

UNITED STATES PATENT OFFICE

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METHOD OF PURIFYING AND SWEETENING
HYDROCARBONS BY COPPER HALIDESWalter A. Schulze and Frederick E. Frey, Bar-
tlesville, Okla., assignors to Phillips Petroleum
Company, Bartlesville, Okla.No Drawing. Application February 28, 1931,
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14 Claims. (Cl. 196—30)

This invention relates to processes of treating gasoline and other hydrocarbon oils to sweeten the same, and it comprises a process wherein the gasoline or other hydrocarbon oil is treated with solutions of copper compounds in the presence of relatively high concentrations of bromide ions; it more specifically comprises a process wherein gasoline is sweetened with an aqueous solution of copper sulfate and sodium bromide; and it further comprises processes wherein gasoline is treated with solutions of copper compounds in the presence of both bromide and chloride ions.

In our copending application, Serial No. 503,326, filed December 18, 1930, we have described and claimed processes wherein hydrocarbon oils, for example, gasoline, are sweetened with copper compounds in the presence of a relatively high chloride ion concentration. In that application, it is pointed out that the disadvantages inherent in the use of copper compounds are avoided provided the chloride ion concentration of the treating solution as well as the acidity thereof is controlled within certain limits.

We have now found that the sweetening in the presence of copper compounds, proceeds at a somewhat faster rate if bromide ions are present, in fact, we find that adding a soluble bromide such as sodium bromide to the solution of copper sulfate containing sodium chloride as described in the prior application increases the rate of sweetening over that when sodium chloride is used alone.

As is well known, crude gasoline contains appreciable quantities of sulfur compounds, for example, mercaptans, and one of the customary refining operations is the destruction or removal of such sulfur impurities. This process is commonly referred to as "sweetening". A "sweetened" gasoline is "sweet" to the doctor test, in that it shows no discoloration when treated with an alkaline sodium plumbite solution containing sulfur.

Although plumbite solutions are still used to a very large extent as sweetening agents, and this reagent still predominates in the refinery, a number of attempts have been made to utilize copper compounds. Copper oxide and salts of copper have been suggested but results have not been very satisfactory. Reaction products of copper and sulfur compounds, undoubtedly of complex structure and soluble to some extent in gasoline, are sometimes formed. Furthermore, following the directions of prior published processes, the sweetening action is incomplete. When using ammoniacal copper sulfate, one of the sug-

gested reagents, the treated gasoline invariably contains soluble copper compounds. Other copper sweetening solutions such as a mixture of chloride and acetate, will sometimes give a gasoline which is sweet to the doctor test immediately after the treatment but, upon standing in the presence of sodium plumbite and sulfur such a gasoline may develop a strong positive doctor test, thus indicating that there are sulfur compounds still in the gasoline which do not develop a positive doctor test until after standing.

In our prior copending application referred to above, we have overcome the foregoing inherent disadvantages and, as stated therein, employ copper solutions containing relatively high concentrations of chloride ions. Our prior copending application, for example, describes treating gasoline at ordinary room temperature, with an aqueous solution containing about eight percent of copper sulfate and about seventeen percent of sodium chloride.

In the present invention, we use sodium bromide or other soluble bromide in place of the sodium chloride described in the prior application.

More specifically, we treat a sour gasoline at room temperature, say 20° or 25° C., with an aqueous solution containing about thirteen percent by weight of copper sulfate pentahydrate and fifteen to twenty percent by weight of sodium bromide. When using sodium bromide instead of sodium chloride, the sweetening is more rapid and is complete within a minute or two at room temperature. The treated gasoline is permanently doctor sweet and free of copper compounds.

Instead of using sodium bromide alone, we find it advantageous to use a mixture of sodium bromide and sodium chloride and replacement of a part of the sodium chloride, described in our copending application, and indicated above, by sodium bromide decreases the time required for complete sweetening.

Our invention may also be practiced by the direct use of copper bromide and an aqueous solution containing about twenty percent of cupric bromide can be used. However, when using cupric bromide alone, care must be taken that the bromide ion concentration is approximately equal to that in a fifteen percent to twenty percent sodium bromide solution which means that the concentration of copper bromide should be in the neighborhood of twenty percent. Mixtures of cupric chloride and cupric bromide are also suitable and the sweetening is somewhat more rapid than when cupric chloride alone is used.

