Patented Feb. 12, 1946 2,394,965

UNITED STATES PATENT OFFICE

2,394,965

REFINING LUBRICATING OIL STOCKS

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No Drawing. Application August 11, 1942, Serial No. 454,409

13 Claims. (Cl. 196—44)

This invention relates to the manufacture of lubricating oils which are especially resistant to oxidation and sludge-formation, and more particularly to the manufacture of oils used in the lubrication of internal combustion motors.

The tendency for lubricating oils to oxidize and deposit sludge particularly in internal combustion engines, is well-known, and many attempts have been made to correct this difficulty. Various refining procedures have been proposed to correct the sludging tendency of motor oils, and inhibitors have been proposed and used for the same purpose. Some highly refined oils seem to have a greater tendency toward oxidation and sludge formation than oils which are less refined, and points to the fact that some natural protective agents are removed by present normal refining methods.

According to the features of the present invention, lubricating oils which are refined by present methods, or which are unrefined, are treated with a hydrated inorganic ferric compound such as hydrated ferric chloride (i. e. ferric chloride containing water of crystallization). This treatment produces only from 1% to 2% by weight of a sludge material but seems to give a very unusual result in that the stability of the oil is enormously increased. The process may be applied to any of the lubricating oil stocks whether produced as overhead distillates or as cylinder stock type products. Such lubricating oils may be treated in their raw state or after they have been refined with the usual refining agents such as sulfuric acid, contact clays, anhydrous aluminum chloride, selective solvents, or other known treating agents. The stock to be treated is preferably a dewaxed stock and may be ready for use or ready for final treatment.

Lubricating oils in these conditions are treated by the process of the present invention by first intimately contacting the oil with from 0.5 to 4% by weight of a hydrated inorganic ferric salt such as ferric chloride. The oil may be heated up to a temperature of about 190° F. and hydrated ferric chloride added with constant stirring after which the mixture is preferably gradually heated to a temperature of about 350° F. The agitation is continued at this final temperature over a period of from 15 to 20 minutes to complete the reaction which causes the formation of a pitch or asphalt-like precipitate which may be separated from the hot oil by settling or filtration. The oil free of this precipitate is then preferably contacted with a neutralizing agent such as slaked lime used in a proportion of from 0.3 to about 1% by weight of the oil and finally treated with from 3% to about 10% by weight of a refining contact clay. The neutralization and clay treating may be carried out simultaneously by mixing the slaked lime with the contact clay, this final treatment preferably being carried out at a temperature of from 350° F. to 550° F. The clay treating agent is separated from the oil by means of a filter press or other suitable means and the oil is ready for use.

The effectiveness of the process of the present invention may be illustrated by reference to the following examples in which the sludge-forming characteristics of the treated oil are compared with those of the untreated oil or with those of the oil when refined by other methods. The invention, however, is not to be construed as limited by these examples.

Example 1

A finished Pennsylvania lubricating oil stock of 30 SAE number which had been refined by contact treatment at relatively high temperature with an acid washed decolorizing contact clay known as "Filtro," was tested by the Indiana oxidation test and found to give 3.3, 23.5, 72.0, and 166.0 mgms. of sludge per 10 grams of oil after twenty-four, forty-eight, seventy-two, and ninety-six hours, respectively, in the testing machine. A portion of this same finished stock was treated with 1.5% by weight of hydrated ferric chloride at a temperature of from 340° to 350° F. for a period of fifteen minutes while agitating the mixture and maintaining the temperature. The resulting treated oil was separated from the sludge precipitate and treating agent, neutralized with slaked lime and finally contacted with 5% by weight of "Filtrol" at a temperature of about 350° F. The resulting product was then tested on the Indiana testing machine and after the same hourly periods mentioned above, the corresponding sludge values were respectively: 1.2, 2.6, 2.3, and 1.9.

Example 2

A Pennsylvania lubricating oil of about 30 SAE number was refined with "Filtrol" under the conditions described in Example 1 and also

with 2.5% of hydrated ferric chloride at a temperature of about 350° F. The resulting refined products were tested on the Indiana testing machine with the following results:

Hours	Mgms. naphtha insolubles in 10 grams of oil	
	"Filtrol" treated oil	Ferric chloride treated oil
24	1.8	6.5
48	17.9	0.2
72	60.6	6.9
96	158.5	49.0

Example 3

A raw Pennsylvania cylinder stock was treated with 1% by weight of hydrated ferric sulfate at the temperatures used for the ferric chloride treatment, neutralized and finally treated with 10% by weight of Filtrol in the manner described in Example 1. The resulting treated oil showed only 0.0, 1.5, 1.7, and 1.0 mgms. of sludge per 10 grams of oil in the Indiana oxidation testing machine after twenty-four, forty-eight, seventy-two and ninety-six hours, respectively.

