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PROCESS FOR SWEETENING SOUR HYDROCARBON OIL

Walter A. Schulze and Albert E. Buell, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

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10 Claims. (Cl. 196—29)

This invention relates to the refining of hydrocarbon products and particularly to the refining of petroleum products containing malodorous sulfur compounds of the mercaptan type. More specifically, it relates to the preparation and use of moist solid reagents comprising copper solutions adsorbed on carriers for sweetening "sour" petroleum hydrocarbon products. The invention is of special value and application for the treatment of light petroleum distillates such as natural gasoline, refinery straight run and cracked gasolines, petroleum solvent naphthas, liquefied petroleum gases and the like.

This application is a continuation of application Serial No. 166,022, filed September 27, 1937.

Such unrefined petroleum products contain mercaptans, commonly called "sour" elements, which give the oil undesirable odor, and render it corrosive and unstable. Until recently these compounds have been customarily removed, or altered, by the so-called "doctor" process, a laborious, cumbersome and very uneconomical chemical treatment with alkaline plumbite and sulphur. In some instances, e. g., natural gasoline, the sweetening action has been accomplished through the use of alkaline hypochlorite solutions, but this method, too, has not proved satisfactory in most cases due to the introduction into the oil of undesirable constituents as bad as those originally present. Recently, however, sweetening of certain petroleum products has been accomplished with much improved results through the use of moist solid copper reagents as described in a copending application by Buell, Serial No. 121,908, filed January 22, 1937 now U. S. Patent 2,094,485 granted September 28, 1937.

One of the principal objects of the present invention is to provide moist solid copper reagents of the proper composition for the treatment of the various types of petroleum products.

Another object of the invention is to extend the scope of the solid copper reagent process so that products which could not heretofore be treated satisfactorily with solid copper reagents may now be treated with excellent results.

Still another object of the invention is to provide solid copper sweetening reagents which will rapidly and effectively convert mercaptans to disulfides without appreciable color change of the oil and without decreasing the stability of said oil.

Still another object of the invention is to set forth the proper flow rates for the treatment of the various petroleum oils over the herein described copper reagents, such flow rates being critical with respect to the quality of the sweetened petroleum product as well as to the life of the reagent.

Another object of the invention is to set forth the proper temperature for treatment of the various petroleum oils with the herein described copper reagents, such temperature being critical with respect to the quality of the sweetened petroleum oils.

We have discovered that the composition of the copper reagent plays a most important role in the production of sweetened oils of good color and good stability. As described in the Buell application, Serial No. 121,908, (Patent 2,094,485) moisture is an essential requirement. In addition to this requirement, we have now discovered that there must be a definite relationship between the amounts of adsorbent carrier, copper and chloride contents, and water.

These so-called solid copper reagents are in fact adsorbent carriers impregnated with aqueous solutions comprising the two components, cupric copper and chloride, which are necessary for the sweetening reaction. The solution is held onto the surface of the adsorbent by adsorptive forces and is retained in place so long as the quantity of the solution does not exceed this capacity. Thus, for any given adsorbent there is a maximum amount of treating solution which can be held by a unit portion of the adsorbent. Also, the various adsorbents differ somewhat in their capacity for the treating solution. For example, with 16 to 30 mesh fuller's earth, this capacity is of the order of about 30 cc. of treating solution per 100 grams of fuller's earth and with charcoal of similar size it is about 20 cc. per 100 grams.

We have discovered now that the concentrations of cupric copper and of chloride in this adsorbed treating solution are extremely critical and must be maintained within certain limits in order to obtain sweetened oils which are of good color and gum stability. We have found too that in order to maintain the reagent in an active state, the concentration of cupric copper and

chloride must be kept within the limits prescribed below.

In the preparation of our solid copper reagents we have found that the total weight of copper sulfate and sodium chloride to that of water should be within the limits of about 0.20 to 0.85. The composition of several typical reagents listed below illustrates this point.

