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METHOD OF REFINING OIL

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This invention relates to the art of treating or refining oils, more particularly to petroleum oils of the type intended for use as lubricants, transformer oils, etc.

The methods in general use for refining such oils vary considerably, depending on individual preferences as well as on variations in the type of oil being handled and the specifications desired in the product. A large number of such processes, however much they differ as to details, include, as one step, treatment of the oil with acid, usually sulfuric acid. Our invention has for its object the improvement of processes of this class, the improvement consisting in increased efficiency of the refining process as well as improved quality of the product. The method of our invention is not intended primarily to replace any of the steps in existing processes, although such a result may follow in some instances. In most cases, however, it is an added step, the inclusion of which, as is more fully explained below, will prove the efficiency and result of the process now in use.

By the method of our invention the oil, after acid treatment, and preferably after removal of acid reaction products, is subjected to a high temperature for a suitable period of time. For example, the oil may be acid treated and neutralized, then heated to 400° to 750° F., for ten to sixty minutes. Preferably air is excluded during this heat treatment. Oil so treated is of a higher quality than oil which has not been heat treated but has otherwise been processed in the same way. It shows less tendency to emulsify with steam or water, and its color is better and more stable. Therefore, this method makes possible the production of an oil of superior quality, or of an oil of the same quality at less expense.

In many instances it is commercial practice to follow acid treatment and neutralization of the oil with contact with an adsorbent material such as fuller's earth or a suitable type of "clay". This adsorption step is primarily for the purpose of removing color bodies from the oil. Our method is particularly advantageous in the case of oils treated in this way. The quantity of oil of standard color which can be produced from a given amount of earth is greatly increased over that produced when the heat treatment is omitted.

The effect of an independent heat treatment as described is apparently a supplement or continuation of the refinement already produced by the acid treatment in that substances formed during acid refinement are made less soluble in the oil and/or react more readily with an adsorbent subsequently applied.

Thus the method is a beneficial addition even to processes in which the oil is heated after the acid treatment (e. g., for redistillation, adsorption, etc.), since it permits control of time and temperature, i. e., control of the reaction, apart from other reactions such as the pyrolysis which is catalyzed by the adsorbent.

We have found that the optimum degree and duration of heat treatment differs considerably for various oils. We are unable to state a general rule which will indicate the time and temperature for optimum results in the case of any and all oils. In general, we have found that, for best results, oils of lower viscosity require heat treatment at a lower temperature and for a shorter time than do oils of higher viscosity.

For example, a lubricating distillate prepared from California crude and having a Saybolt viscosity of 100 at 100° F., was found to respond satisfactorily to a procedure in which the oil was raised from 500° F., in about six minutes, and held at 550° F., for about four minutes. Another distillate from the same crude which had a Saybolt viscosity of about 1000 at 100° F., was raised from 500° F., to 650° F., in about thirteen minutes and was held at 650° for about forty minutes. These conditions are not critical for the given oils, however, because we have observed that, within reasonable limits, there is an apparent reciprocal relation between the duration of heating and the degree of temperature. Heating for a longer time at 600° F., will produce results equivalent to a shorter time at 650° F. In view of the increased time required as the temperature is lowered, we regard 400° F. as the lowest temperature which can be used in practice. Lower temperatures would require unreasonably long times for the accomplishment of the desired results. The maximum allowable upper limit will vary for different oils. Temperatures are not permissible at which material cracking occurs, nor are temperatures permissible at which substantial fractions of the oil will vaporize. In the case of some oils, a temperature of 500° F. cannot be exceeded for one or the other of the above reasons. In any case, temperatures higher than 750° F. cannot be used.

No matter where the herein described heat treatment is practiced with relation to the other steps of the refining process, it should be carried out in the absence of any solid agent of large surface or porosity, such as fuller's earth or adsorbent clay. Such materials tend to promote

the formation of color bodies, especially at high temperatures.

