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PROCESS FOR SWEETENING LIGHT HYDROCARBON OILS

Arnold R. Workman, Malverne, N. Y., assignor to Cities Service Oil Company, New York, N. Y., a corporation of Pennsylvania

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This invention relates to improvements in the art of sweetening sour oils and more particularly to the sweetening of sour oils where the sourness is caused by the presence of mercaptans.

Most of the processes now used for the sweetening of such oils, especially light petroleum distillates of the type of straight run, natural and cracked gasolines, and straight run and cracked kerosenes belong to the well-known plumbite and copper sweetening types of processes.

In general the process of the present invention may be regarded as an improvement on the copper sweetening processes presently employed in the art, since it is based on the discovery that sour hydrocarbon distillates containing mercaptans can be effectively sweetened by intimately contacting the sour distillate with cupric phosphate. The process of the present invention differs radically from the commercial copper sweetening processes and avoids many of the disadvantages which they obviously include.

The theory and practice of copper sweetening is decsribed in substantial detail by Conn in "Refiner" for March 1941, pages 53 to 61. This article describes the reactions involved in converting mercaptans into disulfides by the use of copper chloride, and emphasizes the necessity of retaining the hydrochloric acid in the treating agent so that cuprous chloride can be revivified by contact with oxygen. The article furthermore describes the "solid process" and the "liquid" or "solution process," and shows sketches of apparatus of various types for carrying out these processes.

The article by Conn also emphasizes the fact that special materials of construction must be employed in order to handle the corrosive materials including hydrochloric acid, especially in the solution process. The presence of hydrochloric acid is regarded as one of the important disadvantages or evils of present copper sweetening methods because of its corrosiveness of equipment, the necessity of using expensive glass-lined vessels, and the loss of chloride as hydrochloric acid from the treating solution. It seems to be universally regarded in the art as indicated by Conn that halide ions, usually chloride, is necessary in the copper sweetening process. Attention may be directed for example to the recently granted Patents Nos. 2,094,485; 2,111,487; 2,225,847; 2,264,220 and 2,284,271-2-3. Even where copper sulfate is used as the copper salt, it is always the practice so far as known to use about an equal or greater weight of sodium chloride (see the Conn article, page 60, and Patent No. 2,284,273, page 4). Some of the patents relating to copper sweetening refer to the use of copper and other metal salts broadly, such as No. 2,042,050, but copper chloride is stressed.

However, it has been discovered that cupric orthophosphate is unusually effective in the sweetening of sour oils, and that this sweetening may be and preferably is effected in the absence of acid and halogen, and at elevated temperatures.

The features of the present invention will be described in connection with certain specific examples, in which various sour gasolines were sweetened.

Example No. 1

A quantity of crystalline cupric orthophosphate was mixed with about four to five volumes of 10 to 16 mesh pumice, wet with water to cause the phosphate to adhere to the particles of the pumice, and then dried at a temperature of about 300° F. The resulting mixture was placed in a column to form a bed and heated to a temperature of 150° F. by means of a jacket heater. East Texas cracked gasoline containing .0057% of mercaptan sulfur, freed of hydrogen sulfide by washing with caustic soda, was intimately mixed with air and passed slowly into the bottom of the column containing the copper phosphate mixture so that intimate contact was obtained. The gasoline was removed from the top of the column, passed through a cooler, and then treated with a solution of sodium sulfite for the removal of small amounts of copper compounds dissolved in the treated gasoline. The gasoline removed from the column was sweet to the doctor test, although the color of the gasoline was off slightly. The importance of the elevated temperature was shown in a similar run when the column temperature was allowed to drop to 80° to 90° F. and the gasoline coming off changed from sweet to sour.

Example No. 2

A sour straight run gasoline was treated in the same manner and with the same materials as in Example No. 1, and sweetened readily without any loss of color.

Example No. 3

A quantity of crystalline copper orthophosphate was mixed with about one and one half times its volume of fine fuller's earth, and about an equal quantity of asbestos fibers. A straight run gasoline previously washed with sodium hydroxide solution to remove hydrogen sulfide was treated by agitating the phosphate mixture with

the gasoline for a period of fifteen minutes at a temperature of 150° F., after which the gasoline was separated out. The treated gasoline had a good color and was sweet.

Example No. 4

A Coastal cracked gasoline containing .0115% of mercaptan sulfur was treated after washing with sodium hydroxide by intimately contacting it with a slurry of powdered cupric orthophosphate in water at 150° F. The contacting was carried out for fifteen minutes, after which the gasoline was separated from the water slurry and found to be substantially sweet although still containing a small percentage of mercaptan sulphur. The fact that the gasoline was not completely sweetened in this particular test was attributed to the circumstance that the amount of gasoline treated was 2½ times the amount of water slurry and that no air was introduced into the mixture. The water slurry was made up from five parts of the cupric orthophosphate to one hundred parts of water by weight. The influence of air on the treating operation was noted in carrying out a test of the type described in Example No. 1, continuous-type operation, which showed that the gasoline came out slightly sour when the air was shut off.

The improved process of the present invention is not restricted to any particular procedure or apparatus, but may be carried out in apparatus described by Conn or any of the patentees cited above. The turbo- or other type mixers and contactors may be used. The process may be of "liquid" or "solution," "slurry" or "solid" type. Cupric orthophosphate is practically insoluble in cold water and only slightly soluble in hot water, so that the carrying out of the process by the solution type operation may be in reality a combination solution and slurry process, since most of the phosphate is solid and only a small proportion of it dissolved in the water solution. In general, the gasoline or other oil to be treated should be freed of hydrogen sulphide prior to contact with the phosphate and should be treated with alkaline sodium sulphite following the contact, in order to remove any traces of copper or copper compounds and H_2S which may be present or dissolved in the treated gasoline. H_2S or free sulfur may be formed under certain conditions. A filter is advisable between the preliminary caustic treatment settler and the copper phosphate treater, for the removal of traces of suspended caustic. Similarly, the sweetened gasoline after alkaline sodium sulfite treatment, may be passed through a sand and salt filter, as in the usual practice.

