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PROCESS OF REFINING MINERAL
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ration of DelawareNo Drawing. Application October 5, 1940,
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9 Claims. (Cl. 196—40)

This invention relates to a process for preparing mineral white oils of a high degree of physical and chemical stability, especially as regards color and chemical inertness to highly polished copper.

White oils are usually prepared from petroleum stocks of about lubricating oil consistency derived from the less paraffinic crudes obtained either as distillates or as residuals. These oils undergo intensive refining to remove substantially all the unsaturated and color forming bodies contained in the crude stocks. The refining is usually effected by treating the oil with sulfuric acid of concentrations between 93% strength and 20% fuming, preferably in a series of additions with the separation of the sludges formed after each reaction, then neutralizing, and treating the oil to remove sulfonic compounds and finishing either by air blowing or clay treatment. The lower strengths of acid may be employed in the initial stages, and the higher strengths of acid employed in the final treating stages. Treating temperatures up to about 180° F. may be employed, the higher temperatures being used only with the lower strengths of acid. The acid may be replaced in whole or in part by aluminum chloride or other known intensive refining agents. It has been found advisable with most stocks, however, to give a final treatment with fuming sulfuric acid. Distillate stocks usually give higher yields of finished oils with slightly lower amounts of reagents than in the case of residual stocks.

The products of such refining consist largely of paraffin and naphthene hydrocarbons and have colors between 16+ and 30+ Saybolt. These highly refined oils are often chemically and physically unstable as a result, presumably, of the removal of certain natural inhibitors considered to be present initially in the oil and believed not to be removed in less intensive refining treatment. This instability gives rise to the development in oils of compounds of poor color and of objectionable taste and odor and also of compounds corrosive to highly polished copper. These are serious defects in white oils, especially in medicinal white oils, which are required to meet the specifications for petrolatum liquidum U. S. P. and in white oils employed as transformer and refrigerator oils which in service come in contact with copper and copper alloyed materials. To eliminate the deterioration products, repurification has been proposed, but such treatment is not favorably considered because it is expensive and somewhat uncertain

in its effect, and furthermore is not a means of remedying a defect apparently in the oil itself due to previous refining treatment. The addition to the oil of compounds similar to those supposedly removed in the intensive refining treatment has the disadvantage in most cases of causing ill effects upon other properties of the oil and the disadvantage also of requiring to be handled separately and blended in the oil in certain limited amounts to achieve the best results.

In the preliminary processing of a suitable stock in this invention, the oil is intensively treated, preferably with a mineral acid such as sulfuric acid, to remove unsaturated and chromogenic compounds as in the prior art. To the thus treated oil about an equal volume of alcohol is usually added, and then 10% aqueous sodium carbonate solution to neutralize the oil. Then the alkaline solution is separated and the oil washed with 50% aqueous alcohol to remove traces of sulfonic soaps, and the alcohol and moisture are removed from the oil by blowing first with steam and then with air. A further refining treatment, the main feature of the present invention, is then given to the oil to effect chemical and physical stabilization. This special processing of the oils obviates the formation of compounds corrosive to highly polished copper, the deterioration of color, and the development of objectionable odors and tastes.

The stabilizing treatment of the highly refined oils is effected by treating the oils with an anhydrous amphoteric metal halide active in Friedel-Crafts reactions in very small amounts, that is less than about 1% by weight of the oil, at temperatures between 30° C. and 100° C. and preferably at about 70° C., followed by removal of the sludge and treatment at about 120° C. with 0.01% to 0.1% of a caustic alkali preferably dissolved in the minimum quantity of a relatively volatile solvent preferably either isopropyl or ethyl alcohol to effect solution or dispersion of the alkali, and then percolating through clay. By the term anhydrous amphoteric metal halide active in Friedel-Crafts reactions as used here and in the claims, is designated the halide of a polyvalent amphoteric metal, such as, aluminum chloride, ferric chloride, chromic chloride, zinc chloride and stannic chloride which hydrolyze in the presence of water. The caustic alkali is dissolved or dispersed in the solvent merely as a means of adding the caustic alkali to the oil in an anhydrous and finely divided state and during the treatment of the oil with the alkali at 120° C., this quantity of the solvent is usually removed.

