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PROCESS FOR CLARIFYING, DECOLORIZING, AND NEUTRALIZING OILS.

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This invention relates to the art of decolorizing, clarifying and neutralizing oils, fats, waxes and similar materials and while not necessarily limited thereto, more particularly refers to such treatment of petroleum lubricating oils. The object thereof is to provide a process wherein the cost in time and operations, as well as in materials, is considerably reduced, and whereby a superior product is obtained.

In the preparation of petroleum lubricating oils from fractions of crude petroleum known as lubricating distillates, it is common practice to treat said distillates with sulphuric acid. This acid treatment effects a considerable removal of coloring matter and other undesirable substances in the oil but does not sufficiently decolorize and clarify the oil for commercial purposes and in addition leaves the same in an acid condition thus rendering it unfit for use. It is necessary therefore to subject the acid oil to a clarifying, decolorizing and neutralizing treatment.

For decolorizing and clarifying the oils, the generally accepted agent has been mineral earth such as fuller's earth and clays, while for neutralization the practice has been to use sodium hydroxide or other alkali. As to the decolorization and clarification, a common method for oils, particularly petroleum lubricating oils, has been to percolate such oils through the fuller's earth or other mineral earth; this method however has the disadvantage that it is tedious and not highly effective. By other methods, the mineral earth in a finely divided form is mixed with the oil, being later removed by filtration or other suitable means. The activity of most mineral earth when used in a raw condition is not high, and in consequence comparatively large amounts are required to obtain any suitable diminution of color. At the same time the process is expensive not only because of the cost of the earth but particularly because of the large amount of oil left in the earth after filtration. To avoid the use of said large amounts of earth, various processes for activating the earth have been developed in order that a considerably smaller amount may be used to bring about a given color reduction. Such activation of the earth has usually been obtained by acid treatment thereof followed by washing with water to remove the acid, and water-soluble reaction products, the earth being used either in the form of a mud or after drying and grinding thereof. This method of activation is expensive not only because of the large amounts of acid and water required but also because of the large mechanical losses of earth during the washing and handling.

As to the neutralization of the oils with alkalis wherein the products of neutralization have been separated by washing with water, the process presents several disadvantages which can be related to the fact that some of the products of neutralization partake of the general characteristics of soap and are active emulsifying agents. Because of the presence of these emulsifying agents the neutralization and washing process involves considerable loss of oil, and if the temperatures of operation are maintained so high that the difficulties from emulsification are decreased an excessive reversion of color often is experienced.

Because of the disadvantage of wet neutralization processes, it has been generally considered that a dry neutralization process would be of value and many attempts have been made to utilize the absorptive properties of active clays or fuller's earth for this purpose. In general however, such treatment of acid oils does not give a product of satisfactorily low acidity, unless either the organic acid content of the oil be extremely low or an excessive proportion of earth be used. Such use of large amounts of earth is expensive, both because of the cost of the earth itself and because of the losses of oil absorbed by the earth. Evidently therefore, it would be desirable to assist the neutralizing effect of the earth by the addition of reagents, and alkalis such as sodium hydroxide, or alkaline earths such as lime, naturally present themselves for this purpose. However if a sufficient amount of alkaline material is used to neutralize the acid in the oil, it is found that considerable proportions of the products of neutralization are not removed by the mineral earth but remain in the oil probably in a dissolved condition, and in consequence after removal of the earth by filtration or other means the oil has an excessive ash content. In other words the effect of the treatment is, to a considerable extent, merely to neutralize the acid impurities in the oil without removing them.

With my present process, a raw earth or clay is used and a considerable degree of acti-

vation for decolorizing purposes is obtained at almost no additional expense over that of raw earth, and the amount of such clay is considerably reduced as compared with use of raw earths as heretofore proposed, while the neutralization step of this process, which employs clay and an alkali, results in the separation of the acid impurities to such an extent that the ash content of the finished oil is satisfactorily low. The decolorizing and clarifying stage does not necessitate the use of any additional equipment over that ordinarily used with raw earth, and the amounts of reagents are so small that the additional costs are almost negligible. Although the degree of activation obtained is sometimes not quite so great as in the usual methods using large amounts of sulphuric acid, yet if the comparison is made on the basis of equal amounts of raw earth originally taken, rather than on a basis of equal amounts of activated earth produced by the two processes, it is found that the present method yields a very satisfactory degree of activation and any difference in the degree of activation by the two methods is much more than compensated by the lower cost of the present method. The neutralization stage is accomplished by the use of only moderate amounts of absorptive mineral earths rather than by the large amounts required when alkaline reagents are not used with the mineral earth.