The sweetening effect of the cupric orthophosphate and air may be somewhat similar to that of cupric chloride sweetening as far as the reduction of cupric to cuprous copper is concerned, but it is believed that the reactions are substantially different, since no acid is used and none is apparently produced in the operation. Alkaline conditions may be used. It is believed that the phosphate redical is reduced to phosphite with the temporary loss of oxygen, later replaced from the air or other source of free oxygen supplied during the process or in a subsequent regeneration step. Copper and phosphorus have a rather unusual relationship because of the existence of the phosphide and the copper-phosphorus alloys such as the phosphor-bronzes, and it may be that the cupric copper and the phosphate radical are reducible to about the same potential or with about the same ease. The phosphite group has a considerable tendency to be oxidized to the phosphate, but in the absence of air or free oxygen or other oxidizing agent, mild reducing agents such as the mercaptans, prevent the oxidation of phosphite to phosphate. Cupric copper or free oxygen (or both) cause rapid regeneration of the phosphate under neutral or alkaline conditions. A cupric phosphate molecule provides a large structure having many active points for conversion of mercaptans encountered in the contact with the oil.

From tests made with other phosphates, it has been determined that about half the mercaptan surfur content of a gasoline can be converted, where the reduction could only occur in the phosphate group. It has therefore been concluded that the copper present with phosphorus of the phosphate radical has a decided joint catalytic effect in promoting the complete sweetening of sour petroleum distillates. It may be that the cupric orthophosphate is not ionized to any appreciable extent to give free copper ions, and that the compound as a whole acts mostly as a catalyst to make free oxygen useable or supply active oxygen or electrons for the oxidation of mercaptans. The process of the present invention in any case is usually effective for the sweetening of sour distillates and does not depend upon any particular theory which may explain the catalytic action of copper phosphate.

The presence of acid with copper phosphate in the solution or slurry process was found to be a detriment, and to give no better results than a non-copper phosphate or a phosphoric acid solution. This was determined by adding powdered cupric orthophosphate to a 10% phosphoric acid solution and using the resulting mixture in an attempt to sweeten the East Texas cracked gasoline treated in Example No. 1. Some reduction in mercaptan sulphur was obtained but the distillate was still sour and still contained a large proportion of the original mercaptan content. Similar results were obtained with a solution of trisodium phosphate and a 10% solution of phosphoric acid.

Instead of using air for carrying out the process substantially pure oxygen or ozone or other source of free oxygen may be utilized. The amount of either of these materials necessary for carrying out the process is readily determined on the basis of the mercaptan content of the oil to be treated. When air or other relatively inexpensive source of free oxygen is used, it is preferable to employ a substantial excess so as to always maintain all parts of the catalyst in the reaction chamber at substantially maximum activity. Even in the use of substantially pure oxygen, any excess discharged from the reaction chamber can be freed of other gases and recycled.

While cupric orthophosphate is the preferred copper compound for use in the process of the present invention, it is to be understood that other cupric phosphates such as the meta-, hypo-, and pyro- may be used, as well as complex cupric phosphates or double salts. Double metal phosphates may be used, such for example as cupric potassium or sodium phosphates. Cuprous phosphates of course may be used but they are converted to the cupric compounds in the process. Various other modifications may be made in the procedure and conditions of the process without departing from the spirit and

scope of the invention as defined by the claims.

Having described the invention in its preferred form, what is claimed as new is:

1. A process for sweetening petroleum oils containing mercaptans, comprising intimately contacting the petroleum oil to be sweetened with a copper sweetening catalyst consisting essentially of cupric orthophosphate in the presence of free oxygen at a temperature of from about 100° F. to 200° F.

2. A process for sweetening petroleum oils containing mercaptans, comprising intimately contacting the petroleum oil to be sweetened with cupric orthophosphate at a temperature of about 150° F.

3. A process for sweetening petroleum oils containing mercaptans, comprising intimately contactng the oil to be sweetened with a copper phosphate at a temperature of at least about 150° F. in the presence of free oxygen and in the absence of halide and acid.

4. A process for sweetening petroleum oils containing mercaptans, which comprises intimately contacting the oil to be sweetened at a temperature of at least about 150° F. with a copper sweetening catalyst consisting essentially of a cupric phosphate.

5. A process as defined by claim 4 in which said phosphate is cupric orthophosphate.

6. A process for sweetening sour petroleum oils containing mercaptans, comprising passing an intimate mixture of free oxygen and the oil to be sweetened through a reaction zone in intimate contact with a substantially dry contact material including a cupric phosphate as a sweetening agent, and maintaining a temperature in said zone of at least approximately 150° F.

7. A process for sweetening sour petroleum oils containing mercaptans comprising intimately contacting the oil to be sweetened with a sweetening catalyst consisting of a copper phosphate in the presence of free oxygen, and carrying out the sweetening operation in the absence of halide and at a temperature between 100° and 150° F.

8. A process for sweetening light petroleum oil distillates containing mercaptans, comprising intimately contacting the petroleum oil distillate to be sweetened with a cupric phosphate at a temperature of at least about 150° F.

ARNOLD R. WORKMAN.