

UNITED STATES PATENT OFFICE

2,527,176

TREATMENT OF OILS CORROSIVE TO COPPER

Charles A. Cohen, Roselle Park, N. J., assignor to
Standard Oil Development Company, a corpo-
ration of Delaware

No Drawing. Application October 4, 1946,
Serial No. 701,087

7 Claims. (Cl. 196-40)

1

This invention relates to the treatment of petroleum hydrocarbons particularly of the white oil type which, during their preparation, have been acid treated to remove undesirable constituents such as olefins, aromatics and the like, and, more particularly, to acid-treated oils which after neutralization and contacting with or percolation through clay are found to be corrosive to copper.

This invention describes a process for the treatment of mineral oil, petroleum products, and process lubricants which are corrosive to the copper strip as described in the Federal Standard Stock Catalog VV-L-791 C, Section IV, Part 5, Method 530.31.

Acid treatment of various petroleum hydrocarbons is a well established art and varies with the character of the particular hydrocarbon and its eventual use. For example, low boiling hydrocarbons from cracked stocks boiling in the gasoline range are treated with small percentages of sulfuric acid varying in concentration from 95-98% for the purpose of removing and polymerizing the more reactive olefinic types of materials and, after caustic washing, the material is generally rerun and cut to specification boiling point. The purpose of this treatment is to remove the gum-forming constituents of the gasoline and improve the storage stability of the product. Desulfurization is generally accomplished at the same time. Higher boiling hydrocarbons, such as kerosene, may be lightly acid treated with weak concentrations of sulfuric acid on order to improve burning quality and odor or may be highly acid treated with strong acids varying from 100% sulfuric acid to fuming sulfuric acid containing 20% by weight of sulfur trioxide. Kerosene treated with strong acids are used as deodorized bases for the preparation of household insecticides. Oils of the white oil type such as medicinal oils, cosmetic oils, transformer oils, refrigerator oils, hydraulic oils, and the like, usually require severe acid treatment and during the process of their refining are subjected to the action of concentrated sulfuric acid varying in strength from 98% to fuming sulfuric acid. Depending on the crude source and the nature of the acid treatment used, these oils when finished may at times be corrosive when tested with the copper strip test.

One of the objects of this invention is to render highly acid-treated petroleum hydrocarbons non-corrosive to copper.

Highly acid-treated oils or white oils are prepared by the drastic acid treatment with sulfuric

2

acid of a hydrocarbon distillate having a viscosity in the range of 30-1000 seconds Saybolt at 100° F. Prior to treatment with fuming sulfuric acid, the oil may be previously solvent extracted, deasphalted, dewaxed, or lightly acid treated to remove certain undesirable constituents. In treating with the acid, it is usual to apply the acid in a number of dumps during which mechanical or air agitation is used. Between successive dumps the mixture is allowed to settle and the sludge drawn-off and discarded. During the process of acid treatment, a substantial quantity of oil-soluble sulfonic acids known as "mahogany acids" are formed and largely remain dissolved in the oil. Prior to finishing the oil, these mahogany acids must be removed either by washing with water or immiscible solvent in the acid state or they may be partially or wholly neutralized with a neutralizing agent such as the oxide, hydroxide and carbonate of the alkali, and alkaline earth metals, and of ammonium, amines, etc., and extracted with water or dilute alcohol in the form of their salts commonly known as "mahogany soaps." The oil after removal of the acidic constituents and after steaming to remove any volatile solvent, if present, but before contacting with or percolation through clay, is known as a "neutral oil." Depending on the initial character of the oil, the strength of the acid used, the temperature of the acid treatment, and the total quantity of acid supplied, the neutral oil will vary in color from about a -10 to a +27 Saybolt color. The colored material remaining in the oil may be hydrocarbon or resinous in nature or may consist of high molecular weight sulfonates which are difficult to remove by ordinary extraction. It is the purpose of contacting with or percolation through clay to remove the last remaining colored material to yield a water-white oil having a Saybolt color of +30 and up. Along with color removal, the oil is improved in taste and odor and other quality specifications such as susceptibility to oxidation and resistance to formation of rancidity when exposed to ultra violet light.

