Patented Aug. 24, 1943

2,327,504

UNITED STATES PATENT OFFICE

2,327,504

REFINING HYDROCARBON OILS

Charles A. Cohen, Elizabeth, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application December 26, 1940, Serial No. 371,779

9 Claims. (Cl. 196—41)

This invention relates to an improved process for refining hydrocarbon oils or waxes. More particularly, it is concerned with the treatment of oils of the white oil type, such as medicinal oils, transformer oils, insecticide base oils, refrigerator oils and cosmetic oils, or lubricating oils, such as spindle oil and motor oil, or petroleum waxes, which have during the process of their refinement been subjected to the action of concentrated sulfuric acid or fuming sulfuric acid.

Heretofore, highly acid-treated oils or white oils were prepared by the drastic treatment of a hydrocarbon oil having a viscosity in the range of 30 to 1000 seconds Saybolt at 100° F. with fuming sulfuric acid, followed by separation of the acid sludge from the oil, neutralization of the acid oil with an alkali, substantial removal of the oil-soluble sulfonic acid salts or "mahogany soaps" from the oil by water washing or by dilute alcohol or other solvent, and steaming of the oil to remove the solvent or other volatile constituents. The oil at this stage is known as a "neutral" oil and may vary in color from about −10 to +20 Saybolt. The colored material remaining in the oil may be hydrocarbon in nature where the conditions or amount of acid treatment used was mild, or may be due to small amounts of organic sulfonic acid salts which are difficult to remove by washing. The "neutral oil" is then finished by contacting with adsorbent clay fines or adsorbent carbon or materials of like nature, such as bauxite or various zeolites, or the oil may be finished by percolation through a bed of adsorbent clay or carbon or the like to give a water-white finished white oil of a +30 up Saybolt color.

In the refining of waxes to improve their color and stability towards heat and light, substantially the same procedure is used as in the refining of oils except that the temperatures used are generally higher in order to keep the wax fluid.

Many oils when finished are, however, corrosive in character and will cause the discoloration of copper in less than two hours when subjected to the copper strip test. This test consists in polishing a strip of thin copper sheet measuring ½" x 3" with tripoli, fine steel wool, or other fine abrasive, immersing the copper strip in a sample of the oil to be tested and heating for from 2 to 3 hours in a steam bath at a temperature of 212° F. The results are rated numerically as follows: No. 1 shows no change in appearance of the original copper strip; No. 2 shows a slight discernable yellow color but is still passable; No. 3 which does not pass (D. N. P.), shows a pronounced bronze coloration; No. 4 shows a deep bronze to red color and No. 5 is blue-black. In severely corrosive oils the copper may have a peacock hue changing to a brassy or silvery appearance.

In testing the corrosive character of refined waxes, the same procedure is used except that a temperature of 300° F. and a time of 16 hours are used.

Oils and waxes which exhibit a poor response to the copper test generally also show poor stability toward heat and light. On exposure of refined oils and waxes to either natural sunlight or toward artificial light which is rich in ultraviolet rays, such as carbon arc or mercury vapor lamps, the oil or wax, if not perfectly refined and free from objectionable by-products, may develop disagreeable odors and tastes which are generally described as garlic, H_2S, cedar and, in bad cases, rancid. Waxes are less prone to develop distinctive odors other than a general rancidity but may quickly go off color.

Ordinarily, oils and waxes which have failed to pass the copper strip test have had to be recycled through the acid treatment in an attempt to make them less corrosive. At times it has been necessary to recycle the corrosive oils through the acid treatment three or four times before an acceptable copper strip test is obtained upon them.

Some success has been had in treating finished white oils or waxes to improve their copper strip test by the use of calcium or magnesium hydroxide. However, this method is not generally applicable to medicinal white oils because oils treated with these reagents acquire an objectionable taste. Also, the quantity of calcium and magnesium hydroxide used is bulky and its removal necessitates additional handling of the finished oil which increases the possibility of contamination. In addition, there are individual cases of corrosive oils when, in order to obtain good copper strip tests by the use of calcium or magnesium hydroxide, it has been necessary to give the oil several teratments with these reagents.

In addition to the above method, which works best on finished white oils, a number of methods have been in use for correcting corrosive oils to improve their copper strip test by chemical treatment of the neutral oil prior to final percolation through clay. For example, it has been found that alcoholic potassium hydroxide in the proportion of one-half to ten pounds of the dry hydroxide per thousand gallons of oil affords some degree of correction when added to the neutral oil at the end of the steaming period, but this method of treating corrosive oils has several notable objections, the chief among these being the sever degradation in color which takes place and the tendency for the finished white oil from the clay percolating filters to run cloudy after a compartively short filter life.

