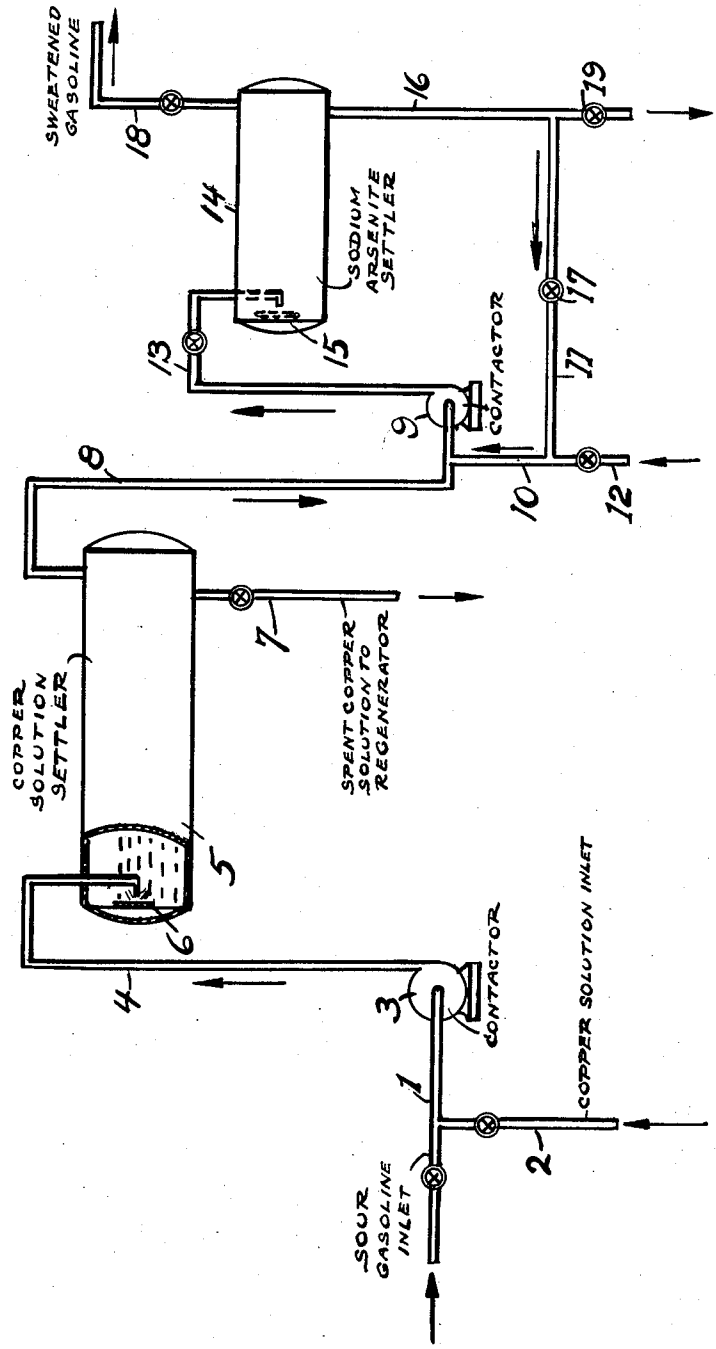
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PROCESS OF REFINING PETROLEUM OILS

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## PROCESS OF REFINING PETROLEUM OILS

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6 Claims. (Cl. 196—30)

This invention relates to a method of treating petroleum oils to improve their stability. It is particularly applicable to the stabilization of hydrocarbon oils which have been treated or sweetened by means of chemical reagents containing copper.

The elimination of mercaptans from petroleum distillates, e. g., gasoline and kerosene, is effected often by employing certain metal salts, and of these, copper salts are particularly effective. However, after treatment with a copper reagent, the treated oils tend to retain small amounts of copper in the form of dissolved or entrained salts, and this copper tends to act catalytically in causing deterioration of the oil, evidenced by the formation of gum (resinous) compounds and color bodies.

In accordance with the present invention, it has been found that the hydrocarbon distillates treated or sweetened by reagents containing copper are effectively freed of copper and thus stabilized by treatment with salts of arsenic acids, particularly basic metal salts of arsenious acids, which may be termed arsenites. The arsenite may be prepared by neutralizing a solution of arsenious acid with a basic metal hydroxide, e. g., sodium hydroxide to form sodium arsenites having the compositional formulae such as $NaAsO_2$, $Na_3AsO_3$, and $Na_4As_2O_5$, or $Na_2As_4O_7$.

A copper treated petroleum oil stock may be intimately contacted with the arsenite solution in an orifice column, centrifugal pump or other suitable mixing device. Another method of obtaining intimate contact between the agent and the copper treated oil is by the use of a carrier, such as clay or fire brick, impregnated with a solution of the arsenite reagent. The copper treated oil may be percolated through a bed of the adsorbent carrier impregnated with the arsenite.

It has been shown that many copper salts which are formed in the copper treating, e. g., copper naphthenates, are soluble in the oil layer; however, the chemical reaction occurring in using the arsenite agent results in a formation of salts which are substantially insoluble in the oil and which may be separated readily therefrom. In some instances, as in the treatment of distillates higher boiling than gasoline, it is preferred to carry out the copper removal operation with the arsenite reagent in the liquid phase so as to form stratified layers, in which the aqueous layer contains the product which may be separated more readily from the oil. This latter procedure may be employed in treating either gasoline or higher boiling distillates such as kerosene.

