Patented Mar. 1, 1932 1,847,623

UNITED STATES PATENT OFFICE

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METHOD OF TREATING OIL

No Drawing. Application filed July 15, 1929. Serial No. 378,570.

This invention relates to a process for treating lubricating oils to produce lubricating oils of the proper characteristics and to produce lubricating oils of desired color.

It is an object of this invention to treat highly viscous lubricating oil with acid under such conditions that the subsequent neutralization by solutions of neutralizing agents shall not create troublesome emulsions.

It is a further object of this invention to treat lubricating oils of over 800 seconds Saybolt Universal at 100° F. and even up to 15,000 seconds Saybolt Universal at 100° F. or even higher viscosity oils, and oils having a viscosity of 55 and higher seconds Saybolt Universal at 210° F., with acid under such conditions that troublesome emulsions are not formed when the acid treated oil is subsequently neutralized by solutions of neutralizing agents.

It is a further object of this invention to treat lubricating oils by acid under such conditions that the inherent green fluorescence of the oil is not destroyed.

It is a further object of this invention to treat lubricating oils with acid under such conditions that the bodies having a blue fluorescence are not formed.

It is a further object of this invention to treat lubricating oil with acid under such conditions that only a minimum loss by sludge formation is obtained.

It is a further object of this invention to treat lubricating oil with sulfuric acid of non-sulfonating and non-oxidizing concentrations to obtain the objects described above.

It is a further object of this invention to treat lubricating oil with sulfuric acid of less than 90% acid strength and preferably of a strength lying between 40 to 90% acid concentration.

A well known process for the production of lubricating oils consists in treating lubricating oil stock with 98% sulfuric acid in varying quantities; removal of the acid sludge formed, by settling, or other means; neutralization of the acid treated oil with caustic soda or equivalent neutralizing agent; washing the neutralized oil with water; and the removal of the last traces of water in order to produce a dry finished oil by heating the washed oil and agitating it with air. Processes are also well known for producing finished lubricating oils which involve treating the finished oil from the above or similar process with fuller's earth or finely divided decolorizing clays. Also, in other processes, clay treatments have been applied at some point after the acid treatment of the lubricating stock, as, for instance, after acid treatment, the oil is treated with clay to produce a finished oil free from acid reaction products and of desired color.

During the treatment of lubricating stocks with 98% acid there is generally a definite and noticeable rise in temperature and evolution of sulfur dioxide gas. This may be taken as an evidence of an oxidizing action.

The lubricating stocks are treated with sulfuric acid in different amounts, in order to produce a finished lubricating oil of red or pale color from the stock which is generally dark green in color and opaque. The amount of sulfuric acid used is generally dependent upon the nature of the stock, for some stocks react more readily to acid treatment than others and give a finished oil of the required color with less severe acid treatment.

Strong sulfuric acid is also a sulfonating agent, and the use of strong sulfuric acid in large quantities on lubricating stocks, definitely tends to produce sulfonated products which promote emulsification during neutralization of the acid oils with caustic soda. These sulfonated products may also appear in some form in the finished lubricating oils, and thereby cause them to have poor de-emulsifying and lubricating properties.

It is known that oxidation does occur in treating these lubricating distillates with strong sulfuric acid. One of the effects of such an oxidation is to impart a somewhat bluish or purplish fluorescence to the acid oil. It is known that strong sulfuric acid is definitely a sulfonating agent and one of the results of the sulfonating action on lubricating distillates is to impart to the acid oil a bluish fluorescence, even more pronounced than obtained by deleterious oxidation effects. When treating certain lower viscosity distil-

lates for the production of spray oils, it has been necessary to use large amounts of 103% sulfuric acid. The acid oils in this case are almost purple in appearance and when attempting to neutralize these acid oils with caustic soda, emulsifying difficulties have been so pronounced that on one occasion the whole volume of oil seemed to emulsify into a semi-solid condition. This tendency must definitely have been occasioned by the presence of material amounts of sulfonated products.

The tendency to emulsify when neutralizing a lubricating distillate has been more pronounced with an increased viscosity of the lubricating distillate, so that it has been almost impossible to treat lubricating stock of higher viscosity than 1200 seconds Saybolt Universal at 100° F. with strong sulfuric acid without encountering serious emulsion difficulties during the neutralization process. This would indicate that the sulfonating action is more pronounced in the case of the higher viscosity distillates, or causes more difficulty during neutralization on account of the higher viscosity of the oils being neutralized.