Briefly stated the invention comprises two stages of oil treatment and is applicable to either acid or neutral oil. The first stage, which serves to decolorize the oil and remove the greater part of the mineral acidity along with a portion of the organic acidity, includes agitation of the oil with raw clay, water and added acid, the mixture being heated, filtered and cooled. The second stage, which serves chiefly to complete neutralization, includes mixing the filtered and cooled oil with clay, water and an alkali such as sodium hydroxide and preferably with the addition of sodium oxalate or some other water soluble compound which forms difficultly soluble calcium salts. This mixture is heated, filtered and cooled thereby yielding a neutralized product of excellent color and very low ash content. The invention resides further in the various steps, features and combinations thereof which will appear from the disclosure of preferred forms herein presented.

Considering the preferred form of invention in detail, the first stage consists in thoroly mixing from 4 to 20% of raw mineral earth in a finely divided state with the oil or fat to be treated, and adding to this mixture an amount of dilute acid solution approximately equal in weight to half the amount of mineral earth used. While more or less solution may be added, it never should greatly exceed twice the weight of the earth, and the amount should preferably be so chosen as not to cause agglomeration or coagulation of the mineral earth, since, if such agglomeration or coagulation takes place, the amount of active surface of the earth is decreased and, in consequence, the decolorizing effect is diminished, unless special provision is made for breaking up the lumps and redispersing the earth in the oil. The acid solution which serves to activate the clay when the mass is heated, consists preferably of an aqueous solution of a strong mineral acid or a strong organic acid in which the acid content is approximately equivalent to 4 mg. of potassium hydroxide per gm. of oil to be treated, but the actual amount of acid to be used will vary according to the amount and kind of mineral earth employed, and the mineral acid content of the oil, if an acid oil is being treated. By the expression "strong acid" is meant an acid either mineral or organic which ionizes freely and serves readily to activate the clay or other mineral earth, for which purpose the most satisfactory acid has been found to be oxalic acid, although sulphuric acid yields approximately the same final color and appears to be the best of the mineral acids. Hydrochloric or phosphoric acid also may be employed, but usually these are not so satisfactory. Other strong organic acids which may be used are, for example, trichloracetic acid or maleic acid. After the addition of the clay and of the acid solution, the mixture is heated rapidly to a sufficiently high temperature to evaporate substantially all the added water, thereby to bring about activation and to give a satisfactory decolorizing effect. For this purpose a temperature approximating three hundred and twenty degrees Fahrenheit has been found very satisfactory although it is possible to use temperatures both lower and higher but below the boiling point of the oil. The spent earth is then removed from the oil or fat by filtering, centrifuging or other suitable means, and, if this stage only is used, as for example upon a neutral oil, the product is cooled to a temperature not greatly exceeding atmospheric for the purpose of preventing reversion of color. However, if the oil is to be treated also by the second or neutralization stage to be hereinafter described, the cooling will be only to such a degree (e. g. 190° to 212° F.) as will avoid excessive evaporation during mixing of the reagents in the oil and the period of their reaction upon it.

The treatment just described results in clarification and decolorization of the oil, and if the oil originally treated be an acid oil, the treatment results also in partial neutralization.

This stage of the invention perhaps can best be set forth by means of an example. To one thousand pounds of a petroleum lubricating oil, which as above indicated may be either

an acid oil or a neutral oil, there is added eighty pounds of a finely pulverized fuller's earth or other absorptive clay or mineral earth in a raw state. This earth or clay is thoroughly mixed with and distributed through the oil at a temperature somewhat but preferably not greatly in excess of ordinary temperature, as for example 120° F. for a viscous cylinder oil. To the mixture there is then added with agitation about fifty pounds of an aqueous solution containing two and one-half pounds of crystallized oxalic acid and about forty seven pounds of water. The temperature of the solution is unimportant, but should be maintained high enough to prevent separation of the acid in solid form. The mixture is then heated to about 320° F. steam being permitted to escape freely as it is formed and the earth being maintained in suspension by agitation or otherwise. The earth is then separated from the oil by filtration, centrifuging or the like, and the oil is cooled to a temperature below that at which the reversion of color is rapid. By operating as in this specific example, the improvement in the quality of typical petroleum lubricating oils may be as follows:

Color, from No. 6 N. P. A. to No. 4 N. P. A.;

Acidity, from an acid number of 5 to 1, or in another example from an acid number of 0.15 to 0.03;

Clarity, from cloudiness to substantial brilliancy.

