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PROCESS FOR STABILIZATION OF COPPER TREATED OILS

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4 Claims. (Cl. 196—30)

This invention relates to a new and useful process for treating hydrocarbon oil. More specifically, this invention relates to a process for stabilizing or preventing the deterioration of hydrocarbon oil which has undergone a purifying treatment with reagents containing copper.

Hydrocarbon oil, particularly petroleum distillates usually contain impurities, including sulfur compounds, which cause the oil to exhibit undesirable properties such as bad odor and gum and color formation. It is customary, therefore, to subject said impure oil to a purifying treatment in order to remove the impurities or to convert them to less objectionable forms, for example, the conversion of mercaptans to disulfides.

The methods of treatment for the removal or conversion of mercaptans make use of various chemical processes, and of these processes, one of the most satisfactory is the process utilizing copper, salts of copper, or solutions containing copper salts.

However, subsequent to treatment with copper-containing reagents, it has been found that many hydrocarbon oils require further treatment or stabilization. This condition is due to the fact that said unstable oils retain from their contact with copper reagents, extremely small quantities of oil-soluble copper compounds. These traces of copper compounds remaining in the oil are responsible for the marked acceleration of reactions which lead to the formation in said oil of color, gum, resinous deposits and polymers; these deteriorative changes seriously impair such properties of the oil as color, gum content and octane number.

One object of this invention is to effect the removal of traces of copper compounds from hydrocarbon oils.

Another object of this invention is to prevent the deterioration of hydrocarbon oil which has been treated with copper reagents by the removal from said oil of small amounts of retained oil-soluble copper compounds responsible for aforesaid deterioration.

A further object of this invention is the production of hydrocarbon oil of good color and stable with respect to gum formation subsequent to treatment with copper-containing reagents.

A further object of this invention is the treatment of oil which retains traces of copper compounds subsequent to sweetening with copper reagents, to remove said copper from the oil, thereby delaying or preventing deterioration.

Another object of this invention is to provide a step in the sweetening of hydrocarbon oil with copper reagents whereby the sweetened oil is stabilized against deterioration by the removal therefrom of retained copper salts.

Another object of this invention is the conversion of oil-soluble copper compounds present in hydrocarbon oil as a result of sweetening with copper reagents to oil-insoluble compounds, said conversion resulting in complete separation of the insoluble copper compounds from the oil.

Schulze and Frey in U. S. Patent No. 1,980,555 described a method for stabilizing an oil treated with copper and which exhibited discoloring and/or formation of resinous matter, polymers and oxidation products; that is, a method of stabilizing the oil by bringing it in contact with an alkaline sulphide solution subsequent to treating with the copper reagent.

We have now discovered that copper treated oils may be stabilized by means other than the alkaline sulfide solution referred to above and that these means involve certain improvements and advantages. This discovery is extremely important in that it clearly defines the conditions which must be met to produce stabilized oils. This discovery likewise makes it possible to divide treating agents into two groups, the first group consisting of those reagents which will effectively remove the hydrocarbon oil-soluble copper compounds and thereby stabilize the oil, and the second group consisting of those reagents which will not remove sufficient quantities of the copper compounds to stabilize the oil.

We have found that copper mercaptides increase in solubility in the oil with increasing molecular weight of the mercaptans. Copper methyl mercaptide is the most insoluble of all the copper mercaptides and is almost totally insoluble in hydrocarbon oils. Copper ethyl mercaptide, the next number in the series, is a little more soluble, yet its actual solubility figure is extremely low. Cupper butyl mercaptides and amyl mercaptides are much more soluble and their solubilities may be determined in the usual manner of precise measurements.

We have now discovered that hydrocarbon oil containing copper methyl mercaptide, and therefore completely saturated with respect to the substance, does not show any of the undesirable reactions mentioned above as resulting from the catalytic effect of dissolved copper compounds. In other words, we have established that the concentration of copper from a saturated solution of copper methyl mercaptide in hydrocarbon oil is too low to cause deterioration of the oils. On the other hand, we have found that if the hydro-

carbon is saturated with respect to copper ethyl mercaptide, the concentration of copper is just sufficient to cause a slow depreciation in the said properties of the oil. Thus, we have established that there is a critical value for copper concentration in the oil, above which deterioration will occur, and below which the oil will be stable as regards gum and color formation in storage.

This improved process of stabilization depends on the effective removal of traces of copper compounds from the contaminated hydrocarbon oil by treating said oil to completely convert the hydrocarbon oil-soluble copper compounds into compounds whose solubility is less than the solubility of the copper salt of ethyl mercaptan. By this means, and the subsequent separation of these more insoluble compounds from the hydrocarbon oil, the deterioration due to dissolved copper compounds in the oil is prevented.

