This invention relates to an improved method for sweetening hydrocarbon distillates.

Distillates which may be treated according to the present process include those of petroleum origin obtained by various methods such as the primary distillation of crude hydrocarbon oils, the cracking of crude petroleum or fractions thereof, the polymerization of normally gaseous olefins from cracking or other processes, etc. Distillates from other hydrocarbon sources, such as coal tar, shale oils, etc., may also be treated by the present method.

Practically all hydrocarbon distillates require some form of treatment to render them of marketable quality, and this is particularly true of cracked products of motor fuel boiling range. Many distillates require little or no treatment other than sweetening which is often supplemented, in the case of cracked gasolines, by the addition of inhibitors to increase storage stability and prevent the formation of color, gum, and other objectional products during the storage period.

Among the sweetening methods which have been used with considerable success is the so-called doctor process employing alkaline solutions of sodium plumbite. Another method is the hypochlorite process wherein gases are sweetened by means of solutions or suspensions of sodium or calcium hypochlorite. The copper sweetening process has been developed in recent years to overcome many of the disadvantages of these methods. It is with improvements in this process that the present invention is concerned.

In one specific embodiment the present invention comprises contacting sour hydrocarbon distillate with a dilute solution of an acidic substance, this term being intended to include materials which yield a solution having a pKa of less than 7 and which in the state of dilution in which they are used are relatively unreactive with the hydrocarbons. Included are mineral acids such as sulfuric, phosphoric and hydrochloric acids; acid salts such as sodium and ammonium acid-sulfate or acid-phosphate; heavy metal halides such as aluminum chloride, iron chloride, zinc chloride, etc.; and organic acids such as acetic acid. Normally, the concentration of the solution is less than 20% in order to prevent undue reaction of the acidic substance with hydrocarbon components of the distillates undergoing treatment. This depends to a large extent on the acidic substance being used. Solutions of sulfuric or phosphoric acid of 1-20% and preferably 1-10% may be satisfactorily used. When using hydrochloric acid, solutions of less than 10% concentration are preferred. When using acid sulfates such as sodium acid-sulfate somewhat stronger solutions may be employed without affecting undesirable secondary reactions. Contacting is carried out at substantially atmospheric temperature.

Treatment with dilute acidic substance may be effected in any suitable manner such as for example mixing the acidic substance with the gasoline in an eductor or Venturi type mixer, by mechanical agitation, by counter-current contacting in a packed column, or similar equivalent devices. A separation step follows in which the hydrocarbon is substantially freed of suspended aqueous solution. In certain cases this is followed by treatment with alkali although this is not always done.

The effect of treatment with dilute acidic substances is to remove colored or color-forming materials which tend to accumulate on the sweetening reagent and later under the influence of air, to redissolve thus throwing the distillate off color and depreciating its other desirable properties such as storage stability.

The clear hydrocarbon distillate is withdrawn from the settler and passed through a drying step, which comprises contacting it with a solid drying agent capable of absorbing water from the hydrocarbon. The reagent may consist of activated alumina, silica gel, calcium sulphate, rock salt, calcium chloride, solid sodium or potassium hydroxide, etc.

The dried distillate is then mixed with air and passed into a primary treating tower wherein the
sweetening reaction occurs by means of a copper-containing sweetening reagent.

The purpose of the drying step is to minimize migration of soluble copper salts through the reagent bed by which results when water is formed during the sweetening reaction. The dried gasoline dissolves a major part of the water formed and removes it so that it cannot accumulate and migration of the salts is stopped.

The sweetening reagent may comprise any suitable solid copper-containing material such as, for example, a mixture of copper sulfate with sodium or ammonium chloride, and an inert filler such as pumice, fuller's earth, firebrick, etc. Impregnated sweetening reagents are also used, these consisting of an adsorbent granular carrier impregnated with mixtures of copper sulfate and an alkaline chloride, or with cupric chloride or other suitable copper compounds. The term "alkaline chloride" is intended to mean chlorides of alkali or alkaline earth metals including the hypothetical metal ammonium.