According to the present invention, it has been found that if substances, such as the various diatomaceous filter aids, or finely ground activated carbon, are added to the neutral oil, after it has been treated with alcoholic KOH or NaOH at 100° C. to 150° C., and the alcohol removed by blowing with air or inert gas, and subsequently filtered to remove the diatom-KOH complex, the neutral oil can then be finished by contacting with adsorbent clay fines or adsorbent carbon, or by percolation through a bed of adsorbent clay or carbon or the like to give a finished white oil of a +30 up Saybolt color which passes the copper test and which comes through the percolation filter without the appearance of any cloudiness or haziness even after 20 times the amount of oil has passed through the clay bed as was obtained without the use of the diatomaceous earth or activated carbon.

In practicing the present invention, the neutral oil is brought up to the working temperature of 100° C. to 150° C. by means of a convenient source of heat, such as a steam coil or by passage through a heat exchanger, and in the case of the heavier oils which may have some water emulsified or suspended in the oil, is previously dried by air-blowing for a short time. When the oil is substantially dry, an alcoholic solution of potassium hydroxide containing from one-half pound to 10 lbs. of dry KOH per thousand gallons of oil treated is added to the oil and thoroughly mixed to effect solution. At the temperatures used, most of the alcohol is evaporated off in a short time and recovered through a condenser. The remainder of the alcohol is removed by air-blowing when the process is operated in a batch still, but it is possible to remove the alcohol by passing the oil downward through a packed tower while blowing countercurrently with a stream of air or inert gas, or the oil containing the KOH and alcohol may be passed in a thin film through or over a heated zone while maintaining a vacuum in the region of the heated zone.

When all of the alcohol has been removed, the alkaline metal hydroxide is dispersed throughout the oil in the form of a colloidal suspension. It is believed that the action of the KOH on the corrosive principles present in the oil is a surface phenomenon, in which the KOH forms an insoluble complex with the corrosive material present, and it is therefore within the province of this invention to add the KOH to the oil in the form of a colloidal dispersion in a non-aqueous medium, such as a finished oil of the same viscosity as the oil being treated or an anhydrous solvent like glycol.

After all of the alcohol has been removed, the oil is cooled to a temperature of from 20° C. to 100° C., preferably 50° C. and then treated with a quantity of filter aid or activated carbon in an amount equal to from 1 lb. to 40 lbs. per thousand gallons of oil. The amount added is preferably from 2 to 4 times that of the weight of dry alkali hydroxide used. Most types of diatomaceous filter earths commercially available are suitable for the practice of this invention, particularly those which fall into the following classification: The natural air dried and ground earths, calcined and ground earths, earths calcined in the presence of alkali and the acid-treated earths. The types of activated carbon which may be used may either be of the natural or acid-treated varieties.

The method of treating the KOH treated oil with the diatomaceous earth or carbon may be varied from either the direct addition of these materials to the oil in the form of a dry powder or they may be previously admixed with a portion of the oil to form a slurry which can then be pumped into the main body of the oil The diatomaceous earth, after it has been added to the oil, may be agitated for a period of from 5 minutes to ½ hour and then filtered through either a plate and frame press, a continuous rotary press, or may be centrifuged out by means of a basket type of centrifuge. In using the plate and frame or rotary type of press, it is advantageous to precoat the press with from 5 to 10 lbs. of the diatomaceous filter aid per hundred square feet of filter press area. The oil so obtained is optically bright and free from haze and is several shades of color lighter than the original KOH treated oil. The oil is then finished by contacting with or percolation through a sorptive material, such as Attapulgus clay, activated carbon, bauxite or natural or synthetic zeolites. The expression "sorptive material" is used to denote those materials which are either active by adsorption or by absorption such as are enumerated above.

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

EXAMPLE

1000 gallons of an acid-treated neutral white oil having a viscosity at 100° F. of 55 seconds Saybolt was treated at a temperature of 115° C. with 5 lbs. of KOH dissolved in substantially anhydrous alcohol. After the addition of the KOH was complete, the oil was air blown until free from alcohol. The oil was then transferred to an agitator, cooled to 50° C. and 20 lbs. of a diatomaceous earth filter aid (commercially known as J-N Standard Super-Cel) was added and the mixture agitated while maintaining the temperature of 50° C. for a period of 15 minutes. The oil was then filtered through a plate and frame press which had been previously precoated with the same filter aid in an amount equal to 5 lbs. of filter aid per hundred square feet of filter press area. After the oil had cooled to atmospheric temperature it was percolated through a bed of adsorbent Attapulgus clay to yield a finished white oil. This resulting oil gave a satisfactory copper test and improved stability toward sunlight. The following table gives the comparative data on the original neutral oil without KOH treatment, the same oil treated with 5 lbs. of KOH per thousand gallons of oil

but without filter aid, and the oil prepared according to the above example:

Table

	A	B	C
	Neutral oil	Neutral oil+Alc-KOH	Neutral oil treated according to Ex. 1
Neutral oil color	+17 Saybolt	+8 Saybolt	+20 Saybolt.
1 hr. neutral oil copper	DNP [1] 4	DNP 5	Pass 1.
2 hr. neutral oil copper	DNP 5	do	Pass 1-2.
3 hr. neutral oil copper	do	do	Pass 2.
Color after percolation	+30 up Saybolt	+19 Saybolt (hazy)	+30 up.
1 hr. copper test after percolation	DNP 4-5	DNP 3 (spotty)	Pass 1.
2 hr. copper test after percolation	DNP 5	do	Do.
3 hr. copper test after percolation	do	DNP 4 (spotty)	Do.
Taste and odor after percolation	Garlic and rancid	Metallic	Pass test.
5 min. natural sunlight stability	DNP H_2S		Do.

[1] DNP is abbreviation for "Does not pass."

What is claimed is:

1. The process of improving the color and reducing the corrosiveness of acid-treated petroleum hydrocarbons having a viscosity in the range of from 30 to 1000 seconds Saybolt at 100° F. on copper which comprises treating the hydrocarbon in its neutral state first with an alkali metal hydroxide at 100° C. to 150° C., cooling the hydrocarbon to from 20° C. to 100° C., adding a finely divided diatomaceous filter aid, agitating and filtering.

2. The process of improving the color and reducing the corrosiveness of acid-treated oils on copper which comprises treating the oil in its neutral state first with an alkali metal hydroxide at 100° C. to 150° C., cooling the oil to from 20° C. to 100° C., adding a finely divided diatomaceous filter aid, agitating and filtering.

3. The process of improving the color and reducing the corrosiveness of acid-treated petroleum hydrocarbons having a viscosity in the range of from 30 to 1000 seconds Saybolt at 100° F. on copper which comprises treating the hydrocarbons in their neutral state first with an alcoholic solution of an alkali metal hydroxide at 100° to 150° C., removing the alcohol, cooling the hydrocarbons to from 20° to 100° C., adding a finely divided diatomaceous filter aid, agitating and filtering.

4. The process of improving the color and reducing the corrosiveness of acid-treated oil on copper which comprises treating the oil in its neutral state first with an alcoholic solution of an alkali metal hydroxide at 100° C. to 150° C., removing the alcohol, cooling the oil to a temperature between 20° and 100° C., adding a finely divided diatomaceous filter aid, agitating and filtering to remove a diatom-alkali metal hydroxide complex from the oil.

5. The process of improving the color and reducing the corrosiveness of acid-treated petroleum hydrocarbons having a viscosity in the range of from 30 to 1000 seconds Saybolt at 1000° F. on copper which comprises treating the hydrocarbons in their neutral state first with an alkali metal hydroxide at 100° to 150° C., cooling the hydrocarbons to from 20° to 100° C., adding a finely divided diatomaceous filter aid, agitating and filtering, and then passing the hydrocarbons through a sorptive material.

6. The process of improving the color and reducing the corrosiveness of acid-treated oils on copper which comprises treating the oil in its neutral state first with an alkali metal hydroxide at 100° C. to 150° C., cooling the oil to from 20° C. to 100° C., adding a finely divided diatomaceous filter aid, agitating, filtering and passing the oil through a sorptive material.

7. The process of improving the color and reducing the corrosiveness of acid-treated petroleum hydrocarbons having a viscosity in the range of from 30 to 1000 seconds Saybolt at 100° F. on copper which comprises treating the hydrocarbons in their neutral state first with an alcoholic solution of an alkali metal hydroxide at 100° to 150° C., removing the alcohol, cooling the hydrocarbons to from 20° to 100° C., adding a finely divided diatomaceous filter aid, agitating, filtering and then passing the hydrocarbons through a sorptive clay.

8. The process of improving the color and reducing the corrosiveness of acid-treated oil on copper which comprises treating the oil in its neutral state first with an alcoholic solution of an alkali metal hydroxide at 100° C. to 150° C., removing the alcohol, cooling the oil to a temperature between 20° and 100° C., adding a finely divided diatomaceous filter aid, agitating and filtering to remove a diatom-alkali metal hydroxide complex from the oil and then passing the oil thru a sorptive clay.

9. The process of improving the color and reducing the corrosiveness of acid-treated oils on copper which comprises treating the oil in its neutral state first with an alcoholic solution of potassium hydroxide in an amount equal to from ½ to 10 lbs. of potassium hydroxide per thousand gallons of oil, heating the mixture to approximately 115° C., blowing with air to drive off all the alcohol, cooling to a temperature between 20° and 100° C., adding finely divided diatomaceous earth in an amount by weight equal to from 2 to 4 times the weight of potassium hydroxide used and agitating, filtering to remove a diatom potassium hydroxide complex and percolating the oil through a bed of sorptive clay.

CHARLES A. COHEN.