Since the deterioration of oil is accelerated in a catalytic manner by dissolved copper salts, it follows that copper salts more insoluble than copper ethyl mercaptide are inactive as catalysts for deteriorative reactions in oil, and likewise possess marked resistance to oxidation processes which would change said insoluble copper compounds to more active forms which would be injurious to the oil.

Oil-soluble copper compounds which may be formed in complex hydrocarbon oil mixtures, particularly in petroleum distillates, are usually mercaptides or salts of acidic components such as cresylic and naphthenic acids. Such compounds may be more soluble than copper ethyl mercaptide, and likewise may not be removed from an oil in which said compounds are dissolved unless the method of treating or stabilization forms therewith copper compounds less soluble than copper ethyl mercaptide. For example, after a cracked naphtha has been in contact with copper oxide, copper carbonate or copper phosphate, sensitive tests show the presence of traces of copper remaining in the naphtha, whereas a portion of the same naphtha after prolonged contact with copper methyl mercaptide shows no evidence of dissolved copper compounds. Further, the small amounts of copper salts present in a cracked gasoline which has been sweetened with a cupric chloride solution may be removed by adding thereto a controlled amount of methyl mercaptan to convert the more soluble copper compounds into the less soluble copper methyl mercaptide. Complete removal of the copper is not effected by treatment of the oil with caustic soda, carbonate or phosphate solutions, or by the addition to the oil of controlled amounts of ethyl mercaptan.

In order to explain more exactly the criterion by which the stabilization of copper-containing oil is judged, the relative solubilities of the copper compounds encountered may be considered.

The sulfides of copper are the most insoluble compounds of the metal. The mercaptides by reason of analogous structure exhibit similar solubilities in water, but are slightly more soluble in oils due to the organic nature of the alkyl or aryl group present in the mercaptide molecule.

The sulfides of copper have a solubility of about 0.00033 gram per liter of water and an infinitesimal solubility in hydrocarbon oils; the solubility of copper methyl mercaptide is approximately 0.000003 gram per liter of cracked naphtha, or about one-hundredth the solubility of copper sulfide in water. These solubility figures are based on extremely sensitive colorimetric tests, especially devised to indicate the presence and concentration of copper in hydrocarbon oil.

The following table shows the approximate solubilities of copper salts in oils, or the extent to which oil-soluble copper compounds are formed by contact of the oils with said copper salts for a 24 hour period.

TABLE I

Copper salt	Hydrocarbon oil	Dissolved copper	Oil-soluble copper compounds, grams per 1000 cc. of oil[1]
		Parts per million	
Copper oxide	Doctor-sweet cracked naphtha	Greater than 1	0.0003 (approximate).
Copper carbonate (basic)	do	do	0.0003 (approximate).
Copper hydroxide	do	do	0.0003 (approximate).
Copper phosphate	do	do	0.0003 (approximate).
Copper cyanide (KCN Sol.)	do	do	0.0003 (approximate).
Copper silicate	do	do	0.0003 (approximate).
Copper sulfite	do	do	0.0003 (approximate).
Copper-n-butyl-mercaptide	do	do	0.0003 (approximate).
Copper-t-butyl-mercaptide	do	10,000	0.300.
Copper-ethyl-mercaptide	do	0.1	0.00003.

[1] Sp. gr. of naphtha taken as 0.75.

It will be seen from the values listed in Table I that complete removal of copper from an oil may not be accomplished by contacting said oil with a reagent to form any of the copper salts listed. This fact is based on experimental data which proves that the deterioration of an oil due to dissolved copper is not prevented unless the copper content of said oil is reduced to a value less than 0.1 p. p. m. as shown in Table II.

TABLE II

Hydrocarbon oil	Dissolved copper	Original color	Color after 7 days' storage	Appearance after 30 days' storage
	Parts per million			
West Texas cracked gasoline	10	+25	—16	Dark brown.
Do	1	+25	—10	Do.
Do	0.1	+25	+12	—16 color.
Do	Less than 0.1	+25	+23	+21 color.
Do	Zero	+23	+23	+21 color.

Thus in order to prevent the deterioration of a hydrocarbon oil which has been treated with a copper-containing reagent, it is necessary to treat said oil in order to reduce the amount of dissolved copper to a value less than 0.1 p. p. m.

This is accomplished according to our invention by converting the copper present in the oil into compounds with oil solubility less than the oil-solubility of copper-ethyl mercaptide.

As examples of the practice of my invention, the following examples are described:

Example I

A sample of cracked gasoline which had been sweetened by treatment with a solution containing cupric chloride was separated from the copper reagent and divided into two parts. One part was stored without further treatment. To the other portion was added a solution of methyl mercaptan in sulfur-free hexane solution, the quantity added being sufficient to cause the gasoline to have a methyl mercaptan content of 0.003 weight per cent. After the addition of the mercaptan, the gasoline was allowed to stand for two hours, after which it was washed with water and stored. The results of this stabilizing treatment are shown below:

Gasoline samples	Copper test	Original color	Color after 7 days' storage	Appearance after 30 days' storage
Cracked gasoline, unstabilized	Positive, greater than 1 P. P. M.	+24	−16	Dark brown, gummy.
Cracked gasoline plus 0.003 percent methyl mercaptan.[1]	Negative, less than 0.1 P. P. M.	+24	+23	+22 color.