Very often distillates and neutral oils will have a good copper test but on processing the neutral oil with clay a poor copper test develops. In a case of the distillate, the presence of small amounts of organic acids such as naphthenic acid act as passivating materials for the surface of the copper and mask the true corrosive character of the oil. In the case of the neutral oils, the presence of small amounts of sulfonic acids or mahogany soaps act in a similar manner on

the surface of the copper and give the appearance of a non-corrosive oil. Percolation of these neutral oils which removes the inhibitor then yields an oil which is corrosive to copper.

While a number of methods for the correction of bad copper tests have been described, such as the treatment of the oil with metallo-organic compounds, strong caustic, such as alcoholic potassium hydroxide, calcium hydroxide, and the like, these materials have the disadvantage of often causing the oil to go off color and off taste in the medicinal grades.

The major object of this invention is to treat an acid-treated petroleum hydrocarbon either in its neutral state or finished state (that is, after treatment with clay) so as to improve the corrosion test when tested with copper.

I have now found that a satisfactory degree of improvement may be obtained by heating and mixing these neutral oils, which are corrosive to the copper test, with solutions of alkali metal chlorites, particularly sodium chlorite. The alkali metal chlorite is used in an aqueous solution which may vary in strength between .02 and 1.0 weight per cent, preferably 0.1 weight per cent; and is applied to the oil in a volume from 2% to 20%, preferably 10%. The choice of concentration is best determined by the nature of the oil for example, its density, viscosity and tendency to form emulsions. For purposes of my invention, I have found that sodium chlorite obtained commercially is suitable. Other alkali metal chlorites and alkaline earth metal chlorites could be used, but on the basis of cost and availability, sodium chlorite is chiefly employed.

The time necessary to complete the reaction is considerably shortened by the use of increased temperature. I have found that a temperature of from about 40° C. to above about 100° C. is adequate, however, a temperature of 80° C. appears most practical. If, however, more rapid separation is required, higher temperatures may be used. In certain instances, it may be desirable to work at superatmospheric pressure, for example, in treating the lower boiling acid-treated material, it may be desirable to use superatmospheric pressures to keep the reactants in the liquid phase. Mechanical agitation, for example, by turbo-mixers, can be used or the oil may be treated in a tank in which a pump picks up aqueous solution of the chlorite, passes it through a heat exchanger to increase the temperature of the solution and brings it into a mixer to accomplish intimate contact of the two phases.

The length of contact between the oil and aqueous chlorite solution depends on the degree of corrosiveness present. For the usual amount of corrosion encountered, the time will vary from 20 minutes to 4 hours depending on the temperature used and the effectiveness of mixing and the concentration of the chlorite. They are all variables best determined by test.

I have found that any emulsions formed by this treatment break readily on standing and the treated oil may be readily separated by known methods. After separation of the treated oil from the chlorite, the oil may be finished where required by additional water washing and/or contacting with or percolation through clay or, in the case of technical oils where the degree of refinement required is not as severe as for the medicinal grades of oil, may be brightened by blotter pressing through a filter press. Neutral oils treated in this manner exhibit no

corrosive action on copper, either in the neutral state or in the finished state after percolation through clay.

While I have disclosed treatment with chlorite on the neutral oil, the same treatment may be used on a finished oil where it is found the finished oil is corrosive to copper. When used on a finished oil, the oil may be further finished after treatment with the chlorite by filter pressing or by repercolation through clay.

In those cases where the corrosion on copper is unusually severe, it has been possible to dissolve the black coating obtained on the surface of the copper with acid and demonstrate that the black coating is predominantly copper sulfide. Experimental evidence has shown that the pure organic sulfides such as the dialkyl sulfides, diaryl sulfide and alkyl aryl sulfides may be added to a non-corrosive oil in a small amount without corrosiveness being imparted to that oil. However, when elemental sulfur in concentrations as low as one part per million is added to the oil or where a compound containing sulfur is a labile form such as a polysulfide linkage is added to the oil, corrosion will be exhibited in the oil due to the tendency of the labile sulfur or elemental sulfur to react under the catalytic influence of the copper and form hydrogen sulfide and other corrosive sulfur compounds. I have now found that the use of alkali metal chlorites under the conditions disclosed above is particularly effective in decomposing and removing all types of sulfur when present in either a free or labile form.