The amount of acid used above approximates one-quarter per cent, being equivalent to an acid number of 2.2 based on the oil. This amount has been found to be very desirable and at the same time probably it is the most satisfactory generally, but it is observed that a somewhat greater amount of acid is used in treating neutral oil than in treating acid oil. However, smaller or greater amounts may be used, approaching even two per cent, which represents an acid number of 23 for sulphuric acid and of 18 for oxalic acid, but such large amounts ordinarily are not used.

The neutralization stage follows the above treatment and serves as well to further clarify and improve the color of the oil. This step comprises thoroughly mixing material amounts of raw mineral earths (usually from four to sixteen per cent) in a finely divided state with the oil or fat to be treated, and adding to this mixture an amount of dilute alkali solution approximating half the weight of the mineral earth used. The dilute solution of alkali preferably consists of an aqueous solution of sodium hyroxide containing alkali somewhat in excess of that equivalent to the acid content of the oil or fat to be treated. As an alternative form, this caustic alkali solution may contain certain salts, since it has been found that the addition of material amounts of such salts results in a diminution of the ash content of the finished product, these salts in particular being sodium salts of comparatively strong acids which form difficultly soluble calcium salts, for example sodium oxalate and sodium fluoride. The actual amount of alkali and of these salts to be used will vary in particular cases according to the acidity of the material to be treated and according to the amount and kind of mineral earth employed. In general, the greater the amount of earth used, the greater should be the excess of alkali over the amount equivalent to the acid content. The amount of salts is preferably increased with the amount of alkali, since in this way the greatest diminution in the ash content is obtained. The amount of alkali solution is preferably so chosen as not to cause agglomeration or coagulation of the earth, since if such takes place the amount of active service of the earth is decreased, and in consequence the decolorizing effect of the earth is diminished and the neutralizing effect of the added alkali is also materially decreased, unless special provision is made for breaking up the lumps and redispersing the earth in the oil. After the addition of the earth and of the alkali solution, the mixture is heated rapidly to a sufficiently high temperature (for example 320° F.) to evaporate substantially all of the added water, and to produce the desired absorptive effect of the mineral earth. The spent earth is then removed by filtration, centrifuging or the like, and the oils cooled to a temperature not greatly exceeding atmospheric temperature in order to prevent reversion of color.

As an example of this neutralization stage, to one thousand pounds of a petroleum lubricating oil such as supplied by the first or decolorizing stage heretofore described, there is added eighty pounds of a finely pulverized fuller's earth or other absorptive mineral earth or clay, in the raw state. The earth is thoroughly mixed and distributed through the oil at a temperature preferably somewhat in excess of ordinary temperatures, but less than the boiling point of the aqueous solution added to the oil, for example 160° F. for a viscous cylinder oil. To the mixture is then added, with agitation, about forty pounds of an aqueous solution containing sodium hydroxide and sodium oxalate. If the oil being treated has an acid number of one milligram of potassium hydroxide per gram of oil, the solution will consist of about one pound of sodium hydroxide, one and two-third pounds of sodium oxalate and about thirty seven pounds of water. The temperature of the solution is unimportant. The mixture is then heated to 320° F., the steam being permitted to escape freely as it is formed, the earth being kept in suspension by agitation or otherwise. The earth is then separated from the oil as by filtration or centrifuging and the oil cooled

to a temperature below that at which reversion of color is rapid. According to this specific example, improvement in the quality of a particular petroleum lubricating oil may be as follows:

Color, from No. 5 N. P. A. to No. 4½ N. P. A.

Acidity, from an acid number of 1.0 to 0.1.

Clarity, from cloudiness to substantial brilliancy, with an ash content of the product of 0.005 per cent.

The amount of caustic alkali in the form of sodium hydroxide as given above approximates 0.1 per cent but for various oils other amounts thereof may be used up to about 0.5 per cent. The amount of sodium oxalate may be varied according to requirements up to a maximum of about four times the quantity of the sodium hydroxide. It is to be particularly noted that the alkali solution preferably should be fairly dilute for the reason that it has been found that when the required amount of alkali is added as a dilute solution the ash content in the product is materially lower than when the alkali is added in more concentrated form. The quantities of solutions and the concentration thereof must be determined, at least in most instances, with this fact in mind. Thus the employment of an oxalate for the purpose of precipitating the calcium, together with the employment of dilute alkali solution, serves to produce a product of satisfactorily low ash content, this content with many oils being unusually low. While the amount of alkali solution usually approximates half that of the clay, it may be increased but not to greatly exceed twice the weight of the clay.