The effect of heat treatment as herein described is of the same general nature in the case of all oils of the lubricating type. However, the degree of modification which this treatment produces in different types and grades of oil varies considerably. In some cases the color of the oil is improved sufficiently to eliminate the necessity for a subsequent decolorizing treatment. In most cases, however, we believe it advisable to follow the heat treatment by treatment with an adsorbent,—even though at a very low rate,—to remove traces of unstable reaction products.

In order to illustrate the practical application of our method, we describe below an example of its actual use by us in the treatment of a medium light lubricating distillate from a California crude petroleum:

The distillate, having been reduced to the desired flash and viscosity (about 990 at 100° F.) by heating under vacuum, was agitated with sulfuric acid, the resulting "sludge" acid removed and the oil washed with a neutralizing agent. The oil was then heated rapidly while being kept in a turbulent condition to prevent local overheating. By reason of the construction of the heater the temperature of the oil rose from 500° F., to 650° F., in approximately thirteen minutes. It was held at 650° F., for thirty-three minutes and was then rapidly cooled to about 320° F. It was then mixed with a finely divided adsorbent earth and the mixture agitated while being held above 300° for about ten minutes. The oil-clay mixture was passed through a filter press to remove the clay, and the oil immediately cooled.

Another portion of the same raw distillate was treated in exactly the same way except that the heat treatment preceding the clay contacting was omitted. The portion which had the heat treatment required only half as much clay to bring it to standard color as did the other portion. In addition to the saving in decolorizing clay effected by this heat treatment, the oil which had been so treated had a much superior "demulsibility" test, i. e., its resistance to the standard test for tendency to emulsify when blown with steam etc., was less. Another noteworthy improvement in the case of this oil was its appearance with respect to fluorescence, or "bloom". The oil which had been heat treated had a much better "bloom" than the other.

Another pair of treatments was made on the same type and grade of oil. These treatments were identical with those described above except that the final decolorizing step was made by percolating the oil through Florida clay (fuller's earth). In this case only 54% as much clay was required to bring the heat treated oil to standard color as was required by the oil which had not had the heat treatment. In other respects, as in the case of the previously described comparative treatments, the quality and appearance of the heat treated oil was superior.

The above examples are illustrative only, many modifications being permissible without departing from the principles of the invention.

Some oils contain substances which are readily oxidized in the presence of air at high temperatures, producing a darkening of the color of the oil. We therefore prefer to carry out our heat treatment in closed apparatus out of contact with air, or in apparatus so designed as to preclude free circulation of air over the oil.

In practice it is, of course, preferable that the oil to be heat treated should be first substantially neutralized by chemical or physical means. The prime purpose of this de-acidification is to avoid corrosion difficulties in the heating apparatus, rather than to ensure the benefits obtainable by separate heat treatment.

We claim:

1. A method of refining petroleum oil fractions of the lubricating oil type previously treated with sulfuric acid, comprising raising the temperature of the oil above 500° F. but below that at which substantial fractions of the oil are vaporized or cracked, digesting the oil at this temperature out of contact with solid adsorbent material for a controlled time sufficient at the digestion temperature to improve the color of the oil, avoiding access of air while the oil is undergoing digestion, then cooling the oil.

2. In the art of refining petroleum lubricating oil wherein the oil is (*a*) treated with acid and the acid reaction products removed and (*b*) the oil is treated with a decolorizing adsorbent the improvement which consists of interposing between these steps the step of digesting the neutral oil, out of contact with adsorbent material, at a temperature of 500 to 750° F. for about 10 to 60 minutes sufficient to increase the efficiency of the subsequent adsorbent treatment by a substantial amount.

3. The method of refining petroleum lubricating oil which comprises subjecting the oil to the following steps in the order named: treating the oil with sulfuric acid, removing the acid and reaction products, heating the neutral oil above 500° F. but less than 750° F., maintaining the oil within this temperature range out of contact with adsorbent material for a controlled period of time upwards of 10 minutes and less than 60 minutes sufficient to lighten the color of the oil and increase its resistance to emulsification.

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