The use of sulfuric acid in oxidizing and sulfonating strength acts to destroy the inherent green fluorescence of the lubricating oil and/or to develop bodies having a blue fluorescence.

When producing finished lubricating oils by the use of strong sulfuric acid, the bluish fluorescence of the acid oil, occasioned by a definite oxidizing and sulfonating action, may be carried on through the treating process, thereby imparting a somewhat bluish fluorescence or "bloom" to the finished oil. This has been considered detrimental, for it destroys somewhat the attractive appearance of the finished product and tends to be indicative of the presence therein of certain deleterious oxidation and sulfonation reaction products.

When treating lubricating stocks with strong sulfuric acid, relatively large amounts of acid sludge are formed, resulting in low yields of finished oil. The large losses thus incurred are not necessary, in that the percent. of substances present in the lubrication stocks which are actually objectionable malodorous substances, and easily oxidized, color or acid forming substances, is really very small, and the treatment with strong acid may involve much more severe chemical reactions than are necessary to produce a finished product of the appearance and quality desired.

The deleterious effects of strong acid resulting from oxidation and sulfonation can be summarized:

1. Imparting a deleterious blue fluorescence to the oil.

2. Large losses of lubricating oil.

3. Causing bad emulsions on subsequent neutralization.

4. Imparting to the finished lubricating oil a content of oxidized and sulfonated material which impair its lubricative properties and impart to it an undesirable emulsifying tendency.

I have discovered and developed, that the treatment of lubricating stocks for the production of finished lubricating oils, may be improved very much and added beneficial results obtained by regulating the acid treatment of the stock so as to minimize the oxidizing and sulfonating action. I have accomplished this by using sulfuric acid of relatively weak strength, and have found that such relatively non-oxidizing and non-sulfonating acids are available in sulfuric acid of concentration ranging from 40 to 90% H_2SO_4. When treating lubricating stocks with such acids, the oxidizing effect as evidenced by evolution of sulfur dioxide and material advance in temperature during acid treatment, is minimized and very much less than when treating with the stronger sulfuric acids. The oxidation effect and temperature rise are diminished with decreasing strength of acid used. Since lubricating stocks are of different "quality" as evidenced by different amounts of strong sulfuric acid required to produce a finished oil of a definitely desired color, it follows that different strength weak acids may be applied to different quality stocks in order to produce a finished oil of the desired color. Stocks that require relatively small amounts of strong acid to produce a red oil of 4 to 5 N. P. A. color, may be successfully treated with sulfuric acid of as low concentration as 40 to 55% H_2SO_4, whereas certain stocks which do not have this high quality, seemingly require sulfuric acid of 75 to 90% strength and, of course, there are other stocks to which can be successfully applied, sulfuric acid with strength in between the ranges specified.

The use of these weak acids definitely results in the formation of very much less sulfonated products which has resulted in less tendency to emulsification during the neutralization process. Also, a decrease in oxidizing and sulfonating actions is definitely shown by less tendency to form acid oils and finished lubricating oils with a bluish fluorescence or "boom". In fact, the finished lubricating oils resulting from treating the lubricating stocks with weak acids, possess a green fluorescence or "bloom". These finished oils are more pleasing in appearance and possess other advantageous characteristics. This treatment does not destroy the green fluorescence in the oil nor does it develop bodies having blue fluorescence.

In the treatment of lubricating stocks with weak acids, very much less acid sludge is

formed than when using strong acids, resulting in increased yields of finished oil. The treatment with weak acids also more nearly adjusts the treatment to that necessary to produce a finished lubricating oil of good lubricating properties, without subjecting it to severe chemical reactions which are not necessary and which may destroy some of the lubricating properties. The treatment of the stocks with weak acid definitely results in a finished lubricating oil less liable to contain sulfonated products therein, and consequently such a finished lubricating oil has superior demulsifying and lubricating properties.

