oil, which solution has been employed at elevated temperatures below decomposition temperature of said salt for removing sulfur compounds from hydrocarbon vapors, the step which comprises passing oxygen-containing gas through the solution at a temperature above 100° F. and not substantially in excess of 375° F.

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