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## TREATMENT OF GASOLINE

Jacque C. Morrell and Wayne L. Benedict, Chicago, Ill., assignors to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This application is a continuation-in-part of our co-pending application Serial No. 65,411, filed February 24, 1936.

This invention relates more particularly to the treatment of gasolines or naphthas which contain sufficient amounts of reactive mercaptans and similar compounds to show a positive reaction by the so-called "doctor" test, or the so-called "sour" distillates.

In a more specific sense, the invention has reference to a new and improved process for treating sour gasolines in either liquid or vapor phase or during distillation, whereby many of the disadvantages inherent in the sweetening of gasolines by the ordinary sodium plumbite-sulfur and the various hypochlorite processes are overcome to a great extent.

Methods of treatment of sulfur-containing gasolines, and particularly cracked gasolines, for the purpose of improving their odor have been proposed since a very early date in the petroleum refining industry. The efficacy of such treatments depends upon the fact that the foul-smelling mercaptans which may be present in very small percentages are converted into soluble organic disulfides which are substantially odorless. Ordinarily, by the methods of sweetening commonly practiced there is no material reduction in total sulfur content as a result of such treatments unless there is some hydrogen sulfide present. In the following paragraphs some of the disadvantages of the more commonly used sweetening processes will be briefly outlined to serve as a basis for comparing the present process with the prior art on this subject.

The oldest known sweetening method is that involving the use of alkaline solutions of sodium plumbite to form soluble lead mercaptides which are then precipitated, after removal of the plumbite solution, by the addition of regulated and minimum quantities of powdered sulfur, to convert the lead mercaptides into black lead sulfide and simultaneously to convert the mercaptans into the corresponding dialkyl disulfides. Some of the disadvantages of this method are that it must be conducted in liquid phase at ordinary atmospheric temperatures, that the plumbite solutions are inconvenient to prepare, that relatively concentrated sodium hydroxide of the order of 30% is commonly used which is a hazard to operators, that emulsions may be encountered, and that the addition of sulfur after agitation with plumbite must be done with caution since any excess over that required for the precipitation of the lead dissolved in the gasoline, increases the sulfur content and renders the gasoline unstable. Furthermore, the so-called "break" on the addition of sulfur is sometimes slow and much time is necessary to insure complete precipitation. In addition to the foregoing disadvantages, it has recently been found in many cases that the presence of any appreciable quantities of disulfides or free sulfur, or particularly the combination of both substances, predisposes the treated product to color and haze instability when exposed to ordinary illumination. Many other treatments to sweeten cracked gasoline are objectionable merely because of undesirable reactions.

It is recognized that a considerable number of processes and methods have been proposed to overcome some of the disadvantages of the treatments mentioned and that a considerable number have aimed to operate in vapor as well as liquid phase. The present invention stands as a contribution to the art of sweetening gasolines or naphthas and particularly cracked gasolines, and may be operated in either vapor or liquid phase though usually the latter is the simplest and most practical.

In one specific embodiment, the present invention comprises the treatment of sour gasolines for the conversion of mercaptans by contact with solid granular materials comprising as their active ingredients members of the class of compounds known generally as copper-ammonium complexes.

Within the concepts of the present invention the term "copper-ammonium" complex is taken to mean those compounds produced by the interaction of either anhydrous ammonia ($NH_3$) or ammonium hydroxide ($NH_4OH$) on cupric salts. In these compounds there are no negative ions combined with the ammonia, and the sweetening action is due to the oxidizing effect of the cupric salts, which are reduced to the cuprous state and may be reoxidized to regenerate the activity of the contact material.

According to the present invention, it is proposed to utilize these complexes preferably deposited on or admixed with relatively inert spacing or carrying materials, in either liquid or vapor phase operations, in which sour gasolines are either percolated cold through stationary granular beds of treating reagent or distilled through towers packed with prepared treating materials.

The complexes themselves and their mixtures with inert carriers may be prepared conveniently

by several methods, the simplest of which is to add ammonium hydroxide to a solution of copper salt in proper quantities to form the complexes, and then either carefully evaporating to obtain the complex as a residue or absorbing the same from solution by the use of an adsorbent granular material such as silica gel, kieselguhr, fuller's earth, clay, bauxite, greensand, etc. Suitable sweetening composites may also be manufactured by intimately mixing finely ground copper salts and an adsorbent earth such as, for example, fuller's earth or kieselguhr and then merely contacting the mass with pure anhydrous ammonia. It is preferable to employ carriers in connection with the present type of treating materials to prevent agglomeration and to improve the structure of composite particles in addition to exposing more effective treating surface.

A number of cupric salts are known to form a variety of addition compounds with ammonia. One of the most familiar of these compounds is produced by adding ammonia to a solution of copper sulfate, the blue solution being due to the presence of a salt having the formula $CuSO_4.4NH_3.H_2O$. These solutions may be evaporated in the presence of carriers such as those already mentioned or the compound may be absorbed from concentrated solutions thereof by adding a granular and relatively inert material thereto. Cupric chloride forms a number of compounds with ammonia such as those listed below:

| | |
|---|---|
| Cupric di-ammino chloride | $CuCl_2.2NH_3$ |
| Cupric tetraammino chloride | $CuCl_2.4NH_3$ |
| Cupric pentammino chloride | $CuCl_2.5NH_3$ |
| Cupric hexammino chloride | $CuCl_2.6NH_3$ |
| Monohydrate cupric tetrammino chloride | $CuCl_2.4NH_3.H_2O$ |
| Dihydrate cupric tetrammino chloride | $CuCl_2.4NH_3.2H_2O$ |
| Tricupric decammino chloride | $3CuCl_2.10NH_3$ |

Cupric bromide and cupric iodide form series which are completely analogous to the one given above for the cupric chloride. These salts obviously will have valuable sweetening effects on sour gasolines of different origin and the compounds themselves have varying properties in regard to stability and volatility so it is not intended to infer that all the alternative sweetening materials are exact equivalents in their sweetening action. As a rule the compounds of cupric chloride are the most practical to use since they are very effective and the cupric chloride is cheaper than the corresponding bromide or iodide.