To illustrate the invention, the following examples are presented:

*Example 1*

A sample of cracked gasoline was sweetened by treatment with copper chloride in a liquid phase to yield a sweetened product which, after water washing and paper filtering, contained copper as indicated by the diphenylthiocarbazone color test. Subsequent treatment of this product with 2% by volume of 10% sodium arsenite produced a copper-free sweet product.

*Example 2*

A sample of cracked gasoline containing added naphthenic acids boiling in the heating oil range was copper chloride treated to yield a sweetened product containing a substantial amount of copper according to the diphenylthiocarbazone color test. This product was found to become definitely degraded in color due to the formation of copper naphthenates in the sweetening. Subsequent treatment of the sweetened product with 2% by volume of 10% sodium arsenite produced a copper free stock and restored to the gasoline its original color prior to the addition of the naphthenic acids. The sodium naphthenates formed as an interface layer between the oil and the treating reagent. This interface layer may be separated and acidified to recover naphthenic acids.

The amount of the arsenite to be employed depends upon the concentration of the copper and the sweetened oil and, in general, the amount required is very small, being of the order of a small fraction of 1% of the oil treated, as, for example, 0.5% to about 0.1%. The use of sodium as the metal constituent of the arsenite is economical, but other alkaline base metals or cation constituents having similar reactivity may be used, as for example, potassium, and the like. The preferred arsenites are those that are more water-soluble.

In the accompanying drawing is illustrated diagrammatically a suitable apparatus and plant set-up for the practice of the invention.

Referring to the drawing, a sour petroleum distillate, such as gasoline, naphtha or other distillate containing mercaptans, is fed into the system through inlet line 1 and is mixed with the copper treating solution from inlet 2 by means of a suitable mixing device such as a centrifugal pump 3 which brings about intimate

mixing and contact. From the mixing device 3, the mixture is led by line 4 into the copper solution settler tank 5 wherein the mixture is sprayed against baffle 6, and an aqueous layer of spent copper solution is settled to the bottom of the tank to be withdrawn through the drain-pipe 7. The copper sweetened oil forms an upper layer in the settler and is withdrawn therefrom through line 8 to the centrifugal pump contactor 9, wherein it is co-mingled intimately with arsenite solution led into the contactor from line 10, said solution containing the required amount of fresh arsenite to replace the amount of arsenite which is not recirculated through line 11, the fresh arsenite being led into the system through line 12. From the contactor 9, the mixture of copper treated oil and arsenite solution is led by line 13 to the settler 14, wherein the mixture is discharged against baffle 15, then permitted to settle and separate into an aqueous layer containing dissolved reaction products of the copper salt and the arsenite. The settled aqueous solution is withdrawn from the bottom layer into settler 14 by line 16 and a portion thereof may be recycled through line 11 and control valve 17, while remaining portions of the spent treating solution are removed from the system through valve controlled line 19. The sweetened product substantially freed of copper is withdrawn from the upper layer of oil in the arsenite treating settler through the valve controlled outlet line 18.

Although the copper removal treatment of this invention is well adapted for a continuous operation, it may be used in making a batch treatment, also. The arsenite treatment may be applied in conjunction with any other treatment of an oil contaminated by copper-containing impurities, as for example, after a washing or filtration. Not only is it useful in purifying an oil after a copper sweetening treatment, but it may be applied in purifying hydrocarbon oils of all characters, lubricants or fuels, which have become contaminated in handling or use by copper-containing impurities.

It is not intended that the invention be limited to the specific examples which have been given for the purpose of illustration, but it is intended that all modifications coming within the spirit of the invention be included in the scope thereof as defined in the appended claims.

I claim:

1. In a process of sweetening hydrocarbon distillate oils containing mercaptans with copper salts forming sweetened products containing small amounts of copper deleterious to the stability of the oils, the improvement which comprises treating the sweetened oil product containing the copper with an alkali metal salt of aresnious acid, and separating from the sweetened oil decomposition reaction products formed from the reaction of copper compounds with said salt.

2. In a process of sweetening a light petroleum distillate containing mercaptans whereby a small amount of copper compounds remain in the sweetened distillate product, the improvement of removing final traces of copper-containing substances from said product which comprises washing said product with an aqueous solution of sodium arsenite.

3. A process for treating a petroleum distillate containing naphthenic acids and mercaptans, which comprises treating the oil with a copper chloride treating agent to form a sweetened oil, separating the sweetened oil from spent treating agent, treating the sweetened oil with an aqueous solution of sodium arsenite, and separating from the oil a solution of sodium naphthenates, and copper-containing impurities.

4. A process for treating a cracked gasoline containing mercaptans, which comprises sweetening the gasoline with a copper compound and thereafter removing copper impurities from the gasoline by treating the sweetened gasoline with a water-soluble arsenite.

5. In a process of sweetening a light petroleum distillate containing mercaptans whereby a small amount of copper compounds remain in the sweetened distillate product, the improvement of removing final traces of copper-containing substances from said product which comprises washing said product with an aqueous solution of potassium arsenite.

6. A process for treating a petroleum distillate containing naphthenic acids and mercaptans, which comprises treating the oil with a copper chloride treating agent to form a sweetened oil, separating the sweetened oil from spent treating agent, treating the sweetened oil with an aqueous solution of potassium arsenite, and separating from the oil a solution of potassium naphthenates, and copper-containing impurities.

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