Example 4

A used crank case motor oil was taken from the crank case of an automobile and four separate parts of it were treated by four different refining agents, one of which was hydrated ferric chloride. In carrying out the treatment with hydrated ferric chloride, a portion of the used crank case oil was percolated through a filter filled with small pieces of pumice stone on which the hydrated ferric chloride was deposited. A similar operation was carried out on another portion of the oil with anhydrous aluminum chloride deposited on pieces of pumice stone. The third treatment consisted in treating a portion of the used crank case oil with 5% by weight of 60° Bé. sulfuric acid, while the fourth treatment consisted in treating a portion of the oil first by washing it with methyl alcoholic caustic soda and then treating it with 5% by weight of 60° Bé. sulfuric acid. All four of the resulting treated oils were neutralized with alkaline material and finally decolorized with 10% by weight of "Filtrol." The Indiana oxidation tests on the final products gave the following results:

Hours	Mgms. of sludge per 10 grams of oil			
	Ferric chloride treated oil	Aluminum chloride treated oil	Sulfuric acid treated oil	Alkaline washed and sulfuric acid treated oil
24	4.2	4.5	8.5	2.5
48	2.4	8.5	33.4	2.6
72	1.9	19.3	10.9	8.9
96	3.2	48.0	49.5	43.0
120	2.2	104.5	79.9	94.3

The values in this table are the sludges determined after the indicated number of hours elapsed during the test.

The data supplied in the foregoing examples show the value of the process of the present invention in the stabilization of lubricating oil stocks. The process of the present invention is primarily adapted for use as a final stabilization process adapted to eliminate constituents which are most readily oxidized or converted to sludge. The contacting of the treated oil with a refining clay after the ferric chloride treatment is primarily for the purpose of improving the color of the oil and for the removal of small proportions of fine particles of sludge suspended in the oil which may not have been removed after the ferric chloride treatment. While the procedure may be varied considerably without departing from the invention, it has been found that the successive treatment of the lubricating oil stock with a hydrated inorganic ferric salt, separation of sludge, neutralization of the oil with lime, and finally contacting the oil with a refining clay, gives excellent results.

The treatment of the oil with a hydrated inorganic ferric salt seldom produces more than about 1.5% of sludge, which in most cases is separated out as a gritty "coky" material. When this sludge is de-oiled and dried, a black powder is obtained in most cases.

The process of the present invention may be carried out in various types of apparatus such as are used in other oil treating processes. The oil might be treated by passing it together with the proper proportion of hydrated inorganic ferric salt through a heating coil, discharging the heated mixture into an agitator where slow agitation of the mixture is continued, withdrawing the treated mixture from the bottom of the agitator and passing it through a filter press or equivalent separating means for the removal of the precipitated sludge constitutents, and thereafter passing the oil mixed with the proper proportion of slaked lime and fine contact clay through a heating coil in which the mixture is heated to a temperature of from 450° to 550° F. The oil-clay mixture is passed to a filter press or equivalent means for the separation of the treated oil. Where the slaked lime is used alone for neutralization, it is sometimes advisable to add some filter-aid such as "Filter-cell" to aid in the removal of the lime.

The process of the present invention is particularly adapted to the treatment of paraffin base oils, but may be applied to the treatment of asphaltic or mixed base oils which have been subjected to a deasphalting treatment. It is the usual practice in the manufacture of lubricating oils from asphaltic and mixed base oils to remove as much as possible of the asphalt by some deasphalting procedure as well as to treat the oil with sulphuric acid or some other refining agent. In these cases the present process should come as a final treatment.

While ferric chloride is preferred, hydrated ferric salts other than those mentioned above may be used, such for example as ferric bromide, ferric nitrate, and other inorganic ferric salts which are soluble, at least to some extent, in water. The degree of hydration may vary considerably, from salts containing a single water of crystallization to what may be termed a concentrated aqueous solution.

The invention is not restricted to any treatment following the ferric salt treatment, although in most cases neutralization with an alkaline agent is desirable. The use of decolorizing clay or other agent while usually preferred, will depend on the oil and purpose for which it is refined.