One method of effecting the invention is to add to the dry neutral, normally refined oil about 0.5% of aluminum chloride, added preferably in the form of a paste made with a small quantity of the oil to be treated, agitating the mixture at a temperature of about 70° C. for about 30 minutes, removing the sludge and filtering, then adding caustic potash preferably dissolved, in the minimum quantity of dry isopropyl alcohol to effect solution and in an amount to give the treating effect of two pounds of caustic potash per thousand gallons of oil, then air blowing for about 20 minutes at a temperature between 100° C. and 135° C., then filtering and percolating through clay.

It is appreciated that the halides, especially the chlorides, of such amphoteric metals as aluminum, zinc, iron and chromium, and the caustic alkalis have been previously employed in treating petroleum oils, but it is believed that the treatment according to the present invention is the first to employ a two step super refining process, involving the use of both an anhydrous higher halide of an amphoteric metal and anhydrous caustic potash as a means of improving the stability of white oil products. Aluminum chloride and the other such anhydrous halides of the amphoteric metals have been used as general treating reagents, and also in the polymerization and cracking of hydrocarbons. The action of these halides is extremely complex, depending greatly on the temperature, the type of hydrocarbon, and the impurities. Aluminum chloride, for instance, at atmospheric temperatures reacts with sulfur and nitrogen compounds present as impurities in crude distillates and in the conversion of unsaturated hydrocarbons to less chemically reactive compounds mainly of a saturated and polymerized nature. When the higher distillates are treated with aluminum chloride, a molecular breakdown or cracking occurs. Aluminum chloride used as a treating reagent upon crude distillates and residuals is about the equivalent of treating such stocks with concentrated sulfuric acid.

In the present invention the amphoteric metal halides such as aluminum chloride are used for treating oils which have been previously intensively refined to remove substantially all the chemically reactive unsaturated and chromogenic compounds. The amounts of the reagents employed in the process of the present invention are considerably smaller than those which have been hitherto used for treating purposes. The use of the anhydrous amphoteric metal halides of this invention is moreover merely one step in a combination treating process. The removal of the sludge formed by the halide does not eliminate from the oil the corrosive compounds. These compounds are apparently finely dispersed in combination with the halide material throughout the oil and it is only by treating with anhydrous caustic alkalies that the corrosive compounds are removed.

In the prior art, aqueous caustic alkalies have been employed largely in neutralizing and doctor sweetening processes. Anhydrous caustic alkalies have also been previously employed as treating reagents for petroleum oils and in the case of U. S. Patent No. 2,110,283, to remove corrosive compounds from white oil stocks. The process of the present invention may therefore be considered as an improvement over this latter process in that the present process is more generally ap-

plicable and that by the prior use of the anhydrous amphoteric metal halide smaller quantities of the caustic alkalies can be employed to achieve the same treating effect on similar stocks. As a result of the use of lower amounts of caustic alkalies better colors are obtained on the neutral oils which are reflected in improved yields in the clay filtering operations by which the oils are usually finished and also haze formation in the finished products is practically eliminated. Indeed, the combination of the treating effects of the anhydrous amphoteric metal halide and the anhydrous caustic alkali effected by the process of this invention overcomes the instability of all type highly refined white oils and renders the products color stable, odorless and in accordance with the specifications of the U. S. Pharmacopoeia which is not generally obtainable by the use of either reagent alone. This combination of metallic halide, preferably aluminum chloride, and an anhydrous caustic alkali, preferably caustic potash, in a minimum amount of alcohol solution to effect solvent dispersion has been found to be a superior treating process for the preparation of white oil products of a high order of chemical and physical stability.