The secondary treating tower may comprise any suitable elongated vertical vessel in the lower section of which is disposed a bed of secondary reagent. The top section of the tower is empty and serves as an air separator. It has a vent controlled by a valve to release residual air. A liquid level controller is used to maintain a layer of liquid over the reagent bed. The liquid level is kept sufficiently below the vent to prevent mechanical loss of distillate with the released air.

The advantage of this particular step is that it dispenses with a separate air separator which is normally used in connection with the copper sweetening process between the primary and secondary treating steps. A further advantage is that it shortens the lapse of time between the primary sweetening step and contacting of the sweetened distillate with the secondary reagent. This has been found to be of particular importance when sweetening cracked gasolines. Results wherein the copper sweetened gasoline has been allowed to stand for even a relatively short time after leaving the primary sweetening tower have shown that the gasoline is no longer readily treated for copper removal and that it has suffered a loss in some of its desirable properties such as color and storage stability. The effects on the gasoline in even as short a time as 15 minutes to 1¼ hour is often sufficient to bring about irreparable damage unless expensive expedients such as redistillation are resorted to.

By using the secondary tower as a combination air separator and treating tower the gasoline from the primary sweetening step is contacted immediately with the secondary reagent and the residual air is removed from contact with the gasoline as efficiently as in the formerly used air separator.

The secondary reagent may suitably comprise a heavy metal sulfide deposited on a filler, for example, coke sulfide on pumice. Other sulfides such as iron sulfide, lead sulfide, etc., or alkali- or alkaline-earth metal sulfides deposited on a carrier such as pumice or fuller's earth may be used.

One embodiment of our process is shown diagrammatically by the accompanying drawing, although this should not be interpreted as restricting the invention to the exact apparatus shown.

Referring to the drawing, hydrocarbon distillate such as gasoline is introduced through line 1, valve 2, pump 3, valve 4, which joins with line 5 and is commingled with a dilute acidic solution passing through valve 6, pump 7 and valve 8. Mixing is accomplished in line 9 and mixer 10 which may comprise any suitable type of mixing apparatus. The mixture passes through settler 11, from which spent acidic solution is withdrawn through valve 12 and line 13. Clear gasoline passes through line 14 valve 15 to gasoline drier 16 which may be, for example, a vertical tower packed with a suitable drying agent in solid form. The dried gasoline is removed through line 17 and valve 18, and valve 20 serve as a means of draining the drier. Air is introduced through line 21, valve 22 and air dryer 23. The air dryer may be similar to the gasoline drier 16 or may comprise merely a knockout drum for removing entrained water. It is not necessary to dry the air completely so that almost any suitable packing material such as wood wool, rock salt, fuller's earth, etc., may be used. Water may be removed from the bottom of the drier through line 24, valve 25. The dried air passes through line 26 and valve 27 which joins with line 17. The air and gasoline mixture is mixed in mixer 28 and enters primary treating tower 29 through distributor 30. Line 31 and valve 32 serve as a means of venting the primary treating tower. The tower is equipped with pressure gauge 33. The tower contains a solid copper-containing sweetening reagent such as one of those previously described. The hydrocarbon distillate and air under pressure of 30-100 pounds per square inch approximately are passed through the sweetening reagent and are removed through line 34 and valve 35 to secondary treating tower 36. Line 37 and valve 38 serve as a means of draining tower 29. Treating tower 36 comprises a vertical tower, the upper section of which is empty and serves as an air separator. Air is withdrawn from the top of the tower through line 46 and valve 46. The gasoline passes downwardly through a layer of granular secondary treating reagent such as zinc sulphide deposited on pumice or other suitable material. The tower is equipped with liquid level controller 39 which acts upon valve 40, said valve being contained in line 41. The tower may be drained through line 42 and valve 43. The tower is equipped with pressure gauge 44.

The following example is given to illustrate the usefulness and practicability of our invention but should not be construed as limiting it to the exact conditions or materials used therein.