According to the preferred method of operation, the two stages, which for convenience may be respectively referred to as the decolorizing stage and the neutralizing stage are both being used in the proper sequence upon average oils to produce a satisfactory marketable product of good clarity, color and low ash content, the first stage serving to decolorize the oil and remove the greater part of the mineral acidity, and the second stage completing neutralization. However where the organic acid content of the oil is quite low, the decolorizing stage alone may be relied upon for neutralizing the oil as well as for decolorizing and clarifying the same. Likewise an oil of good color and intermediate acid content might be treated by the second or neutralizing stage alone, since this step will produce clarification and a limited amount of decolorization in addition to neutralization. But for average use neither step separately employed will be sufficient.

The above two-stage double filtration process may be modified from the standpoint of economy by omission of the first filtration, thus making the process a two-stage, single filtration procedure. In this case, it is necessary before proceeding with the second stage to cool the mixture of oil, acid and clay to around 200° F. in order to prevent excess evaporation of water when the second-stage reagents are added and before these reagents have had an opportunity to act on the oil. It is also necessary to use somewhat larger amounts of alkali than when double filtration is employed due to the large amounts of adsorbed acids in the first-stage clay. According to this modification the amount of alkali would be increased in general to about 0.35%, or in particular cases up to about 1.0%. This phase of the process is valuable from the standpoint of economy and is good for certain types of oil.

It is also within the scope of the invention, to operate upon an alkaline oil, that is an oil containing soaps, by treating with clay and a dilute acid, for example oxalic acid as before stated, to assist in the removal of the soaps present and to tend toward a product of low ash content.

Throughout the specification and claims where either of the terms "clay" and "earth" is employed, the same is intended to include any clay, fuller's earth, other mineral earth or the like suitable for such purposes. And where the term "oil" is used the same is intended to include oils, fats, waxes and oleaginous substances in general unless otherwise limited. Also it should be noted that the term "alkali" or "caustic alkali" is intended to include potassium hydroxide or the like as well as sodium hydroxide and that corresponding substitution may be made wherever advantageous or desirable.

I claim:

1. The process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils, comprising commingling the oil with about 4 to 20 percent of raw clay together with water in amount approximating half the weight of the clay, and acid approximating one quarter percent of the substance treated, heating, separating the clay, agitating the oil with about 4 to 16 percent of a fresh amount of clay, adding a dilute alkali solution containing alkali less than one-half percent of the substance treated, heating and removing the clay.

2. The process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils, comprising commingling the oil with clay, together with water and acid, the acid not substantially exceeding two percent of the weight of the oil, heating, removing the clay, adding a second quantity of clay and dilute alkali solution containing alkali not substantially exceeding one-half percent of the substance treated, heating to drive off the water and removing the clay.

3. The process of decolorizing and neutralizing oleaginous substances including pe-

troleum lubricating oils, comprising treating oil with clay and a dilute acid solution containing acid not substantially exceeding two percent of the oil, heating, removing the clay, adding a second quantity of clay and treating with a dilute alkali solution containing alkali in amount not substantially exceeding one-half percent of the oil and in the presence of a salt of an acid whose calcium salt is substantially insoluble in water.

4. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising mixing clay with acid, treating oil therewith, and in a separate treatment treating the oil with clay and an alkali solution.

5. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising commingling oil with an acid and clay, removing the clay and adding to the oil a second quantity of clay, together with an alkali solution.

6. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising mixing an oil with clay and a strong acid and then treating the oil with clay and an alkali solution.

7. A process of decolorizing and neutralizing petroleum lubricating oils comprising mixing the oil with clay, acid and water, heating below the boiling point of the oil to vaporize the water and treating the oil with clay and an alkali.

8. A process of decolorizing and neutralizing petroleum lubricating oils comprising treating the oil with clay, a strong acid and water, heating below the boiling point of the oil to decolorize the oil, removing the clay, and treating the oil with a second quantity of clay and an alkali.

9. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising commingling the oil with clay and a strong organic acid, and treating the oil with a second quantity of clay and an alkali.

10. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising commingling the clay with oxalic acid, treating a quantity of oil therewith and treating said oil with another quantity of clay and an alkali.

11. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising commingling clay with a strong organic acid and treating oil therewith.

12. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising treating a quantity of oil with clay and oxalic acid.

13. A process of decolorizing and neutralizing petroleum lubricating oils comprising mixing an oil with clay and an acid solution, and heating below the boiling point of the oil to expel excess water.

14. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising mixing an oil with clay and a strong organic acid and heating to vaporize water and to decolorize the oil.

15. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising mixing an oil with clay and an oxalic acid solution and heating to vaporize excess water.

16. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and acid and with a second quantity of clay and a solution of alkali, and heating, thereby vaporizing water and aiding decolorization.

17. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and an acid, removing the clay, and then treating the oil with a second quantity of clay and an alkali solution sufficient to neutralize the acid and heating, thereby vaporizing excess water.

18. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and an acid, removing the clay and then treating the oil with clay, an alkali and an oxalate.

19. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and an acid, removing the clay, and then treating the oil with a second quantity of clay, an alkali and a salt of an acid whose calcium salt is substantially insoluble in water.

20. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and an alkali solution and vaporizing water by heating the mixture.

21. A process of decolorizing and neutralizing acid oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and an alkali solution sufficient to neutralize the acid and heating, thereby vaporizing excess water.

22. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising treating an oil with clay, an alkali and an oxalate.

23. A process of decolorizing and neutralizing oleaginous substances including petroleum lubricating oils comprising treating an oil with clay, an alkali and a salt of an acid whose calcium salt is substantially insoluble in the mixture.

24. A process of decolorizing and neu-

tralizing oleaginous substances including petroleum lubricating oils comprising mixing clay with an alkali solution, treating an oil with the mixture, vaporizing excess water by heating the oil mixture, and removing the clay from the oil.

25. A process for refining oils comprising commingling the same with clay in the presence of an alkali solution, heating said mixture to obtain a good decolorization and vaporizing water by such heating.

26. A process of treating oleaginous substances having acid reactions including petroleum lubricating oil comprising treating the oil with clay in sufficient quantity to decolorize the oil and at the same time subjecting the oil and clay to the action of a caustic alkali solution, and heating the mixture thereby vaporizing at least a substantial quantity of the water of the solution.

27. A process of decolorizing and neutralizing acid oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and with a dilute alkali solution, and heating the oil while in contact with said solution and thereby expelling water and producing decolorization.

28. A process of producing decolorized oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and a dilute alkali solution in the presence of each other, said solution containing water sufficient to wet the clay and insure good contact of the clay with the oil, but insufficient to cause agglomeration, and vaporizing water from the mixture by heating the same.

29. A method of refining acid petroleum oils comprising the steps of subjecting the oil to the action of clay in contact with a water solution of alkali sufficient to neutralize the oil, and heating the mixture thereby vaporizing water and effecting decolorization.

30. A method of refining petroleum oils containing organic acidity comprising the steps of subjecting such acid oil to the action of a decolorizing quantity of clay at the same time with subjection of the action of an excess of alkali solution, and heating the mixture to effect decolorization.

31. A process according to claim 30 wherein alkali is present in the form of a water solution thereof and the heating is carried on to produce vaporization of the water.

32. A process for treating petroleum oils comprising commingling clay with an alkali solution in quantity sufficient to produce a moist clay, mixing oil with such moist clay, and heating the mixture thereby vaporizing moisture from the mixture and producing good decolorization of the oil.

33. A process for refining petroleum oils comprising acid-treating the oil, then treating the oil with alkali to neutralize the oil, establishing an excess of alkali in the oil, treating the oil with clay whereby the clay acts upon the oil in the presence of said excess of alkali, and heating the mixture to effect decolorization.

34. A process for treating petroleum oils comprising commingling the oil with a decolorizing clay in decolorizing quantities and with an alkali solution in the presence of each other, and vaporizing excess water from the mixture by heating and thereby effecting good decolorization.

35. A process of treating oleaginous substances including petroleum lubricating oils comprising treating an oil with clay sufficient to decolorize the oil and in the presence of an alkali solution containing water approximating the amount of the clay.

36. A process of producing decolorized oleaginous substances including petroleum lubricating oils comprising treating an oil with clay and a dilute alkali solution in the presence of each other, said solution containing water sufficient to wet the clay and insure good contact of the clay with the oil, but insufficient to cause agglomeration.

37. A process of refining oil which comprises the steps of treating oil with an alkali solution and contacting the alkaline oil containing excess of alkali solution with clay and removing the clay.

38. A process of refining oil which comprises treating acid oil with clay and adding an alkaline solution to the thus treated oil and contacting the alkaline oil containing excess of alkaline solution with clay and removing the clay.

39. A process for treating oleaginous substances including petroleum lubricating oils, comprising treating an oil with clay sufficient to decolorize the oil and in the presence of an alkali solution containing water amounting to between one half and twice the amount of the clay.

Signed at Oleum, in the county of Contra Costa, and State of California, this 7th day of January, A. D. 1926.

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