In the preparation of such highly refined petroleum products as the white oils, an important controlling test is that of determining under specific conditions corrosion to highly polished copper. In the usual test in this regard a copper strip is mechanically polished with an inert abrasive material such as Tripoli powder on a dampened reclaimed towel or other cloth material free from sizing. The strip is freed of the abrasive material by dusting with a clean dry cloth and then wiping with filter paper. The size of the copper strip which is employed is convenient for placing in a four ounce sample bottle, that is, strips measuring 1/2 inch by 3 inches. The polished strip is then placed in a clean dry four ounce bottle containing sufficient oil to immerse completely the strip. The bottle is stoppered with a clean stopper and placed in a constant temperature bath at a temperature of 210° F. for two hours. At the end of the two-hour period, the sample is removed from the bath and the appearance of the copper strip compared with the appearance of a similarly polished copper strip which has been heated in an adjacent four ounce bottle containing air. The presence of corrosive copper substances in the oil sample is indicated by the difference in discoloration between the copper strip immersed in the oil sample and on the blank copper strip. The results are reported as:

		Remarks
(1) Same as blank	#1	Pass
(2) Slight reddish discoloration	#2	Pass
(3) Definite reddish discoloration	#3	Does not pass
(4) Reddish discoloration with slight iridescence or brassy appearance	#4	Does not pass
(5) Extensive iridescent, brassy or black discoloration	#5	Does not pass

Sunlight taste and odor test

50 cc. of oil in clean four ounce bottle, stoppered with clean cork stopper is exposed to natural sunlight. At certain intervals of time (5, 10, 15, and 60 min.), the sample is tested to determine

if the taste or odor have been affected by the sunlight. A poor oil will develop garlic or sulfurous odor after exposure for as short a period of time as 5 minutes. Oils which are not appreciably affected by exposure to sunlight for the entire length of the test are desirable.

The following examples will serve to illustrate the invention and the novelty over prior art procedures. The invention, however, is not limited by the following examples. The examples are presented merely for purposes of illustrating the invention.

Example 1

An oil of lubricating consistency having a viscosity of 90-100 seconds Saybolt at 100° F. derived from a Mid-Continent crude was treated with 44% of its volume of 20% fuming sulfuric acid, the sludge separated, and the oil phase neutralized with a 10% aqueous solution of sodium carbonate, then washed several times with 50% aqueous isopropyl alcohol solution to remove the oil soluble sulfonates, and then blown with steam and then with air to remove traces of alcohol and moisture present. The resultant oil had a Saybolt color of 19+, a No. 5 copper test value, and an ash value of less than 0.01%. Five samples of this oil were taken and treated as follows:

I. Aluminum chloride in the amount of 0.5% (wt./volume basis) in the form of a paste was made with a small quantity of the oil and added to the bulk of the oil. The aluminum chloride was kept suspended in the oil during the treatment for 30 minutes, at 75° C., by active agitation. The gelatinous sludge remaining in the oil after treatment was removed by contacting with filter aid and then passing through a Buchner funnel. The oil was then steamed for 10 minutes at 110° C. to remove hydrogen chloride and odors which had developed during the treatment with aluminum chloride, then dried by filtering through absorbent paper. The oil was then treated, at 120° C., for 20 minutes with 0.025% (wt./volume) of caustic potash dissolved in the minimum quantity of isopropyl alcohol. The alcoholic solution was then separated and the oil was air blown at 120° C. for 20 minutes to remove all traces of alcohol. The oil at this stage had a Saybolt color of 21+. The oil was then percolated through Attapulugus clay (30-60 mesh) at room temperature. The resultant oil was tasteless, odorless, had a Pass No. 1 copper test value, and had a color of +30 Saybolt. The oil did not develop any sulfurous odors when exposed to natural sunlight for a period of 60 minutes. The oil had a Saybolt viscosity at 100° F. of 86 seconds, and at 212° F. of 38 seconds.