A sour West Texas cracked gasoline was contacted with 5% by volume of a 2% solution of sulfuric acid, the gasoline was separated and passed into a drying step where it was contacted with activated alumina. The dryer consisted of two towers which were used alternately, the material in one reactor being dried and regenerated while the other was in operation. Regeneration was carried out by heating the activated alumina while passing dry air through it continuously to remove water.

The dried gasoline was mixed with approximately 6 cubic feet of air per barrel of gasoline and passed into a copper sweetening step. The sweetening reagent consisted of a mixture of copper sulphate, ammonium chloride and pumice. The gasoline was passed downwardly through the reagent under a pressure of 60 pounds per square inch. The sweetened gasoline containing residual air was passed to the secondary treating tower. The upper section of the tower was used as an air separator from the top of which the air was
released. In this way there was a minimum lapse of time between sweetening with the copper reagent and the treatment of the gasoline to remove dissolved copper therefrom, which is one of the advantages of the present process. Residual air was withdrawn from the top of the tower. The gasoline passed through the secondary treating agent which comprised zinc sulfide deposited on powder. The finished treated gasoline was withdrawn from the bottom of the secondary treating tower and passed to storage.

The properties of the sweetened product are compared in the following table with those of the original sour gasoline, the gasoline copper-sweetened but not previously treated with dilute acid, and the gasoline which has been pretreated with dilute acid, copper-sweetened, passed through an air separator and then through the secondary treater to remove dissolved copper.

<table>
<thead>
<tr>
<th>Gasoline</th>
<th>Original, sour</th>
<th>Not acid pretreated copper sweetened</th>
<th>Acid pretreated copper sweetened</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Separate air separator and secondary treater</td>
<td>Combined air separator and secondary treater</td>
</tr>
</tbody>
</table>

Color 2 Saybolt 30 6 10
Oxygen bomb stability induction 210 130 100 700
Original, min. original gasoline 425 230 300 480
Copper dist. test Me. 0.06 MIL 110 95 75 120
Original gasoline 100 100 120
Original gas. 40.0% Comm. Inhib 30 60 90 12

The results show that the acid pretreatment with an air separator and secondary treater yielded a gasoline of improved properties over those obtained when the gasoline was not acid pretreated, but that the properties other than the doctor test were slightly poorer than those of the original sour gasoline. When using the combined air separator and secondary treater following copper-sweetening of acid pretreated gasoline, the properties of the sweetened gasoline were improved still further.

During the operation of the plant, the advantage of drying the gasoline prior to copper sweetening was demonstrated by the fact that migration of the copper salts through the reagent bed was minimized. When operating without an air dryer, it was necessary to remove the sweetening reagent at intervals of approximately 30-40 days, remix it in order to produce a uniform reagent mass, and return it to the tower. This was necessitated by migration of salts resulting in the development ofchanneling due to migration of the salts. When operating according to the present invention, a period of 90-90 days’ operation was possible without the development of channeling.

We claim as our invention:
1. In the treatment of sour hydrocarbon distillates with a copper-containing sweetening agent in the presence of oxygen-containing gas, the method which comprises introducing the mixture of distillate and gas from the sweetening step into the upper portion of a vertical chamber having a free space in its upper portion and a layer of copper-removing agent in its lower portion, separating the gas from the distillate in said free space of the chamber and permitting the separated distillate to gravitate through said layer, whereby to minimize the time interval between the sweetening of the distillate and the removal of dissolved copper therefrom.

2. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous mineral acid solution of a concentration not substantially above 20%, whereby to remove colored and color-forming bodies without undue reaction on the hydrocarbon components of the distillate, drying the thus treated distillate to remove water therefrom, mixing an oxygen-containing gas with the dried distillate and contacting the resultant mixture with a copper-containing sweetening agent, introducing the mixture of distillate and gas from the sweetening step into the upper portion of a vertical chamber having a free space in its upper portion and a layer of copper-removing agent in its lower portion, separating the gas from the distillate in said free space of the chamber and permitting the separated distillate to gravitate through said layer, whereby to minimize the time interval between the sweetening of the distillate and the removal of dissolved copper therefrom.

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