Patented Jan. 20, 1942

2,270,248

UNITED STATES PATENT OFFICE

2,270,248

TREATMENT OF HYDROCARBON DISTILLATES

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No Drawing. Application July 28, 1939, Serial No. 287,005

8 Claims. (Cl. 196—30)

This application is a continuation-in-part of our copending application Serial Number 253,619, filed January 30, 1939.

This invention concerns the treatment of hydrocarbon distillates prior to sweetening with copper compounds. More particularly, the process relates to the pretreatment and sweetening of hydrocarbon distillates such as gasoline, kerosene, and the like, which may be obtained by the primary distillation or cracking of crude petroleum oil, shale oil, coal tar, etc., or fractions thereof.

Practically all hydrocarbon distillates, and particularly those of gasoline, naphtha, and kerosene boiling range, require some form of refining treatment in order to make them of marketable quality. Among the methods which have been used for treating such distillates is treatment with sulfuric acid, various metal salts, adsorbents, such as fuller's earth, etc.

Another method which has wide application in the treatment of cracked products particularly, is the use of various inhibitors to prevent or minimize the formation of color, gum, and odor as well as loss in antiknock qualities of the product.

Regardless of the other treatments which may be used it is usually necessary to subject light hydrocarbon distillates to a sweetening step in order to improve the odor thereof. A sweetening process which has been widely used is the so-called doctor or sodium plumbite method. Another method particularly useful with straight-run and natural gasolines is the hypochlorite sweetening method. Still another method which has become increasingly important in recent years is the copper-sweetening process involving the use of solutions or solid mixtures of various copper compounds. It is with improvements in this process that the present invention is concerned.

The advantages of the copper-sweetening method over plumbite sweetening and other commercially practiced processes, is that it yields, in many cases, distillates of improved color and gum stability and, in the case of gasolines, superior octane number with and without added tetraethyl lead. The ease of regeneration of the reagent and operation of the plant are such as to make the copper-sweetening process still more advantageous in a great many instances. Various methods such as the addition of air or oxygen have been practiced whereby sweetening of the distillate and regeneration of the reagent are continuous. When solid granular reagents are used, the process has the advantage that there is little or no emulsion formation, a condition which generally occurs during doctor sweetening and which results in loss of distillate and chemicals.

Many hydrocarbon distillates following copper sweetening contain minute quantities of copper either dissolved or in suspension after the sweetening reaction has been completed. As a result there is often a loss in color and gum stability of the sweetened distillate. Various methods have been proposed for removing the offending compounds and in the majority of cases such methods are effective for restoring the color and stability of the sweetened product. Among the compounds useful for this purpose are the heavy metal sulfides, such as those of zinc, iron, lead, etc., as well as the alkali metal and alkaline earth-metal sulfides.

In one specific embodiment our invention comprises treating petroleum distillates such as gasoline, naphtha, kerosene, etc., with a solution of a hydrogen halide acid of 0.5–10% concentration, separating the distillate, sweetening said distillate with a copper-sweetening reagent, and finally treating said sweetened distillate with a secondary reagent to remove dissolved copper compounds therefrom.

In some cases copper-sweetening reagents, whether used in granular form or as aqueous solutions, become contaminated with highly-colored tar-like material, which upon exposure to air becomes partially soluble in the distillate, so that a marked discoloration of not only the reagent but the distillate as well results. These tar-like substances become soluble in gasoline when contacted with air, and since it is necessary to supplement the continuous addition of oxygen-containing gas by blowing the copper-sweetening reagents with air at intervals in order to regenerate them, particularly when using solid reagents, these highly-colored reaction products must be removed. In practice this is done by washing the solid reagent with straight-run or natural gasoline until a major portion of the coloring materials have been removed. This adds considerably to the cost of processing, and even so fails to remove all of the colored material from the sweetening reagent, and as a consequence a permanent discoloration of the main body of the distillate to be sweetened sometimes results. The contaminating materials likewise have a deleterious effect on the susceptibility of gasolines to inhibitors, and tend to increase gum formation. The fouling of the reagent tends to be accumula-

tive so that in some cases it eventually becomes difficult or impossible to produce a satisfactory product, and as a consequence the reagent must be discarded while still active insofar as the sweetening reaction itself is concerned.

When using solid granular sweetening reagents containing cupric halides it has been found that there is a gradual decrease in the activity of the sweetening reagent and that eventually this activity is reduced to a point where further reactivation is ineffective and the reagent must be discarded. The reason for this loss in activity has not been entirely explained but apparently is related to the development of water-insoluble copper compounds, which have little or no benefit, insofar as sweetening activity is concerned, in the sweetening reagent. This, in turn, appears to be related in some fashion to a reduction in halide ion content of the sweetening reagent.

We have found that the loss of sweetening activity, and the accompanying development of water-insoluble cupric copper, as well as loss in halide content, and the discoloration effects on the reagent and distillate, can be minimized and in some cases entirely eliminated by treating the distillate prior to the copper-sweetening step with dilute solutions of hydrogen halides such as hydrochloric acid. The acid used will depend on the composition of the sweetening reagent. Thus, hydrochloric acid will be used to pretreat gasolines to be sweetened by reagents containing chlorides of copper, while hydrobromic acid will be used for pretreating gasolines to be sweetened by reagents containing bromides of copper. The concentration of acid used is of the order of 0.5–10% and is preferably 1–5%. The distillate, after pretreatment with the dilute acid, is separated by well-known methods. Entrained or suspended acid solution should be removed prior to the sweetening step, but the distillate is not neutralized. The treated distillate is then passed through a bed of the copper-sweetening reagent together with air or oxygen-containing gas. After sweetening, the distillate is treated with a secondary reagent such as zinc sulfide, for the removal of dissolved copper compounds therefrom.