In the event that cupric bromide is used in much lower concentration than that given above, additional sodium bromide should be added to the treating solution so that the bromide ion concentration is approximately equivalent to that in a fifteen to twenty percent sodium bromide solution. The copper concentration in the treating solution can vary over rather wide limits, from, for example the chemical equivalent of the mercaptans to be destroyed up to fifteen or twenty percent, and in fact, good results are obtained when the treating solution contains but one percent of copper sulfate and fifteen percent of sodium bromide. It is understood of course that the most economical copper concentration, as well as the bromide ion concentration will be determined for any particular gasoline to be treated. Aside from considerations of expense, the copper concentration can vary widely.

Various methods of mixing the treating solution with the gasoline can be used. Briskly agitating the two together is satisfactory, although somewhat better results are obtained if the gasoline is allowed to issue from atomizers in the lower part of a body of treating solution. As the gasoline passes upward through the solution, it assumes a fine state of dispersion, and good contact of gasoline and treating solution is easily obtained in this manner.

The volumetric ratio of treating solution to gasoline can vary over wide limits, but when using ratios in the neighborhood of but one volume of solution to five or more of gasoline, better results are obtained if the acidity of the solution is kept between neutrality and one hundredth normal. Undesirable acidity tends to develop when high ratios of gasoline to treating agent are employed, as well as when very low concentrations of copper, in the neighborhood of one percent, are used in the treating solution. In all cases, in our process, we work on the neutral or acid side and do not use alkaline copper solutions. A detrimental excess of acid is easily overcome by adding sufficient alkaline material such as sodium hydroxide to the treating solution when the acidity appears to approach the upper limit stated. Acidity in excess of that stated is to be avoided, since it slows up the sweetening action, or even renders it incomplete. Our treating agent works best in neutral or slightly acid solutions. If desired, the acidity of the treating solution can be controlled by adding a buffer substance such as sodium phosphate and a little mineral acid, say hydrochloric, which will keep the acidity of the solution within desired limits. The use of buffer substances to control acidity is a common and well understood procedure.

During the sweetening treatment with copper solutions containing bromide ions as described above, we find it advantageous to introduce air or oxygen into the solution, while the sweetening action is progressing. This helps to regenerate the copper compounds and restore their activity, and when an oxidizing gas is used, little or no control of acidity is required.

After the gasoline or other hydrocarbon oil has been sweetened with cupric bromide, or an aqueous solution of copper sulfate and an alkali metal bromide, the gasoline is then given an ordinary water wash. Sometimes, after the water wash, the gasoline has a yellowish color. We have found that this may be removed by storing the oil after the water wash in the presence of a small amount of water for a few hours, or by

washing the gasoline with an aqueous solution of soluble cyanide such as sodium cyanide.

After the gasoline has been sweetened in accordance with the foregoing, it can be treated with sulfuric acid in ways well known to desulfurize the gasoline. We find that we can get increased desulfurization with sulfuric acid when the acid treatment follows our sweetening process. While the explanation of this is probably obscure, we believe that it is due to the fact that our sweetening process converts the mercaptans in the gasoline to disulfides and that these are more easily removed by the acid than are the mercaptans themselves.

This acid treatment step is carried out in the customary manner. For example, we can agitate the gasoline with about two and one-half pounds of 66° Baumé sulfuric acid per barrel of gasoline, separate off the sludge and then wash the gasoline with water until acid-free. The gasoline may thereafter be distilled.

Although we have more specifically referred to copper sulfate and sodium bromide, it is to be understood that other copper salts as well as other soluble bromides, for example, potassium bromide are, of course, suitable, but generally speaking, we find that from the economical point of view, an aqueous solution containing copper sulfate and sodium bromide is preferable. Generally speaking, the optimum concentration of bromide, whether it be derived from a soluble alkali metal bromide, or from cupric bromide, is roughly equivalent to that contained in a fifteen to twenty percent sodium bromide solution. It is to be understood, however, that we do not expressly limit ourselves to this concentration. Some gasolines may require more or less bromide ion than that stated above.

When treating gasoline or other oils which have received a preliminary treatment with sulfuric acid, it is best to intimately contact such oils with a solution of a cupric salt in strong alkali before sweetening the acid treated gasoline in accordance with the foregoing description. We have found effective for this purpose a solution of five percent copper sulfate in a thirty-five percent sodium hydroxide solution containing a stabilizer such as about three percent of glycerol or five to ten percent of cane sugar. After briefly contacting the acid treated gasoline with such an alkaline copper solution, we then apply our sweetening process as described.