It is to be understood that the invention is not restricted to any particularly theory whether catalytic or purely chemical by which the hydrated inorganic ferric salt accomplishes the results obtained and reported.

Having described and illustrated the invention, what is claimed as new is:

1. A process for manufacturing lubricating oils which are resistant to oxidation and sludge-formation, comprising contacting a sludge-forming lubricating oil with from 0.5 to 4% of a hydrated inorganic ferric salt at a temperature of from about 340° F. to 400° F., said salt being substantially free of water except for water of crystallization, continuing the contacting for a substantial period of time after which the sludge resulting from the treatment is separated from the oil, neutralizing the treated oil and finally contacting it with a decolorizing clay to produce an oil of desired color which is resistant to oxidation and sludge-formation.

2. The process for manufacturing lubricating oils which are resistant to oxidation and sludge-formation, comprising contacting a lubricating oil stock which gives relatively high sludge results in oxidation tests with from 0.5 to 4% of a hydrated water-soluble inorganic ferric salt which is substantially free of water except for water of crystallization, gradually heating the mixture of oil stock and salt following the initial contact until a temperature of from 340° to 400° F. is reached to thereby cause the formation of sludge-like constituents, and thereafter separating the resulting sludge and the treating agent from the oil stock.

3. A process as defined by claim 2 in which the treated oil is neutralized with a small proportion of slaked lime.

4. A process as defined by claim 2 in which said salt is ferric chloride.

5. A process as defined by claim 2 in which said salt is ferric sulfate.

6. A process for manufacturing lubricating oils which are resistant to oxidation and sludge-formation, comprising contacting the sludge-forming lubricating oil to be treated at a temperature of approximately 200° F. with from 0.5 to 4% by weight of hydrated ferric chloride which is substantially free of water except for water of crystallization, gradually heating the mixture following the initial contact until a temperature of from 340° F. to 400° F. is reached, thereafter separating the sludge formed by the reaction together with the treating agent from the oil, neutralizing the oil with a small but sufficient proportion of slaked lime, and contacting the oil with a refining clay at a temperature of from 350° F. to 550° F.

7. The process for manufacturing lubricating oils which are resistant to oxidation and sludge-formation, comprising contacting a sludge-forming lubricating oil stock which gives high results in oxidation sludge-forming tests with from 0.5 to 4% of hydrated ferric chloride which is substantially free of water except for water of crystallization, agitating the ferric chloride in contact with the lubricating oil stock at a temperature of approximately 350° F. and thereby causing the formation of an asphalt-like sludge, and separating the resulting sludge and chloride treating agent from the treated oil.

8. The process for manufacturing lubricating oils which are resistant to oxidation and sludge-formation, comprising contacting a sludge-forming lubricating oil stock which gives high results in oxidation sludge-forming tests with from 0.5 to 4% of a hydrated inorganic ferric salt which is substantially free of water except for water of crystallization, agitating the oil and ferric salt for a substantial period at a temperature of not less than about 190° F. and in the absence of any added water thereby causing precipitation of the more readily oxidizable constituents of the lubricating oil stock to asphalt-like material, and separating the resulting asphalt-like precipitate from the treated oil stock.

9. A process for manufacturing an improved motor lubricating oil which is highly resistant to oxidation and sludge-formation, comprising intimately contacting a refined motor lubricating oil stock which gives relatively high results in oxidation tests with from 0.5 to 4% of a hydrated inorganic ferric salt which is substantially free of water except for water of crystallization, intimately agitating the oil stock and salt for a substantial period of time at a temperature of not less than about 190° F., to thereby cause precipitation of the more readily oxidizable constituents of the oil to form a sludge, and separating the resulting sludge together with the treating agent from the resulting purified motor oil.

10. A process for manufacturing lubricating oils which are resistant to oxidation and sludge-formation, comprising contacting a raw lubricating oil stock which gives high sludge results in oxidation tests with approximately 1.5% of hydrated ferric chloride which is substantially free of water except for water of crystallization, carrying out the contacting operation at a temperature of from 340° to 350° F. to produce asphalt-like sludge material, and separating the resulting sludge from the treated oil.

11. A process as defined by claim 2, in which approximately 2.5% of ferric salt is contacted with the oil stock.

12. A process as defined by claim 2, in which approximately 1% of said ferric salt is contacted with the oil stock.

13. A process as defined by claim 2, in which the oil stock treated is a used crank case motor oil.

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