Any suitable copper-sweetening reagent comprising cupric halides may be used. For example, mixtures of ammonium, sodium, potassium, calcium, etc., chlorides with copper sulfate, either impregnated or admixed with a suitable carrier, such as pumice, fire brick, fuller's earth, diatomaceous earth, porcelain chips, etc., may be used. The sweetening treatment is normally carried out at a temperature of approximately 60–120° F. and preferably of the order of 70–90° F. Contact with the acid solution and treatment with the secondary reagent are also carried out in the same temperature range. The secondary reagent may suitably be a heavy metal sulfide such as zinc sulfide, iron sulfide, lead sulfide, etc., or may comprise solutions of alkali-metal or alkaline earth-metal sulfides. When the heavy metal sulfides are used such as, for example, zinc sulfide, the reagent is deposited or otherwise dispersed on suitable carriers such as pumice, fuller's earth, diatomaceous earth, etc. If desired a slurry of the secondary reagent can be used.

The apparatus in which the reaction may be carried out is not a special feature of the present invention, but may comprise any suitable well-known design of contactor for carrying out the dilute acid treatment as well as the various steps of the copper-sweetening treatment. Preferably the copper-sweetening treatment is carried out in packed towers or other suitable types of contactors wherein granular or powdered reagents may be contacted with the distillate.

The following examples are given to illustrate the practicability and usefulness of our process but should not be construed as limiting the invention to the exact conditions given therein.

Example 1

A West Texas cracked gasoline was sweetened by means of a mixture of copper sulfate, ammonium chloride, and pumice, the mixture being made in the ratio of 1:1:2 parts by weight of the reagents in the order named. The gasoline was mixed with air and passed over the reagent at a temperature of 75° F. At intervals beginning at approximately 1000 barrels of gasoline per ton of reagent the flow of gasoline was interrupted and the reagent was blown with air to regenerate it. It was then washed with straight-run gasoline to remove a portion of the highly-colored reaction products and used again to sweeten the cracked gasoline. As the treatment proceeded the intervals between periods of blowing became shorter until, after a total of approximately 10,000 barrels per ton had been passed through the reagent, a permanent discoloration of the gasoline occurred and the interval at which regeneration was necessary was reduced to approximately 250 barrels per ton.

After 11,500 barrels per ton had been passed over the reagent it would no longer sweeten the gasoline satisfactorily. Examination of the reagent showed that it was dark brown in color and there was very little water-soluble cupric copper present.

The reagent was replaced with a fresh mass. The gasoline prior to sweetening was washed with an aqueous solution of 1.5% hydrochloric acid. The gasoline was allowed to settle and was passed through a sand filter in order to remove any entrained acid solution. The clear gasoline was then passed over the sweetening reagent as previously described. It was found necessary to regenerate the reagent at intervals of approximately 2000 barrels per ton, and after 12,000 barrels per ton had been passed through the reagent no decrease in activity could be observed. After 30,000 barrels per ton the reagent was still substantially as active as when first put into the plant. Moreover, examination of the reagent showed no discoloration and only a small amount of water-insoluble cupric copper.

Example 2

A fraction of hydrocarbon distillate suitable for use as a dry cleaner's naphtha was sweetened in the presence of air by the reagent mass described in Example 1. This naphtha boiled in the range of 300–400° F., and contained 0.04% mercaptan sulfur. After a yield of approximately 3200 barrels per ton the distillate could no longer be sweetened by the reagent. Blowing with air had practically no effect and it was necessary to discard the sweetening reagent entirely. In this case there was no discoloration of either the naphtha or the sweetening reagent. About 75% of the cupric copper compounds present were water insoluble.

The reagent was replaced and the operation continued as before except that the naphtha was given a preliminary wash with 1% by volume of 2.0% hydrochloric acid prior to the sweetening step. After a yield of 6000 barrels per ton the reagent was as active as when first introduced

into the plant. Analysis showed that there had been substantially no loss in chloride content, and that there was very little insoluble cupric copper formed.

We claim as our invention:

1. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous hydrogen halide solution, separating the distillate from the solution and then treating the same with a sweetening agent containing combined copper and a combined halogen.

2. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous hydrogen halide solution of a concentration of the order of 0.5–10%, separating the distillate from the solution and then treating the same with a sweetening agent containing combined copper and a combined halogen.

3. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous hydrogen chloride solution, separating the distillate from the solution and then treating the same with a sweetening agent containing combined copper and combined chlorine.

4. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous hydrogen chloride solution of a concentration of about 0.5–10%, separating the distillate from the solution and then treating the same with a sweetening agent containing combined copper and combined chlorine.

5. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous hydrogen halide solution, separating the distillate from the solution and then treating the same with a copper halide.

6. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous hydrogen chloride solution, separating the distillate from the solution and then treating the same with a copper chloride.

7. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous hydrogen chloride solution, separating the distillate from the solution and then treating the same with a sweetening agent comprising copper sulfate and ammonium chloride.

8. A process for sweetening sour hydrocarbon distillates which comprises treating the distillate with an aqueous hydrogen chloride solution of a concentration of about 0.5–10%, separating the distillate from the solution and then treating the same with a sweetening agent comprising copper sulfate and ammonium chloride.

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