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TREATMENT OF OILS CORROSIVE TO
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4 Claims. (Cl. 196-40)

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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 is also concerned with the treatment of compositions which may be predominantly petroleum hydrocarbon in character comprising mixtures of acid-treated hydrocarbons and simple or polymerized ester types of materials which may be added to improve the lubricating qualities of the petroleum hydrocarbons.

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 in 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

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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 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 applied, 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 test in the medicinal grades and cannot be used when the oil is compounded with materials which will react with strong alkalis.

Another 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 normal alkali metal sulfites, particularly sodium sulfite. The alkali metal sulfite is used in an aqueous solution which may vary in strength between 2 and 18 weight percent and is applied to the oil in a volume from 5 to 25%. The choice of concentration is best determined by the nature of the oil, for example; its density, viscosity and tendency to form emulsions. 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 pressures, 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 the aqueous solution of sulfite, 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 sulfite 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 mixer and the concentration of the sulfite. 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 sulfite, the oil may be finished where required by 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 sulfite 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 sulfite 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 in 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 sulfites 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 production of elemental sulfur during the course of treatment which reacts with the alkali metal sulfite to form a non-corrosive thiosulfate which remains in the aqueous solution.

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 a copper strip in the oil to be tested and heating 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.

I have found that because of the substantial neutral character of the reagent used, my treatment can be used with oily compositions containing phenolic inhibitors, oil-soluble dyes and esters, all of which are unaffected by the treatment. 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.

I have found that normal alkali metal sulfites, for example, ammonium sulfite, potassium sulfite, and sodium sulfite, preferably in aqueous solution, are all effective reagents for my disclosed

treatment, however, sodium sulfite is the cheapest and is readily available commercially. Alkaline earth metal sulfites can also be used but they are insoluble in water and can be used in a dry state or in aqueous suspension.

If the oil, before sulfite treatment, is found to be acidic in nature or if the oil develops acidity during sulfite treatment, it is advisable to add alkali in the form of hydroxide or carbonate to counteract the acidity of the oil, that is, to make it neutral before sulfite treating.

With regard to the prior art, it is recognized that alkali sulfites have been used for the treatment of acid-treated oils, for example, U. S. Patent 2,257,914 to Sylvan R. Merley, describes a process for neutralizing a sulfuric acid-treated oil with aqueous solutions of alkali metal sulfites. It is noted in Merley's disclosure that alkali metal sulfite solution is used as the neutralizing agent in place of the customary hydroxide or carbonate. Merley's method is inapplicable and not feasible for the uses contemplated in this invention in that at no time, is the sulfite used for the neutralization of any acidity. My use of the sulfite is restricted to those oils which are perfectly neutral in character or which purposely contain a slight excess alkalinity in order to fix any hydrogen sulfide formed during process of treatment. Furthermore, any sulfonate formed during acid treatment is removed by washing with water or dilute alcoholic caustic treatment before applying sulfite treatment. Merley treats acid-treated naphthas which contain only a small amount of acid readily removable by water washing and which contain only traces of sulfonic acids so low in molecular weight as to be readily water-soluble without the formation of bad emulsions. On the other hand, the oils which I treat with sulfite have been treated with fuming sulfuric acid. In their acid state, therefore, they contain high concentrations of acid and high concentrations of sulfonic acids in comparison with those present in Merley's treatment. The neutralization with aqueous alkali sulfites of my highly acidic oils would produce severe emulsions which would not break without the use of additional materials such as alcohol which would be undesirable since the solubility of sulfite in dilute alcohol becomes quite low, and in order to accomplish complete neutralization of the acidity, it would require enormous amounts of alcoholic sulfite.

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

Example 1

A paraffinic base oil having a viscosity of about 52 seconds Universal Saybolt at 100° F. which had been treated to produce a white oil with fuming sulfuric acid, the sludge separated, the acid oil 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 in its neutral state at boiling temperature and atmospheric pressure with 20% by volume of a 10% by weight solution of sodium sulfite for 1 hour. The layers were allowed to separate and the oil finished by clay percolation. The original oil, without any treatment with sulfite and after percolation through the same type of clay, showed a highly corrosive copper strip rated as a #9, while after treatment with sodium sulfite, a strip was obtained and rated as #1.

Example 2

A compounded hydraulic oil comprising a mixture of a 32 Saybolt viscosity oil and a 60 viscosity oil, both of which had been acid treated, containing in solution an acryloid polymer, a phenolic inhibitor, and an oil-soluble dye, showed a bad copper strip test and failed to pass the 168 hr. corrosion specification for such a mixture as specified in Federal Specification AN VVO-366-B. Treatment of this oil mixture with 20% by volume of a 10% by weight solution of sodium sulfite at 70° C. for a period of 2 hours gave a product which when finished by filtration through a filter press, had a satisfactory copper test and satisfactorily passed the above-identified corrosion specification, with no adverse effect on any of the other physical tests.

Example 3

A Mid-Continent base white oil having a viscosity of 85 seconds Saybolt at 100° F. which had been produced by conventional acid treatment, separation of the sludge, neutralization of the acidity with sodium carbonate, extraction of the sulfonic bodies with dilute isopropyl alcohol, steamed to remove the alcohol and finished by percolation through clay to produce a finished white oil was found on inspection to be off odor and taste and showed a poor response to the copper corrosion test. This oil was treated with 20% by volume of a 15% solution of sodium sulfite using mechanical agitation at a temperature of 80° C. for a period of 2 hours. The lower sulfite layer was removed, the clear bright oil layer finished by blotter-pressing through a plate and frame filter press. The oil finished in this manner showed good odor and taste and gave a good copper corrosion test. Repercolation of a portion of this oil through an additional quantity of clay yielded a satisfactory oil with respect to quality tests and copper corrosion. The untreated oil, when treated with an equivalent quantity of water for the same period of time and temperature showed no improvement either with or without additional clay percolation.

Example 4

A synthetic lubricant consisting predominantly of di-2-ethyl hexyl sebacate was found on inspection to possess a poor copper test. Materials of this type are normally not corrosive to copper but are subject to contamination with materials which may be corrosive to copper and in this instance, the origin of the corrosive material appeared to be one of contamination. The usual method of treatment such as redistillation under high vacuum and blowing with inert gas failed to yield any improvement. Treatment of this ester with 10% by volume of a 5% solution of sodium sulfite at reflux temperature for a period of one hour followed by simple paper filtration in order to finish the ester gave a satisfactory corrosion-free product, which met specifications as to pour, free acidity, and so forth.

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 oil non-corrosive to copper, said oil having been treated with strong sulfuric acid, the sludge having been removed, the acid treated oil having been neutralized with a neutralizing

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agent, the product of neutralization having been extracted with an immiscible solvent, and the residual immiscible solvent having been removed from the oil, and the resulting oil having been treated with clay, which comprises treating the said oil with an aqueous solution of a normal alkali metal sulfite.

2. A process for preparing petroleum hydrocarbon oil non-corrosive to copper; said hydrocarbon oil having been treated with strong sulfuric acid, the sludge having been removed; the acid having been neutralized with a neutralizing agent, the product of neutralization having been extracted with an immiscible solvent, the residual immiscible solvent having been removed from the oil; and the resulting oil treated with clay, which comprises treating the finished oil with an aqueous solution of a normal alkali metal sulfite at a temperature of from 40° C. to about 100° C. for a period of time from about 20 minutes to 4

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hours and separating the oil from the aqueous solution.

3. A process according to claim 1 in which the normal alkali metal sulfite is sodium sulfite.

4. A process according to claim 2 in which the normal alkali metal sulfite is sodium sulfite.

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