While no limitation is to be had to the theory of reaction, it is believed that the mechanism of treatment involves oxidation of sulfur, sulfide or polysulfide to sulfuric acid during the course of treatment and subsequent fixation of the sulfuric acid by alkali or removal by water washing.

The copper strip test mentioned above consists in polishing a strip of thin copper sheet measuring ½ in. x 3 in. with a fine abrasive, immersing the copper strip in the oil to be tested and heating for 3 hours in a steam bath at a temperature of 212° F. The results are rated numerically as follows: (1) shows no change in appearance of the original copper strip; (2) shows a slight discernible yellow color but is still passable; (3) which does not pass (D. N. P.), shows a pronounced bronze coloration; (4) shows a deep bronze to red color; (5) blue-black. In severely corrosive oils the copper may have a peacock hue changing to a brassy or silvery appearance. These silvery corrosive oils are rated number 6 to 10.

My treatment produces improved quality tests. For example, taste and odor are improved, ability to resist deterioration by sunlight is improved, susceptibility of the oil to oxidation is decreased, the physical properties of the oil remain unchanged and, of course, corrosion to copper is substantially decreased.

All types of oils may be treated by my method particularly paraffinic and naphthenic type oils.

In high viscosity oils which are acid-treated, there is encountered a polysulfide type of corrosive sulfur which usually exhibits an orange to reddish copper strip. In the lower viscosity oil range, that is, with kerosenes and gas oils, which are acid-treated, there is encountered a free sulfur type of corrosive sulfur which usually exhibits a copper strip varying in hue from peacock hue to a black scaly deposit. The latter indicates a severe type of corrosion. Where indications are that the latter type of corrosive sulfur is present,

I find that the condition is corrected by treatment of the corrosive oil with sodium chlorite.

While not bound by any mechanism whereby the corrosive sulfur is removed, I may say that a possible mechanism is the oxidation of the sulfur by sodium chlorite to sulfuric acid, and fixation of the sulfuric acid with alkali normally present in commercial sodium chlorite (sodium chlorite commercially contains about 15% of sodium carbonate), or which may be extraneously added. The oil may be left in the acid state and the acidity removed prior to finishing by water washing or other means.

It has long been known in the art to treat certain hydrocarbon oils with hypochlorite solutions. The development of the art of treating with hypochlorites is well summarized in "Chemical Refining of Petroleum" by V. A. Kalichevsky and B. A. Stagner, Second Edition, American Chemical Society Monograph Series No. 63, Reinhold Publishing Company, 1942. However, it is well recognized in the art that hypochlorite salts, as desulfurizing agents, can only be used in strongly alkaline media. Adjustment of the pH to either the neutral point or an acid range results in the liberation of free chlorine, and undesirable chlorination of the oil thereby results.

On the other hand, the metal chlorites are effective desulfurizing reagents in either the neutral, acid or alkaline state and the active reagent is chlorine dioxide (ClO_2) which is absent from any of the hypochlorite processes.

The effectiveness of my invention will be more clearly illustrated by the following example:

Example 1

A paraffinic base oil having a viscosity of about 35 seconds Universal Saybolt at 100° F. which had been treated to produce a white oil with fuming sulfuric acid, neutralized with sodium carbonate, alcohol washed to remove sulfonic bodies, and steamed to remove the alcohol, was found to be highly corrosive to copper.

The above acid-treated oil was refluxed at boiling temperature and atmospheric pressure with 10% by volume of a 0.1% by weight solution of sodium chlorite for 1 hour. The layers were allowed to separate and the oil finished by a water wash and brightened by paper filtering. The original oil, without any treatment, showed a highly corrosive copper strip rated as #9, and developed a rancid and garlic-like odor when exposed for a short time to sunlight. After treatment with the chlorite, the oil gave a No. 1 copper strip test and exhibited satisfactory stability to sunlight. The spent chlorite liquor gave a positive indication of sulfate ion being present when tested by standard method.

Numerous modifications may be made in the process by those skilled in the art without departing from the scope of the invention described.