The effect of the treatment of lubricating stocks with weak acids as evidenced by a reduction in the tendency of emulsification when neutralizing the acid oil, has made it possible to successfully treat lubricating stocks of very high viscosity. It was formerly impossible to economically and advantageously treat stocks above 1200 viscosity Saybolt Universal at 100° F. with strong sulfuric acid in amount required to give commercial oils, and even in the neighborhood of 800 seconds emulsions have made said treatment almost economically impossible. Stocks have now been successfully treated with weak acid with viscosities as high, and even higher, than 15,000 Saybolt Universal at 100° F. It is well known that in order to produce commercial oils of required viscosity at 210° F. ranging from 55 seconds Saybolt Universal to 150 seconds Saybolt Universal, that oils of varying viscosity at 100° F. are required, depending upon the source or nature of the crude oil. Thus, for example, whereas an oil of 800 to 1,200 viscosity seconds Saybolt Universal at 100° F. would be required to produce a finished lubricating oil of 55 to 70 seconds Saybolt Universal at 210° F., if produced from a western or naphthene base crude, on the other hand, an oil of approximately 450 to 800 seconds Saybolt Universal viscosity at 100° F. would be required to produce a finished lubricating oil of 55 to 70 seconds Saybolt Universal at 210° F., if produced from an eastern or paraffine base crude. All of the above oils, when treated with strong acid in the neighborhood of 98% acid in sufficient quantities to give commercial oils ranging from 55 to 150 seconds Saybolt Universal and higher at 210° F., produce emulsions of such tenacity as to render the processes both difficult and uneconomical and impossible of commercial exploitation. Whereas, such oils, when treated with the process herein described, that is, with weak acids of 90% and less concentration, the desired oils may be produced without any substantial difficulty as to emulsions on neutralization. This is a distinct advantage, for it has opened new fields for the economical production of lubricants of high viscosity which have a general application.

In the treatment of high viscosity stocks of above 800 seconds Saybolt at 100° F. with strong acid, as previously described, the oxidizing and sulfonating actions were always increased by the necessity of treating these stocks at somewhat advanced temperature, in order to reduce the viscosity so that proper settling of reaction products would take place at atmospheric pressure. The use of weak acids permits treating at much higher temperatures than were formerly practical. By using acids of less than 90% concentration, I have been able to avoid the bad emulsions which have made treatment of these high viscosity oils impossible. The advance in temperature of treatment when using weak acids, does not result in the increased oxidizing and sulfonating action as when using strong acid, so that stocks of high viscosity have been treated at temperatures as high as 250° F. with weak acids, without the evolution of sulfur dioxide in near the quantity as when treating with strong sulfuric acid at temperatures of nearer 100° F. In similar manner the treatment of high viscosity stocks at high temperatures has not resulted in the formation of sulfonated bodies to the extent that these high viscosity acid oils cannot be successfully neutralized in open agitators at ordinary pressures.

While these elevated temperatures may prove necessary for these very high viscosity oils, it tends to increase the oxidizing and sulfonating effect of the acid and therefore tends to oppose the advantage of the dilution of the acid. It is, therefore, preferred to work at as near normal temperature as possible, consistent with the rapid and adequate settling of sludge, and for oils of 800 seconds or less, heating is avoided and reaction proceeds at as low a temperature as consistent with proper settling of sludge and reaction products.

Another advantage of the use of weak acids lies in the possibility of utilizing waste acids obtained by washing the acid sludge derived from treating lubricating stock with different cencentration acids. When employing 98% sulfuric acid or stronger sulfuric acid for acid treating lubricating stocks, the waste acid derived from washing this acid sludge is generally of 40% to 55% H_2SO_4 content. This waste acid is a so-called "black acid", for it contains a material percentage of finely divided carbonaceous material. The ordinary means for the utilization of this waste acid is to concentrate it in the proper type of concentrating plant to a concentration as high as 90% H_2SO_4 or higher. However, the production of black acids of 40 to 55% strength allows these black acids to be used directly for acid treating certain lubricating stocks of high quality. On stocks which are not of such high quality then, these black acids can be used by fortifying them with strong sulfuric acid so that they have an

H_2SO_4 content of above 55% and possibly up to about 85%. The concentration to which they can be economically fortified naturally depends on the cost of the fortifying acid as compared with the cost of concentrating the "black acids" to the desired strength. Figures show that the black acids can be fortified to a concentration of about 80% economically, as compared with concentrating them to this concentration. They can be fortified to concentrations less than 80% even more economically as compared to concentration. Certain stocks have such a quality that permits the use of 70 to 85% acid and these stocks have been successfully treated with acids of this concentration made by fortifying black acid.