II. The second sample of the oil was treated similarly to the first sample except that the 0.025% (wt./volume) caustic potash was dissolved in the minimum amount of water to effect solution. The thus treated oil failed to pass the copper corrosion test.

III. The third sample of the oil was treated with 0.5% of anhydrous aluminum chloride (wt./volume basis) added in the form of a paste made with a small quantity of untreated oil, then incorporated in the body of the oil, and maintained suspended in the oil by agitation for 30 minutes. The gelatinous sludge was separated by contacting the filter aid and filtering through a Buchner funnel. The oil was steamed for 10 minutes at 110° C. to remove hydrogen chloride and other mal odors which had developed in the oil during treatment with aluminum chloride. The resultant oil had a Saybolt color of 26+, and

after percolation through Attapulugus clay (30-60 mesh) gave a No. 5 copper test.

IV. A fourth sample of the oil was treated at 120° C. for 20 minutes with 0.025% (wt./volume) of caustic potash dissolved in the minimum quantity of isopropyl alcohol to effect its solution. The thus treated oil had a Saybolt color of 10+. After percolation through clay (30-60 mesh) the resultant oil was tasteless, odorless, and had a +30 Saybolt color. The thus treated oil had a No. 4 copper test and developed a garlic odor on exposure to sunlight for 5 minutes.

V. The fifth sample of oil was percolated through Attapulugus clay (30-60 mesh). This oil was tasteless and odorless and had a Saybolt color of 30+. It gave a No. 5 copper test and developed a garlic odor upon exposure to sunlight for 5 minutes. The Saybolt viscosity at 100° F. was 86 seconds, and at 210° F. was 38 seconds.

It is demonstrated by the treating of the five samples of the oil that a combination treatment of aluminum chloride followed by alcoholic potash improves both the color, odor, taste, and chemical stability of the oil as regards inertness to highly polished copper. The oil without such treatment is shown to be definitely unstable in regard to color, odor, taste, and corrosiveness towards highly polished copper. It is only the combination treatment with aluminum chloride, followed by alcoholic potash that is effective in producing highly stabilized oil. It is also demonstrated that the small amount of aluminum chloride employed has no effect whatever on the viscosity of the oil.

Example 2

In a test to demonstrate the effect of the presence in the oil of soluble sulfonates, 0.06% of a purified oil soluble soap was added to a sixth sample of the oil used for subsequent treating in Example 1. The blended oil after percolation through 5% clay gave a No. 2 copper test rating. The refining action inherent in the process of the invention is not associated therefore with the removal of any sulfonic compounds from the oil.

Example 3

The effect of treating reagents other than aluminum chloride in small quantities is shown by another series of treatments of the same base normally refined oil as previously employed.

I. 1% by volume of 20% fuming sulfuric acid was added to the oil and agitated for one hour. The oil was treated with an equal volume of isopropyl alcohol solution containing 0.025% (wt./volume) of caustic potash and filtered through several sheets of absorbent paper. After percolation through Attapulugus clay (30-60 mesh), the oil gave a No. 5 copper test.

II. The oil was treated with an 0.5% anhydrous ferric chloride at 75° C. for 30 minutes. The reagent was added in the form of a paste. The oil was then filtered free of sludge and treated at 120° C. with an equal volume of an isopropyl alcoholic solution containing 2 pounds of caustic potash per thousand gallons of oil to be treated. The alcoholic solution was separated and the oil phase air-blown at 120° C. for 20 minutes to remove traces of alcohol. The oil at this stage of the treatment showed a below -15 Saybolt. The oil was then percolated through Attapulugus clay (30-60 mesh). The resultant oil was tasteless, odorless, and had a color of +30 Saybolt. The oil also gave a No. 1 copper test. Furthermore, the treated oil did not develop any mal odor

upon exposure to natural sunlight for 60 minutes.