What is claimed is:

1. A process for preparing petroleum hydrocarbon oils non-corrosive to copper which comprises treating the hydrocarbon oil with concentrated sulfuric acid ranging in strength from 98% sulfuric acid to fuming sulfuric acid having 20% by weight of sulfur trioxide, removing the sludge, neutralizing the acid-treated oil with a neutralizing agent, extracting the products of neutralization with an immiscible solvent, removing residual immiscible solvent from the oil, and treating the resulting oil with an aqueous solution of an alkali metal chlorite, and thereafter treating the resulting oil with clay.

2. A process according to claim 1 in which the alkali metal chlorite is sodium chlorite.

3. A process for preparing petroleum hydrocarbon oil non-corrosive to copper which comprises treating the hydrocarbon oil with concentrated sulfuric acid ranging in strength from 98% sulfuric acid to fuming sulfuric acid having 20% by weight of sulfur trioxide, neutralizing the acid-treated oil with a neutralizing agent, extracting the product of neutralization with an immiscible solvent, removing residual immiscible solvent from the oil and treating the resulting oil with an aqueous solution of an alkali metal chlorite at a temperature of from 40° C. to about 100° C. for a time of from about 20 minutes to 4 hours and separating the oil from the aqueous solution, and thereafter treating the resulting oil with clay.

4. A process for preparing petroleum hydrocarbon oils non-corrosive to copper which comprises treating the hydrocarbon oil with concentrated sulfuric acid ranging in strength from 98% sulfuric acid to fuming sulfuric acid having 20% by weight of sulfur trioxide, removing the sludge, neutralizing the acid-treated oil with a neutralizing agent, extracting the products of neutralization with an immiscible solvent, removing residual immiscible solvent from the oil, treating the resulting oil with clay, and treating the finished oil with an aqueous solution of an alkali metal chlorite.

5. A process for preparing petroleum hydrocarbon oils non-corrosive to copper which comprises treating the hydrocarbon oil with concentrated sulfuric acid ranging in strength from 98% sulfuric acid to fuming sulfuric acid having 20% by weight of sulfur trioxide, removing the sludge, neutralizing the acid-treated oil with a neutralizing agent, extracting the products of neutralization with an immiscible solvent, removing residual immiscible solvent from the oil, treating the resulting oil with clay, and treating the finished oil with an aqueous solution of an alkali metal chlorite at a temperature of from 40° to about 100° C. for a period of time from about 20 minutes to 4 hours and separating the oil from the aqueous solution.

6. A process for preparing petroleum hydrocarbon oils non-corrosive to copper which comprises treating the hydrocarbon oil with concentrated sulfuric acid ranging in strength from 98% sulfuric acid to fuming sulfuric acid having 20% by weight of sulfur trioxide, removing the sludge, neutralizing the acid-treated oil with a neutralizing agent, extracting the products of neutralization with an immiscible solvent, removing residual immiscible solvent from the oil, whereby said oil has a good copper corrosion test, and treating the resulting oil with an aqueous solution of an alkali metal chlorite, and thereafter treating the resulting oil with clay.

7. A process for preparing petroleum hydrocarbon oils non-corrosive to copper which comprises treating the hydrocarbon oil with concentrated sulfuric acid ranging in strength from 98% sulfuric acid to fuming sulfuric acid having 20% by weight of sulfur trioxide, removing the sludge, neutralizing the acid-treated oil with a neutralizing agent, extracting the products of neutralization with an immiscible solvent, removing residual immiscible solvent from the oil, whereby said oil has a good copper corrosion test, treating the resulting oil with clay, whereby said oil has a poor copper corrosion test, and

7

treating the finished oil with an aqueous solution of an alkali metal chlorite, whereby said oil has a good copper corrosion test.

CHARLES A. COHEN. 5

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,908,273	Taylor -----	May 9, 1933
2,028,998	Schulze et al. -----	Jan. 28, 1936

8

Number	Name	Date
2,110,283	Archibold -----	Mar. 8, 1938
2,179,008	Campbell -----	Nov. 7, 1939
2,382,753	Treseder -----	Aug. 14, 1945

OTHER REFERENCES

- Sachanen, "Conversion of Petroleum," pages 337, 343-345, 347. Copyright 1940 by Reinhold Publishing Corp., New York, N. Y.
- 10 Kalichevsky et al., "Chemical Refining of Petroleum," page 198. Copyright 1942 by Reinhold Publishing Corp., New York.