Table I

	Per cent by weight			Ratio: $\frac{\text{salts}}{H_2O}$
	Fuller's earth	Copper sulfate plus sodium chloride	Water	
Reagent No. 1	62.4	11.6	26.0	0.45
Reagent No. 2	69.8	5.7	24.5	0.23
Reagent No. 3	84.2	2.8	13.0	0.21
Reagent No. 4	78.3	5.7	16.0	0.28
Reagent No. 5	74.4	11.6	14.0	0.83

The copper sulfate and sodium chloride need not be employed in the ratio of one mol of the former to two moles of the latter but, preferably, less than one mol of cupric copper to more than two moles of chloride. The ratio of chloride to water should be held within the limits of 0.05 to 0.35 as shown by several typical reagents in Table II.

Table II

	Per cent by weight		Ratio: $\frac{\text{chloride}}{H_2O}$
	Chloride	Water	
Reagent No. 1	3.52	26.0	0.14
Reagent No. 2	2.13	24.5	0.09
Reagent No. 6	3.83	17.8	0.22
Reagent No. 7	4.10	13.0	0.31
Reagent No. 8	1.47	26.2	0.06

The treating solution containing the requisite cupric copper and chloride may be prepared, of course, from any soluble salts producing the cupric copper and chloride ions in solution.

If the copper solution on the adsorbent is too concentrated with respect to chloride, i. e., if it has a chloride to water ratio greater than 0.35, the reagent when placed in service for sweetening oils such as vapor recovery gasolines, kerosenes and the like, will cause a decrease in Saybolt color and in gum stability of such oils. With very high chloride to water ratios, hydrochloric acid will be given off the reagent and will contaminate the oil; simultaneously the treated oils will contain soluble copper compounds which cause rapid deterioration of the product and oftentimes it may even react sour to the doctor test.

On the other hand, if the copper solution on the adsorbent is too dilute with respect to chloride, i. e., if it has a chloride to water ratio less than 0.05, the sweetening reaction will be too slow and hence there will be a rapid migration of the copper compounds through the filter bed in the direction of flow of the oil. This migration of the copper is equivalent to spending of the reagent and hence cannot be permitted. Thus, it is imperative that the chloride to water ratio be maintained, as we have discovered, within the limits of 0.05 to 0.35.

The following examples are given as illustrative of the results secured with solid copper reagents when treating several typical oils.

Example I

A sour vapor recovery gasoline from Mid-Continent crude was treated over a copper reagent containing 2.13 per cent chloride and 22.0 per cent water on 16 to 30 mesh fuller's earth, a chloride to water ratio of approximately 0.10. The treated product was completely sweetened, contained no trace of copper, was +30 Saybolt color, and showed no color or appreciable gum formation during two months storage. More than 1000 volumes of the gasoline per volume or reagent were treated without any detectable migration of copper in the reagent bed.

On the other hand, when some of the same vapor recovery gasoline was treated with a copper reagent having a chloride to water ratio of approximately 0.40, the treated product was only +16 color and showed appreciable gum formation during a short storage period. Similarly, when a copper reagent having a chloride to water ratio of approximately 0.03, the treated product contained copper and showed rapid deterioration in color and gum stability during a few days storage. At the same time it was noted that much of the copper migrated through the bed and was carried out with the gasoline.

Example II

A sour kerosene of 43.6° A. P. I. gravity and a mercaptan sulfur content of 0.024 per cent was treated with a copper reagent comprising by weight 0.87 per cent cupric copper, 2.13 per cent chloride, 1.37 per cent sodium, 1.31 per cent sulfate, 24.5 per cent water and 69.82 per cent 16 to 30 mesh fuller's earth. This reagent has a chloride to water ratio of 0.09. At a treating rate of 3 volumes per hour per volume of reagent the product was 28 to 29 color, was entirely free of copper and was stable in storage. A reagent with a chloride to water ratio of 0.37 gave an extremely yellow product of very undesirable characteristics. Also, a reagent with a chloride to water ratio of 0.04 gave both an unsatisfactory product and unsatisfactory service.