The treatment according to the invention improves the stability of white oil products in at least four respects; namely, color, odor, taste, and development of corrosiveness towards highly polished copper. As a result of processing oils according to the invention, it is noted also that the yields in the clay filtering operations by which the oils are usually finished are improved. This treating effect upon normally refined oils of lubricating oil consistency is common to all the higher valent halides of the amphoteric metals which hydrolyze in the presence of water in combination with caustic alkalis dissolved or finely dispersed in an organic solvent which readily vaporizes from the treated oil. The halides of the trivalent elements however, particularly aluminum chloride and ferric chloride have been found to be preferable in combination with potassium hydroxide dissolved in either isopropyl or ethyl alcohol. In addition to the improvement of white oil products of lubricating oil consistency, highly refined oils in the naphtha and kerosene boiling ranges can also be advantageously treated by the method of the present invention. The products obtained in such cases are suitable for the preparation of solvents, lacquers, spray compositions and in the preparation of similar type materials.

While the invention has been described in detail, and a number of illustrated examples have been given, it is to be understood that the invention is not limited thereby but same have been given for the purpose of conveying an appreciation of the scope and nature of the invention. It will be obvious to those skilled in the art that variations of the process can be made within the spirit of the invention.

What is claimed is:

1. The process of refining mineral white oils which comprises, treating a petroleum oil with sulfuric acid of above 95% concentration to remove substantially all the unsaturated and color-forming bodies, separating the sludge, neutralizing the oil with an alkaline solution, separating the alkaline solution, treating the oil with about 50% aqueous alcohol to remove sulfonate soaps, treating the resultant product with from about .5% to 1% of an anhydrous metallic chloride selected from the group consisting of aluminum chloride, ferric chloride, chromic chloride, zinc chloride and stannic chloride, separating the sludge so formed and then treating the oil with from about .01% to 1% of an anhydrous caustic alkali.

2. Process according to claim 1 in which the

anhydrous metal chloride is that of a trivalent element.

3. Process according to claim 1 in which the anhydrous metal chloride is aluminum chloride.

4. Process according to claim 1 in which the caustic alkali is caustic potash.

5. Process of refining mineral white oils which comprises, treating a petroleum oil of lubricating oil consistency with sulfuric acid of concentrations between 93% strength and 20% fuming in a series of additions to remove substantially all the unstable and color-forming bodies, separating the sludge after each addition, then neutralizing the oil with an aqueous alkaline solution, separating the aqueous solution, treating the oil with an about 50-50 water isopropyl alcohol mixture to remove sulfonate soaps, treating the oil with steam and then with air to remove traces of isopropyl alcohol and water, then treating the oil with an anhydrous metallic chloride selected from the group consisting of aluminum chloride, ferric chloride, chromic chloride, zinc chloride and stannic chloride in an amount between about .5% to 1% by weight of the oil, separating the sludge so formed, treating the resultant oil with an anhydrous alcoholic solution of 0.01% and 0.1% of a caustic alkali and then treating with clay.

6. Process according to claim 5 in which the anhydrous metallic chloride is aluminum chloride.

7. Process according to claim 5 in which the caustic alkali employed is caustic potash.

8. Process according to claim 5 in which the anhydrous metallic chloride is aluminum chloride and the caustic alkali employed is caustic potash.

9. Process of refining mineral white oils which comprises treating a petroleum oil of lubricating oil consistency with 20% fuming sulfuric acid in a series of additions to remove substantially all the unsaturated and color forming bodies, separating the sludge after each addition, then neutralizing the oil with a 10% aqueous solution of sodium carbonate, separating the aqueous solution, washing the oil several times with a 50% aqueous isopropyl alcohol solution to remove oil soluble sulfonates, treating the oil with steam and then with air to remove traces of isopropyl alcohol and water, then treating the oil with 0.5% of aluminum chloride for 30 minutes at 75° C., separating the sludge so formed, treating the resultant oil at 120° C. with 0.025% of caustic potash dissolved in a minimum quantity of isopropyl alcohol, blowing the oil at 120° C. to remove the alcohol and then percolating through clay.

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