On a certain stock it has been definitely shown that the use of 83% H_2SO_4 results in the production of an oil of less desirable characteristics than the use of 80% H_2SO_4. It is difficult to define absolutely the proper strength acid for each stock so as to insure a minimum oxidizing and sulfonating action, but the decrease of such actions is definitely noticed when reducing the strength below 90% H_2SO_4. Beneficial effects have been obtained by the use of 60 and 70% H_2SO_4, but the use of these acids depends upon the quality of the stock being treated, since in order to produce a finished oil of a certain color, it might be necessary to use very large amounts of acids of this concentration, whereas, materially less amounts of acid of a strength of 80 to 90% could be employed to produce the same color. However, in the case of the use of a stronger acid, the beneficial effects on the neutralization of minimizing the oxidizing and sulfonatng actions will not be as noticeable as in the case of the use of a weaker acid. Finished oils of still more pleasing green fluorescence, or bloom, and of somewhat better demulsifying and lubricating qualities, could be produced with the relatively weaker acid, but the economy of the process might make it preferable to use the relatively stronger acid. It, therefore, appears that for every oil there is an optimum concentration of acid beyond which the sulfonation and oxidation effect increases to a deleterious extent and below which excessive amounts of acid must be employed.

After the acid treatment of the various stocks with weak acids, the strength of which is chosen according to the "quality" of the stocks, the acid oils are freed from sludge by settling or other means; the acid treated oils then neutralized with caustic soda, and the neutralization reaction products removed by settling or other means; and then washed with water. After water washing, the oils are dropped into a "blow pan" where they are heated and blown with compressed air to remove traces of water. The oils produced in this manner are more free from deleterious reaction products, such as oxidized and sulfonated products, and are characterized by a less pronounced bluish fluorescence, or bloom. Also, a materially increased yield of finished oil is produced than when using strong acid. The heating of the oil in the blow pan, and blowing it with compressed air, results in some oxidation of the oil and tendency to form again a bluish fluorescence; therefore some other method for obtaining a product of even more pleasing appearance and of somewhat better characteristic and quality preferably should be used.

After acid treating the lubricating stock, it is then neutralized as usual, and the reaction products removed by settling or other means. The neutralized oil is then clay treated without washing the neutralized oil with water. The clay treatment consists in mixing the neutralized oil with various amounts of finely divided decolorizing clay and heating this mixture to a relatively advanced temperature, for example, 250° F. to 330° F. and removing the clay by a filtration process or equivalent means. Such a procedure is somewhat more economical, for the water washing of the oil has been eliminated as well as the heating of the oil in the blow pan and agitating it with compressed air. The clay has a decolorizing action as well as an absorbing action for reaction products, and the use of clay permits the use of less acid to obtain the same color of finished oil as compared with the process where clay is not used. The omission of either or both of the steps of water washing the neutralized oil and then blowing it free from traces of water, and substituting therefor, a clay treatment, results in the production of a finished oil of more pleasing appearance. The oil produced in this manner is characterized by a distinct greenish fluorescence, or bloom, and is more free from deleterious reaction products than the oils which have not been clay treated, due to the absorbing action of the clay in further removing these deleterious reaction products.

Oils of pleasing appearance and excellent quality naturally can also be obtained by clay treating the acid treated oils after neutralization and after water washing these neutralized oils.

Also oils of pleasing appearance and good quality may be obtained by clay treating the oils which have been produced from the blow pan. Naturally, the elimination of the steps discussed, results in a more economical process, and the choice of steps is occasioned by the cost of the finished product and the pleasing appearance and quality thereof.

Oils of pleasing appearance and excellent quality also can be obtained by treating with weak acid lubricating oil which has previously been neutralized or had its acidic constituents substantially removed. These acidic

constituents can be variously removed by distilling the crude oil with caustic soda or equivalent chemical, or treating the distillate with a neutralizing agent either in the vapor phase during the distillation process or in the liquid phase after condensing. After treating the substantially neutral distillates, produced in this manner, with weak sulphuric acid, the acid remaining in the oil may be removed by washing with water, treating with a neutralizing agent or treating with an absorbing and decolorizing clay. The neutralizing agent and/or the clay acts to remove acid and acid reaction products from the oil. In every case, the use of weak sulphuric acid imparts a pleasing green fluorescence to the finished oil and results in the production of the finished oil substantially free from oxidized and sulphonated material in an economical manner.

