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PROCESS FOR REMOVING COPPER COMPOUNDS FROM COPPER-SWEETENED HYDROCARBON OIL

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This invention relates particularly to the treatment of the lower boiling naphthas and gasolines produced in the straight run distillation and in the cracking of petroleum though it may also be applied to analogous low boiling distillates produced in the primary distillation of any naturally occurring hydrocarbonaceous materials or in the secondary distillation of their primary tars.

More specifically the invention is concerned with improved methods for treating crude primary gasoline boiling range distillates to render them sufficiently stable and pleasing in appearance and odor from a sales standpoint.

Primary naphthas and gasolines quite uniformly require some type of chemical treatment to eliminate objectionable constituents of a colored, odorous or gummy character. Color has been variously attributed to suspended asphaltic and resinous materials, oxidized hydrocarbons, nitrogen compounds and even to some pure hydrocarbons. The objectionable odors are principally due to sulfur compounds of which the chief offenders are the sulfur alcohols or mercaptans. The gummy or potential gum-forming constituents are heavy hydrocarbon polymers or highly unsaturated hydrocarbons such as conjugated diolefins respectively.

It is the object of chemical treatments to remove sufficient quantities of the groups of impurities mentioned above until they are reduced to a point corresponding to a finished gasoline. The conventional treatment consists in the primary use of sulfuric acid of graded strength to remove unsaturates and to some extent sulfur and nitrogen compounds followed by neutralizing and redistilling to leave high boiling polymers and sludge reaction products as a residue. The application of so-called "sweetening" agents may be practiced either before or after the distillation following acid treatment or may be applied to distillates which have not received any acid treatment. These "sweetening" reagents apparently transform the foul smelling mercaptans into the relatively odorless and stable dialkyl disulfides by chemical reactions involving oxidation with the removal of the mercaptan hydrogen and the condensation of the residual radicals.

The oldest and best known sweetening treatment involves the use of sodium plumbite solutions followed by the addition of minimum amounts of sulfur to precipitate lead from the initially formed lead mercaptides and form the desired organic disulfides. Owing to the numerous operating difficulties attending the use of plumbite such as the tendency to emulsion formation and the danger of having to use too much sulfur to "break" the lead from solution, numerous other sweetening treatments have been proposed and some have attained commercial importance. The use of hypochlorites has been found applicable to certain distillates, principally those of a straight run character and another development has involved the use of copper compounds and it is with improvements in this last named type of sweetening process that the present invention is concerned.

In one specific embodiment the present invention comprises the treatment of copper-sweetened hydrocarbon oils for the removal of color and undesirable dissolved constituents by percolating said hydrocarbon oils through granular material consisting of a double sulfide of sodium and zinc made by fusing together equimolecular proportions of the two compounds.

Owing to the relatively small percentages of compounds involved in the sweetening reactions, the course of copper-sweetening from the chemical standpoint is not entirely certain. In such sweetening processes a large number of copper compounds may be employed either in a dry state or in solution and while in some cases there may be some actual removal of sulfur by combination with copper, there may in other cases be merely the formation of copper mercaptides or a true oxidizing action depending upon the character of the copper salt employed. Cupric chloride as such has given good results or mixtures of a copper salt such as copper sulphate and salts such as the chlorides of sodium, potassium, calcium, magnesium, and ammonium. In order to provide greater contact surface it is advantageous to use earthy or clay-like materials such as fuller's earth with the various copper salts and mixtures thereof with the chlorides mentioned. It is therefore not possible to state exactly what reaction products are present in a copper-sweetened gasoline such as, for example, a cracked gasoline, to cause an increase in color in the treated product, but it has been quite generally observed that this increase in color occurs. There are some indications that it may be due to copper mercaptides and that it may be due in part to oxidized compounds depending upon the copper compounds employed and the conditions of treatment.

It has been determined as a basis for the present invention that exceptionally good results are obtainable in the clarification and decolorizing of copper sweetened gasolines by employing as a

supplementary treatment the filtering or percolation of the sweetened gasoline through granular material consisting of a double sulfide of sodium and zinc, the formula of which may be written: $ZnS \cdot Na_2S$. As already stated, the exact reactions involved in the final decolorizing and stabilizing of sweetened gasolines are not well defined and reliance is therefore placed principally upon the good experimental results which have been uniformly obtained by the use of the present type of double salt. In general better results have been obtained with the double salt than with either substance alone, sodium sulfide being of a soft and soluble character and sphalerite alone being of a dense and compact character so that less effective contact surface is available for a given size particle.

The double sulfide of zinc and sodium may be employed in finely divided condition as a so-called "contact" material which is stirred with gasoline and then filtered off in continuous filters or it may be mixed with about an equal weight of such inert substances as fuller's earth or kieselguhr and used as a tower filler, depending upon the nature of the gasoline to be treated and in some cases the equipment available in commercial plants.

The decolorizing and clarifying of the stocks treated may be due to some extent to mechanical entrainment of finely divided suspended particles but is evidently due principally to reactions of a rather obscure character involving the conversion of dissolved reaction products and particularly copper mercaptides into dialkyl disulfides on the one hand and copper compounds on the other. It is to be noted that copper is below hydrogen in the electro-chemical series and there is a possibility that the initial reactions may involve the replacement of the copper in the reaction products by the zinc or sodium in the double sulfide used with subsequent or concurrent decomposition of the newly formed mercaptides to reprecipitate the metals and regenerate the efficiency of the contact masses.

By the term "chloride of an alkali metal" as used in the above specification is meant the chlorides of sodium and potassium as well as the alkaline earth metals calcium and magnesium and the hypothetical metal ammonium.

The following example is given to indicate the efficiency of the proposed supplementary treatment for copper sweetened gasolines though it is not intended to limit the scope of the invention in exact correspondence therewith.

To manufacture the treating reagent 14 parts by weight of sodium sulfide crystals and 50 parts by weight of finely ground sphalerite were intimately mixed mechanically and heated to 130° C. to a fused mass which had a dark gray color. This material was ground to a powder and mixed with about an equal weight of 30–60 mesh fuller's earth after which it was placed in a vertical filter and used for the secondary treatment of a cracked West Texas gasoline which had been sweetened by means of a mixture of cupric sulfate and ammonium chloride mixed with crushed firebrick. The following table indicates the important effects of the secondary treatment including the change in color and the improvement in the induction period and response to an inhibitor.

Treatment	Color	Induction period	Induction period+.05 % of inhibitor*
		Minutes	
None, sour	10	215	360
Copper sweetened, no sec. treat.	−13	140	205
Copper sweetened, + double sulfide	6	240	335

*A selected wood tar fraction.

The nature of the present invention and its practical aspects are evident from the foregoing specification and the example although neither section is intended to be unduly limiting.

I claim as my invention:

1. A process for removing copper compounds from copper-sweetened hydrocarbon oils which comprises treating the copper-sweetened oil with a double sulfide of zinc and sodium in solid form.

2. A process for removing copper compounds from copper-sweetened hydrocarbon oils which comprises treating the copper-sweetened oil with a metal sulfide in solid form, said sulfide comprising the solid fusion product of zinc sulfide and sodium sulfide.

3. A process for removing copper compounds from copper-sweetened hydrocarbon oils which comprises percolating the copper-sweetened oil through a bed of granular solid material containing a double sulfide of zinc and sodium.

4. A process for removing copper compounds from copper-sweetened hydrocarbon oils which comprises percolating the copper-sweetened oil through a bed of granular solid material containing the solid fusion product of zinc sulfide and sodium sulfide.

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