In the majority of instances the present process is most conveniently practiced by simply pumping a sour distillate through a bed of treating material in liquid phase at a rate consistent with proper sweetening. Ordinary temperatures usually suffice but elevated temperatures and pressures may be employed if found necessary or advantageous. In some instances treatments may be conducted under mixed phase conditions. The operation of pumping a sour distillate through a bed of granular material in order to sweeten it is about the simplest procedure that could be proposed, and constitutes a definite improvement over the various methods of sweetening which employ aqueous solutions of salts of copper and other materials.

In the case of vapor phase treatments some precaution may be necessary in conducting treatments by the preferred treating reagents in regard to the temperature selected since some decompose at moderately elevated temperatures and if found necessary the oil vapors to be treated may be passed over the contact mass at a sub-normal temperature by the use of vacuum. The exact temperature employed will in practically all cases be a matter of trial on account of the various factors involved.

Obviously the present process may not effect a complete treatment of certain distillates, particularly cracked distillates which may require as a preliminary step the use of sulfuric acid or an equivalent type of treatment to selectively remove gum-forming olefins though in some instances the distillates may be sufficiently sweetened and stabilized by the use of an inhibitor after the sweetening treatment. It is sometimes necessary to employ a reactant precipitant to eliminate dissolved copper mercaptides from distillates treated by the present process. Such may include hydrogen sulfide itself or aqueous or alcoholic amonium sulfide or ammonium polysulfide. The ammonium sulfides including the polysulfides are preferred. The need for this supplementary washing and precipitating will be readily determinable after the treatment of any particular gasoline boiling range distillate. Another method of ridding the treated distillates of dissolved copper mercaptides is to expose them to sunlight or other equivalent radiant energy such as, for example, ultra-violet light. Under these conditions the copper precipitates either as oxide or sulfide and leaves soluble organic sulfides which are colorless and odorless. The copper precipitates may be either settled or filtered from the treated stocks, and a convenient method of operation is to pump the treated materiel either after use of a chemical precipitant or a source of illumination through a bed of fuller's earth or other equivalent filtering material to finish the treatment.

The following example illustrative of the results obtainable by the use of the present process is introduced to assist in indicating the useful character of the invention though not with the intent of limiting its scope only to the data presented.

A copper-ammonium complex was formed by passing ammonia through a warm solution of cupric chloride until approximately four molecules of ammonia had been introduced for one molecule of cupric chloride. This solution was mixed with fuller's earth of approximately 10–30 mesh in an amount so that on evaporation of the water the composite contained approximately 20% by weight of cupric chloride.

This material was charged to a vertical cylindrical treating tower and a sour Mid-Continent West Texas gasoline from a vapor phase fuller's earth treating plant was pumped through in liquid form. The material came through sweetened until about 3500 bbls. of distillate had been pumped per ton of treating reagent, after which the material was revivified by oxidation. It was found that an ammonium sulfide wash was necessary to maintain the color of the effluent but that the doctor test was negative at all times.

The nature and scope of the present invention can be seen from the foregoing specification and limited numerical data introduced although neither section is intended to be unduly limiting.

We claim as our invention:

1. A process for sweetening sour hydrocarbon

distillates which comprises treating the same with a solid adsorbent material having adsorbed thereon an additive compound of a copper salt and ammonia.

2. A process for sweetening sour hydrocarbon distillates which comprises treating the same with a solid adsorbent material having adsorbed thereon an additive compound of copper sulfate and ammonia.

3. A process for sweetening sour hydrocarbon distillates which comprises treating the same with a solid adsorbent material having adsorbed thereon an additive compound of a cupric halide and ammonia.

4. A process for sweetening sour hydrocarbon distillates which comprises treating the same with a solid adsorbent material having adsorbed thereon an additive compound of cupric chloride and ammonia.

5. A process for sweetening sour hydrocarbon distillate which comprises treating said distillate with a solid adsorbent material having adsorbed thereon the complex formed when treating a copper salt with ammonia.

6. A process for sweetening sour hydrocarbon distillate which comprises treating said distillate with a solid adsorbent material having adsorbed thereon the reaction product of a copper salt with an aqueous solution of ammonia.

7. A process for sweetening sour hydrocarbon distillate which comprises treating said distillate with a solid adsorbent material having adsorbed thereon the reaction product of a copper halide with ammonia.

8. A process for sweetening sour hydrocarbon distillate which comprises treating said distillate with a solid adsorbent material having adsorbed thereon the reaction product of copper chloride and ammonia.

9. A process for sweetening sour hydrocarbon distillate which comprises treating said distillate with a solid adsorbent material having adsorbed thereon the reaction product of copper sulfate and ammonia.

10. A process for sweetening sour hydrocarbon distillate which comprises treating said distillate with a solid adsorbent material having adsorbed thereon the reaction product of a solution comprising essentially as its active ingredient a copper salt and ammonia.

JACQUE C. MORRELL.
WAYNE L. BENEDICT.