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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of hydrocarbon distillates and more particularly the copper sweetening of hydrocarbon oils of gasoline boiling range.

The copper-sweetening process has been developed during recent years as an improved method for sweetening hydrocarbon distillates. The method has eliminated or minimized many of the disadvantages inherent in the other sweetening methods which have been widely used in the past, namely, the plumbite sweetening method, hypochlorite sweetening method, etc. The present invention relates to improvements in copper sweetening processes involving the use of solid copper-containing reagents.

In one specific embodiment the present invention relates to a process for sweetening sour hydrocarbon distillate which comprises removing hydrogen sulfide and water from said distillate in a primary treating step by contact with a treating agent consisting essentially of a substantially anhydrous mixture of a polyhydroxy alcohol and an hydroxylamine, separating the distillate, sweetening it in the presence of air with a solid copper-containing sweetening reagent, removing copper from the sweetened distillate, regenerating the aforesaid treating agent by first heating in the presence of steam to remove hydrogen sulfide, then distilling the water therefrom, and finally returning the regenerated treating agent to the aforesaid primary step.

Many hydrocarbon oils, and particularly those of gasoline boiling range, contain hydrogen sulfide in solution, and are, moreover, usually saturated with water. The most common method of removing hydrogen sulfide from gasoline and other hydrocarbon distillates has been by treating them with aqueous solutions of alkali metal hydroxides, slurries of lime, brucite, etc. The removal of hydrogen sulfide prior to copper sweetening is a necessary step since if this is not done, the sweetening reagent is gradually rendered inactive, due to the precipitation of copper sulfide which, under the conditions employed, is not a sweetening reagent.

The removal of water from the distillates prior to sweetening when using solid copper sweetening reagents is of benefit since it has been observed that due to the formation of water in the sweetening reaction, a certain amount of migration of salts through the sweetening mass occurs, followed by their recrystallization at other points in the reagent bed, and this results in channelling so that at intervals the reagent must be removed from the contacting apparatus, thorough-

ly mixed, and returned to the treater. At times sufficient water forms that part of the salts are dissolved out and actually removed from the system and thus their utility is lost. The removal of dissolved water from such distillates prior to copper sweetening tends to minimize salt migration and channelling because the water is partially or completely removed by the dry distillate as fast as it is formed. The amount of water formation can be calculated from the mercaptan sulfur content of the sour distillate and by regulating the water content of the distillate charged, it becomes possible to balance the water removed against that formed and prevent substantial changes in moisture content of the sweetening reagent. It is possible to remove the water formed during the sweetening step substantially completely providing the gasoline contains less than 0.05% of sulfur in the form of mercaptan sulfur.

We have found that the use of a treating agent consisting essentially of a mixture of a polyhydroxy alcohol and hydroxylamine can be used to remove hydrogen sulfide and a major portion of the dissolved water from hydrocarbon distillates. By regulating the amount of treating agent in relation to the amount of gasoline, it is possible to control the amount of dehydration to any desired point. Among the polyhydroxy alcohols useful in this drying operation are ethylene glycol, diethylene glycol, glycerine and the like. The hydroxylamines include mono-, di-, and tri-ethanolamine, the corresponding propanolamines, etc.

Contacting with the mixture is normally carried out at a temperature of approximately 60–120° F. and a pressure of substantially atmospheric or slightly superatmospheric, say of the order of 50–150 pounds per square inch. After being sufficiently saturated with hydrogen sulfide and water, the treating mixture is regenerated in a separate system by being heated to a temperature of approximately 200–300° F., heated steam being usually passed through the hot reagent mixture to drive off hydrogen sulfide. After this step, the flow of steam is stopped and heating is continued to remove moisture. This regeneration step may be carried out in any suitable type of apparatus. The operation is similar and requires apparatus similar to that used for regenerating spent caustic alkali solutions which have been used to remove mercaptans from gasoline. It usually consists of a vertical tower containing plates or trays over which the solution is trickled. A reboiler section in the bottom of

the tower may contain both open and closed steam coils so that the removal of hydrogen sulfide and water can be readily accomplished successively.

After being dried and desulfurized, the distillate is mixed with approximately 2-10 cubic feet of air per barrel and passed over solid copper-containing reagent to effect sweetening. Such a reagent may comprise mechanical mixtures of sodium or ammonium chloride with copper sulfate deposited on a carrier, or may consist of inert carriers impregnated with cupric chloride or other suitable copper sweetening reagents. The distillate is removed from the copper sweetening step and subjected to a final treating step wherein dissolved copper is removed. This may be accomplished by contact with a heavy metal sulfide, or an alkali- or alkaline-earth metal sulfide.

The following example is given to illustrate the usefulness and practicability of our process, but should not be construed as limiting it to the exact conditions given therein.

A Mid-Continent cracked gasoline containing 0.35% mercaptan sulfur and having hydrogen sulfide dissolved therein was contacted in a countercurrent manner with a solution consisting of a mixture of equal parts of ethylene glycol and diethanolamine. The gasoline was separated and found to be free of hydrogen sulfide and water. It was mixed with five cubic feet of air per barrel of gasoline and contacted with a mixture of copper sulfate, ammonium chloride, and pumice. The gasoline was recovered, separated from air and passed over zinc sulfide deposited on pumice to remove dissolved copper. The sweetened gasoline was inhibited and sent to storage and found to meet all market requirements for a gasoline of this quality. A total yield of 50 barrels of gasoline per pound of sweetening reagent was obtained in this manner.

The operation eliminated the use of a sodium

hydroxide treatment for hydrogen sulfide removal, reduced treating expenses because the drying agent could be used over and over again in the process, and extended the life of the sweetening reagent. Before operating according to the manner described, it was necessary to remove the reagent from the sweetening plant and remix it at intervals of approximately 30 days. After the present process was installed, it was necessary to remove the reagent only once every three months. It was observed over this period of time that substantially no change in the moisture content of the sweetening reagent occurred. During periods of operation as previously carried out, a certain amount of the copper reagent was removed from apparatus in solution in the water which accumulated as a result of water formation during the sweetening operation, but after installation of the present process no such loss occurred.

We claim as our invention:

1. In the sweetening of hydrocarbon distillates containing hydrogen sulfide and water by contact with copper-containing sweetening agents which are deleteriously affected by hydrogen sulfide and water, the improvement which comprises treating the distillate, prior to its contact with the sweetening agent, with a substantially anhydrous mixture of an aliphatic polyhydroxy alcohol and an aliphatic hydroxylamine to remove hydrogen sulfide and water therefrom.

2. The improvement as defined in claim 1 further characterized in that said alcohol comprises ethylene glycol.

3. The improvement as defined in claim 1 further characterized in that said hydroxylamine comprises diethanolamine.

4. The improvement as defined in claim 1 further characterized in that said alcohol comprises ethylene glycol and said hydroxylamine comprises diethanolamine.

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