[1] This gasoline was doctor sweet; no trace of mercaptan after two days.

Example II

A sample of the same gasoline described in Example I was similarly treated except that the stabilizing reaction was brought about by the addition to one portion of the gasoline of sufficient sour vapor recovery gasoline to amount to 2 per cent by volume. This vapor recovery gasoline contained approximately .01 weight per cent of methyl mercaptan. The results of this stabilization are illustrated below:

Gasoline samples	Copper test	Original color	Color after 7 days' storage	Appearance after 30 days' storage
Cracked gasoline, copper treated, unstabilized	Positive, greater than 0.1 P. P. M.	+24	−16	Dark brown.
Cracked gasoline, copper treated, plus 2 percent (vol.) of sour vapor recovery gasoline.[1]	Negative, less than 0.1 P. P. M.	+24	+23	+22 color.

[1] This gasoline was doctor sweet.

Example III

To a sample of doctor sweet cracked gasoline was added solid copper ethyl mercaptide and shaken until the oil was saturated with the copper compound and an excess remained. Portions of this gasoline were then treated with various reagents to form copper salts less soluble than copper ethyl mercaptide. Samples of each portion of gasoline stabilized with the various reagents were then stored for comparison with a stored sample of the original gasoline and with the original gasoline saturated with copper ethyl mercaptide. The tabulation of results is given below:

TABLE III

No.	Gasoline samples	Copper test	Original color	Color after 7 days' storage	Color after 30 days' storage
1	Cracked gasoline, no additional treatment.	Negative	+24	+22	+21
2	Cracked gasoline, saturated with solid copper-ethyl-mercaptide.	Positive, approx. 0.1 P. P. M.	+24	+16	−10
3	#2 sample, added 0.006 percent methyl mercaptan, followed by water wash.	Negative, less than 0.1 P. P. M.	+24	+22	+21
4	#2 sample, plus 2 percent sour vapor recovery gasoline containing 0.01 percent methyl mercaptan.	Negative, less than 0.1 P. P. M.	+24	+21	+20
5	#2 sample, intimately contacted with alkaline aqueous solution of dithizone.	Negative, less than 0.1 P. P. M.	+24	+22	+21
6	#2 sample, contacted with ammoniacal solution of alpha-benzoinoxime.	Negative, less than 0.1 P. P. M.	+24	+22	+21
7	#2 sample, contacted with aqueous solution of thionalide.	Negative, less than 0.1 P. P. M.	+24	+22	+21
8	#2 sample, contacted with aqueous solution of 5.7-dibromohydroxyquinoline.	Negative, less than 0.1 P. P. M.	+24	+22	+21
9	#2 sample, contacted with ammoniacal solution of diethyldithiocarbonate.	Negative, less than 0.1 P. P. M.	+24	+22	+21

These examples are illustrative of the manner in which deterioration is prevented in hydrocarbon oils containing soluble copper compounds, according to the practice of this invention and the critical value for allowable copper concentration in oil which is stable with regard to color and gum formation in storage is thus disclosed.

We claim:

1. In the treatment of hydrocarbon oil with copper reagents, the steps of stabilizing the treated oil, comprising contacting said oil with a reagent comprising methyl mercaptan, which forms copper compounds having solubilities in the oil below that of copper ethyl mercaptide, and separating said copper compounds from the oil.

2. In the process of sweetening hydrocarbon oil with copper reagents, the step of stabilizing the sweetened oil to prevent deterioration due to retained oil-soluble copper salts which comprises adding a small amount of methyl mercaptan to the said oil to form the less soluble copper methyl mercaptide, and removing the copper methyl mercaptide from the oil.

3. A process for treating hydrocarbon oil sweetened with copper reagents to prevent deterioration due to retained oil-soluble copper salts, which comprises contacting said oil with a sufficient quantity of a reagent comprising methyl mercaptan to reduce the concentration of the copper in the oil below that in a saturated solution of copper ethyl mercaptide.

4. A process for treating hydrocarbon oil sweetened with copper reagents to prevent deterioration due to retained oil-soluble copper salts, which comprises contacting said oil with a sufficient quantity of a reagent comprising methyl-mercaptan to reduce the concentration of the copper in the oil below the critical value of 0.1 part per million.

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CERTIFICATE OF CORRECTION.

Patent No. 2,222,122. November 19, 1940.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, second column, line 41, for "Cupper" read --Copper--; page 2, Table II, in the column headed "Original Color", last line thereof, for "+23" read --+25--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 21st day of January, A. D. 1941.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.