Our invention is applicable to the treatment of cracked gasoline, kerosene and other hydrocarbon oils, natural gasoline, gaseous or liquefied natural gas, and various hydrocarbon gases containing sulfur, and the term hydrocarbon fluid in the appended claims as intended to be comprehensive. The removal of hydrogen sulfide from a gas containing the same, can be achieved by the use of our treating solution by passing the gas through the solution in any one of a number of ways. It is advantageous, for example, to allow the gas and treating solution to flow in counter-current relation in a tower. Our treating solution destroys the hydrogen sulfide yielding elementary sulfur. When treating gases containing mercaptans, the organic disulfides formed as reaction products when using our treating agent, are not highly volatile and can be extracted from the gas by the use of an absorbent oil. This for instance can be done by floating the absorbent oil on the surface of the body of treating solution through which the gases pass.

After use, the cupric sweetening solutions can

be regenerated by simply blowing air there-through or by adding if necessary a copper salt thereto and adjusting the bromide ion concentration and acidity in accordance with the foregoing requirements. When regenerating the spent cupric solution with air or oxygen, it is best to work at a temperature of around 50° C. The regeneration of cupric chloride solutions is rapid at lower temperatures, but when regenerating cupric bromide solutions, we have found that moderately elevated temperatures give better results. The regeneration may also be accelerated by using air enriched with oxygen, air under pressure, or ozonized air. The spent treating solutions can be regenerated for use a number of times, and, after regeneration, are returned to the process.

From the foregoing it is believed that the process may be readily understood by those skilled in the art, and it is apparent that various changes may be made in the steps of the process, without departing from the spirit of the invention, as expressed in the claims.

What is claimed and desired to be secured by Letters Patent is:

1. In the process of removing mercaptans and hydrogen sulfide from fluids containing the same, the step which comprises treating the fluid with an aqueous copper salt solution having a bromide ion concentration approximately equivalent to that in a fifteen to twenty percent solution of sodium bromide.

2. In the process of sweetening hydrocarbon fluids, the step which comprises treating the fluid with an aqueous copper salt solution having a bromide ion concentration approximately equivalent to that in a fifteen to twenty percent solution of sodium bromide and maintaining the acidity of the solution during the treatment below one hundredth normal.

3. The process of sweetening hydrocarbon fluids, which comprises treating the fluid with an aqueous copper salt solution containing bromide and chloride ions in quantity approximately equivalent to that in a fifteen to twenty percent solution of a mixture of sodium bromide and chloride.

4. The process of sweetening hydrocarbon fluids, which comprises treating the fluid with an aqueous copper salt solution containing bromide and chloride ions in quantity approximately equivalent to that in a fifteen to twenty percent solution of a mixture of sodium bromide and chloride, and maintaining the acidity of the copper solution during treatment between neutrality and one hundredth normal.

5. The process of sweetening hydrocarbon fluids, which comprises treating the fluid with an aqueous copper bromide solution having a bromide ion concentration approximately equivalent

to that in a fifteen to twenty percent solution of sodium bromide.

6. The process of sweetening hydrocarbon fluids, which comprises treating the fluid with an aqueous copper salt solution containing bromide and chloride ions the concentration of which is approximately equivalent to that in a fifteen to twenty percent solution of a mixture of sodium bromide and chloride, and maintaining the acidity of the copper solution between neutrality and one hundredth normal.

7. The process of sweetening gasoline, which comprises treating the gasoline with an aqueous solution of copper sulfate and alkali metal bromide, the halogen ion concentration in the solution being approximately equivalent to that in a fifteen to twenty percent solution of sodium bromide.

8. The process of sweetening gasoline, which comprises treating the gasoline with an aqueous solution of copper sulfate and alkali metal bromide, the halogen ion concentration in the solution being approximately equivalent to that in a fifteen to twenty percent solution of sodium bromide, and maintaining the acidity of the solution between neutrality and one hundredth normal.

9. The process of sweetening gasoline, which comprises treating the gasoline with an aqueous solution of copper bromide having a bromide ion concentration approximately equivalent to that in a fifteen to twenty percent sodium bromide solution.

10. The process of sweetening gasoline, which comprises treating the gasoline with an aqueous solution of copper bromide having a bromide ion concentration approximately equivalent to that in a fifteen to twenty percent sodium bromide solution, and maintaining the acidity of the solution between neutrality and one-hundredth normal.

11. The process as in claim 7, wherein an oxygen containing gas is introduced into the copper solution during the treatment of the gasoline therewith.

12. The process as in claim 7, wherein the sweetened gasoline is treated with sulfuric acid to desulfurize the gasoline.

13. The process of sweetening hydrocarbon fluids which comprises treating the fluid with an aqueous copper salt solution containing a total bromide plus chloride concentration approximately equal to the halogen concentration in a fifteen to twenty per cent solution of sodium bromide.

14. The process set forth in claim 3, wherein a gas containing free oxygen is passed into said solution, whereby the latter is regenerated.

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