In the conversion of mercaptans to disulfides by means of oxygen from the air and these catalytic solid copper reagents, water is formed in an amount proportional to the percent of mercaptan sulfur in the sour oil. This water of reaction, if in excess of that soluble in the oil, will be left in the reagent and will dilute the copper solution adsorbed thereon. Moreover, since most of the sweetening is done in the initial portion of the reagent bed, most of the dilution will occur first in this section instead of being uniformly distributed throughout the filter bed. If an oil is very high in mercaptan content, considerable dilution of the solution on the reagent will take place and periodically the solution will need concentration. On the other hand, if the oil is very low in mercaptan content, it may actually extract water from the copper solution on the adsorbent and tend to make the solution too concentrated. When a reagent is used in such service, it is frequently diluted so as to maintain the chloride to water ratio within the proper limits.

We have found too that the chloride to water ratio may be more readily maintained and that less migration of the copper takes place through the filter bed when salts which readily form hydrates are added to the treating solutions along with the cupric copper and chloride. Examples of such substances are sodium sulfate, magnesium sulfate, calcium chloride and the like.

We have discovered too inasmuch as the various oils show varying degrees of stability that much improved results may be obtained during sweetening with solid copper reagents if the reagents are selectively chosen for the particular stocks to be treated. For example, we have found that for extremely unstable stocks, best results may be secured through the use of reagents having a chloride to water ratio near the bottom of our prescribed limits i. e., 0.10 to 0.05, whereas for the exceptionally stable stocks extremely satisfactory and most economical results may be obtained through the use of reagents having a chloride to water ratio near the top of our prescribed limits, i. e., 0.35 to 0.25. For example in the treatment of natural gasoline, the chloride to water ratio of the new treating reagent may be 0.25 to 0.35, for refinery straight run gasoline it may be 0.25 to 0.15, for vapor recovery gasoline, kerosene and heavy naphthas it may be 0.05 to 0.15. It is obvious from these figures that the reagent for treating natural gasoline requires less attention to maintain it in the proper range than the reagent for the straight run gasoline and the straight run gasoline less than the reagent for the vapor recovery gasoline or kerosene.

Since vapor recovery gasolines and kerosenes are representative of the unstable oils treated by the solid copper reagents, particular attention is directed to the variables which influence the treatment of these stocks. As stated above, it is preferable to use reagents with the chloride to water ratio in the lower range, the reagents in the higher ranges causing some color loss. Two other important factors are the flow rate and the temperature as illustrated in Table III.

Table III

	Ratio: $\frac{\text{chloride}}{H_2O}$	Flow rate, volumes per hour	Temperature °F.	Color
Kerosene A	0.09	4.2	76	+29½
Do	0.09	2.3	76	+28½
Do	0.09	4.2	106	+24−
Do	0.09	3.3	97	+26+
Do	0.21	3.0	77	+20
Do	0.21	6.0	77	+22

All of the fractions were completely sweet, did not contain any copper and were quite stable in storage. Nevertheless, it is quite obvious that the most desirable results were secured from the reagent with the 0.09 chloride to water ratio. Likewise the higher the operating temperature, with the flow rate and reagent composition being constant, the greater the color loss during treatment. Also, with the temperature and the reagent composition unchanged the color loss decreased with an increased flow rate. When treating with the reagents having a low chloride to water concentration, e. g., 0.09, the preferred flow rate is two to three volumes per hour per volume of reagent with a maximum of about five or six volumes per hour. At higher flow rates rapid deterioration of the reagent occurs during the treatment of heavy oils such as kerosenes or heating oils. Also, the oils may be contaminated with copper compounds.

Treating temperatures of 70 to 90° F. are preferred, although higher or lower temperatures may be used. If higher temperatures are to be employed with a relatively color unstable stock, then the reagent employed for treating this stock should have a lower chloride to water ratio than the one which could be used at a lower operating temperature.

These solid copper sweetening reagents during use may be maintained within the proper limits of chloride to water either in situ or by removing from the towers and readjusting in the proper direction.

We claim:

1. A process for sweetening sour hydrocarbon oils relatively unstable with respect to color and gum formation comprising admixing air with said oils and passing them in contact with a solid sweetening reagent comprising a solid adsorbent carrier impregnated with a solution of a cupric salt and a soluble chloride, the chloride to water weight ratio of said reagent being maintained within the limits of from 0.05 to about 0.25, and containing between 13 and 26 per cent water.