The preferred process for the manufacture of finished lubricating oils, at present, involves the following steps: treatment of the lubricating stock or distillate with sulfuric acid in concentrations varying from 40 to 90% H_2SO_4; removing the acid sludge by settling or other means; neutralizing the acid oil with caustic soda solution or equivalent neutralizing agent; removal of excess caustic soda solution and some reaction products by settling or other means; mixing of the neutralized oil with finely divided absorbing and decolorizing clay in amounts varying roughly from 10 pounds to 30 pounds of clay per barrel of neutralized oil; heating the mixture of neutralized oil and clay to a temperature varying roughly from 250° F. to 330° F.; the oil and clay are then filtered and the filtered oil is centrifuged whereby any traces of clay which may have come through the filter press will be removed, the centrifuged oil being then cooled and sent to storage.

The method of treating or refining lubricating oil stock herein described, is well adapted to accomplishing the purpose for this invention, but various modifications may be made in the details of the process without departure from the spirit of the invention, and the invention is, therefore, not limited to the specific processes described for the purpose of illustrating the invention, but includes all such modifications as come within the scope of the claims.

I claim:

1. A method of refining lubricating oil of a viscosity greater than 1000 seconds Saybolt Universal at 100° F. which comprises treating said oil with sulfuric acid of 40 to 90% acid concentration, separating the acid sludge and neutralizing said acid treated oil.

2. A method of refining lubricating oil of a viscosity greater than 1000 seconds Saybolt Universal at 100° F. which comprises treating said oil with sulfuric acid of 40 to 90% acid concentration and separating the acid sludge.

3. In the treatment of lubricating oil which generates a blue bloom on treatment with strong sulfuric acid, the step of treating said oil with sulfuric acid having an acid concentration of 40–90% to produce an oil having a green bloom.

4. In the treatment of lubricating oil having a green bloom which is destroyed or impaired upon treatment with concentrated sulfuric acid, the step of treating said oil with sulfuric acid having an acid concentration of 60 to 90%.

5. A method of refining lubricating oil stocks which comprises treating the oil with sulfuric acid of 40% to 90% H_2SO_4 content; removing the acid sludge; neutralizing the acid oil; removing the excess of neutralizing agent and reaction products; mixing the neutralized oil with comminuted solid absorbent material; heating the mixture of neutralized oil and absorbent material to a temperature of 200° F. to 350° F.; removing the absorbent material; centrifuging the filtered oil to remove traces of absorbent material and pumping the finished oil through a cooling coil to storage.

6. A method of refining lubricating oil stocks which comprises treating the oil with sulfuric acid of 40 to 90% H_2SO_4 content; removing the acid sludge by settling; neutralizing the acid oil with a neutralizing agent; removing the excess of neutralizing agent and reaction products; washing neutralized oil with water; heating the washed oil and blowing with compressed air or other agent to remove last traces of water.

7. A method of refining lubricating oil stocks which comprises treating the oil with sulfuric acid of 40 to 90% H_2SO_4 content; removing the acid, mixing the acid oil with comminuted solid adsorbent material, heating the mixture of acid oil and adsorbent material to a temperature of 200° F. to 350° F., removing the adsorbent material by filtration, centrifuging the filtered oil to remove traces of adsorbent material and pumping the finished oil through a cooling coil to storage.

8. A method of refining lubricating oil of a viscosity higher than approximately 55 seconds Saybolt Universal at 210° F. which comprises treating said oil with sulfuric acid of 40–90% concentration and separating the acid sludge and neutralizing said acid treated oil.

9. A method of refining lubricating oil which comprises treating oil with sulfuric acid from 40 to 90% sulfuric acid content, removing the acid from the oil and treating said acid treated oil with an agent capable of separating the residual acid reaction product in the oil from said oil.

10. A method of refining oil which com-

prises generating a neutral lubricating oil fraction and treating said neutral oil with weak acid from 40 to 90% sulphuric acid concentration, separating the acid from said oil and treating said oil with an agent capable of removing said acid reaction product from said oil.

Signed at Los Angeles, in the county of Los Angeles and State of California, this 28th day of June A. D. 1929.

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