2. A process for sweetening kerosenes and heavy naphthas which comprises passing said stock admixed with air over a solid sweetening reagent comprising a solid adsorbent carrier impregnated with a solution of a cupric salt and a chloride, the chloride to water ratio of said reagent being between 0.05 and 0.15, and containing between 13 and 26 per cent water.

3. A process for sweetening sour hydrocarbon oils relatively unstable with respect to color and gum formation which comprises passing said oils admixed with air in contact with a solid sweetening reagent comprising a solid adsorbent carrier impregnated with a solution of a cupric salt and a soluble chloride, said reagent having a chloride to water ratio between the limits of 0.05 and 0.35 and a total salt to water ratio between the limits of about 0.20 and 0.85, and containing between 13 and 26 per cent water.

4. In a process for sweetening sour hydrocarbon oils relatively unstable with respect to color and gum formation by means of a solid sweetening reagent comprising a solid adsorbent carrier impregnated with a solution of cupric chloride, the improvement comprising maintaining the chloride to water ratio of said reagent between the limits of 0.05 and about 0.25 and the water content between 13 and 26 per cent.

5. A process for sweetening sour hydrocarbon oils relatively unstable with respect to color and gum formation which comprises passing said oils admixed with air over a solid sweetening reagent comprising a solid adsorbent carrier impregnated with a solution composed of cupric copper, a chloride and magnesium sulfate, said reagent having a chloride to water ratio between the limits of 0.05 and 0.25, and containing between 13 and 26 per cent water.

6. A process for sweetening sour hydrocarbon oils relatively unstable with respect to color and gum formation which comprises passing said oils admixed with air over a solid sweetening reagent comprising a solid adsorbent carrier impregnated with a solution composed of cupric copper, a chloride and calcium chloride, said reagent having a chloride to water ratio between the limits of 0.05 and 0.25, and containing between 13 and 26 per cent water.

7. In a process for sweetening sour hydrocarbon oils relatively unstable with respect to color and gum formation by means of a solid sweetening reagent comprising a solid adsorbent carrier impregnated with a solution of a cupric salt and a chloride, the step of maintaining the water content between 13 and 26 per cent and the chloride to water ratio of said reagent between the limits of 0.05 and 0.25 by the addition to the copper salt treating solution of an inorganic salt capable of forming hydrates and selected from

the group consisting of sodium sulfate, magnesium sulfate, and calcium chloride.

8. A process for sweetening a sour hydrocarbon oil which comprises passing such an oil in admixture with free oxygen over a solid sweetening reagent comprising a solid adsorbent carrier impregnated with an aqueous solution containing between 13 and 26 per cent water and containing cupric ions, a soluble chloride, and an amount of an inorganic salt of a metal of non-variable valence, capable of forming a crystalline hydrate in which is incorporated water of crystallization and selected from the group consisting of sodium sulfate, magnesium sulfate and calcium chloride, sufficient to effect a stabilization of the water content of said solid reagent.

9. In a process for sweetening a sour hydrocarbon fraction by passing said fraction over a solid copper sweetening reagent in admixture with sufficient free oxygen to maintain the activity of said reagent, said reagent comprising an adsorbent carrier impregnated with an aqueous solution containing cupric ions and chloride ions, the improvement which comprises maintaining the composition of said reagent such as to comprise between about 60 and 85 per cent by weight of granular adsorbent material, a weight ratio of chloride to water between about 0.05 to 0.35, and a molar ratio of copper to chloride of not more than 0.5.

10. An improved process for sweetening a hydrocarbon oil which is both sour and relatively unstable with respect to color and gum formation, which comprises treating said oil in the presence of free oxygen and a solid copper sweetening reagent comprising a solid granular adsorbent material on which is adsorbed an aqueous solution containing cupric ions and chloride ions, and maintaining the composition of said solid reagent such as to comprise between about 60 and 85 per cent by weight of granular adsorbent material, a weight ratio of chloride to water between about 0.05 and 0.25, and a molar ratio of copper to chloride of not more than 0.5.

WALTER A. SCHULZE.
ALBERT E. BUELL.