Patented Feb. 9, 1943 2,310,812

UNITED STATES PATENT OFFICE

2,310,812

METHOD OF MANUFACTURING OILS OF HIGH STABILITY

Friedrich Schick, Berlin-Schoneberg, Germany; vested in the Alien Property Custodian

No Drawing. Application July 6, 1938, Serial No. 217,726. In Germany July 9, 1937

9 Claims. (Cl. 196—39)

In the utilisation of mineral oils it is often necessary to mix different hydrocarbon oils. For instance, it is customary to adjust the properties of commercial oils to the specific requirements of the respective use by mixing oils of different origin. Furthermore, in order to improve the quality of oils which are not per se high-grade oils, it has been proposed to blend such oils with paraffinic or more saturated hydrocarbon oils.

Some oils have been found not to be readily miscible with each other. Gradually, as time goes on during storage or use or under the action of heat, separations are formed in such mixtures to a larger or smaller extent. Blended motor oils show for instance formation of sediments, of carbon and coke, causing clogging of injector nozzles; blended lubricating oils show an unexpectedly high ageing tendency and sludge formation. Not always the sediments may be seen microscopically; often they are recognized only by giving bad results in tests, or they appear as inhomogeneous components when testing the oils by optical means.

On the one hand it was suggested to blend only oils with similar physical properties, e. g., with a definite range of densities, and on the other hand it has been endeavored to improve the miscibility or the quality of the mixture by refining the components most intensively. But the first mentioned measure limits considerably the number of utilizable oils and the second one causes a considerable loss of oil, apart from the necessary high consumption of refining agents. It is well known that by intensive treatment of individual oils with sulphuric acid, valuable components of the oil, such as unsaturated components of motor fuel oils and naphthenic hydrocarbons and other constituents of importance for the oiliness of lubricating oils, are eliminated or chemically changed. It has also been proposed to employ diluents when treating mineral oils with acids, in order to reduce the viscosity of the mixture, or to diminish the intensity of the reaction.

It now has been found that a surprising improvement of the properties of the mixed oils and the like may be attained in a simple manner, by first blending the initial oils produced as usually by distilling or refining and subsequently treating the mixture with refining or precipitating agents. For the last mentioned purpose inorganic and organic acids may be used, particularly sulphuric and hydrochloric acid, furthermore salts and other metallic compounds, doctor solution, alcohol and so on.

From this it follows that it is possible and sometimes even necessary to use much smaller amounts of refining agents than otherwise are required and used for refining purposes. For instance, generally 1% of sulphuric acid, but often, particularly with motor fuel oils, even 0.5% and still less are fully sufficient, whereas hitherto a multiple of this quantity was needed, if similar effects could be reached at all. The quantity of refining agents required will of course somewhat vary, depending on the kind and on the proportions of the oils in the mixture to be treated, on the saturation of one of the components, on the nature and chemical composition of the other component, on its content in aromatics, naphthenes, its ageing index (Indiana-test, Nowack-test, sludge-test, etc.), and so on. The precipitates caused by such treatment with the refining agents are obtained in such a form as is readily separated from the oil.

If desired, the use of a chemical refining agent may be avoided and the impurities may be separated as a precipitate by the action on the oil mixture of an electric field, e. g., by applying electrical discharges, or cataphoresis of direct or alternating currents, and so on.

The improved treatment according to the present invention generally causes a considerable enhancement of the resistance of the oils to ageing. Moreover often an improvement of the colour and of the other properties of the oils results as compared with the refining of the individual oils followed by blending. Furthermore the saving of refining agents, particularly when operating with sulphuric acid, is remarkable and due to this fact, the oils are better preserved and the refining losses are lessened. Besides, the combined effect of the "mutual deflocculation" of the oils mixed and of the coagulation produced in the mixture by the sulphuric acid generally results in an improved separation of the acid sludge.

With the present procedure it is possible to blend oils of good lubricating quality and cold test, such as naphthenic oils, but which do not suffice with regard to some other test, e. g., the viscosity index, with oils unobjectionable in the latter respect, e. g., a highly paraffinic oil, in order to obtain, with a proper after-treatment according to the present invention, a blended or mixed oil satisfactory in every respect.

The present invention, which affords the possibility to treat and improve mixtures of oils of a relatively high degree of saturation and oils of a relatively low degree of saturation, has been found to be particularly satisfactory for mixtures

of distillates and residual lubricating oils manufactured from German raw oils and from oils of similar character, with Pennsylvanian oils, the so called Bayonne oils or synthetic lubricating oils produced by Fischer's method, and furthermore for mixtures of distillate oils or such oils as are refined with sulphuric acid, or with raffinates obtained by means of selective solvents, e. g., such as obtained by the process of the U. S. patent application Ser. No. 94,290.

For the refining after mixing according to the present invention the following mixtures may be considered: mixtures of fresh oils with aged ones, of fresh oils with cracked products obtained from said fresh oils, of more refined oils with less refined oils, and in general of oils having relatively high ageing indices with oils having relatively low ageing indices.

The process may be also applied to crude or unrefined oils. Such mixtures may be made exclusively from unrefined oils, or even refined oils may be blended with unrefined ones, the novel feature consisting in the possibility of improving oils by first mixing oils of different character and then refining this mixture.

It has already been proposed to precipitate pitch-like particles from tars by adding crude oil and hydrochloric acid for obtaining products that are more ready workable. In such treatment, however, a considerable part of valuable oils is carried down into the precipitate and thus lost. Furthermore, oil containing slight quantities of mineral acids has been admixed with heavy carbonaceous oils to separate the carbon. Finally, the regeneration of old oils has been tried by treating same in the proportion of 1:100 with a refining mixture consisting of fresh oil and sulphuric acid. Otherwise, hitherto Engler-Höfer's view maintained in their book "Das Erdöl" was shared that heterogeneous oils, e. g., Russian and Galician lubricating distillates should not be refined together but individually and that only the finished products should be mixed. However, it now has been found that in a very great number of cases the manufacture of mixed oils can be simplified and improved by treating according to the present invention the mixture of the crude or unrefined oils with refining means. Thus the individual refining of the components may be dispensed with completely or partly. Of course, it is necessary that such oils are combined which differ in their properties in the aforesaid manner, if the indicated improvements both for the refining process itself and for the refining effect in comparison to the treatment of the individual components shall be obtained.

Thus, unrefined distillates of crudes of various origin may be blended with one another, e. g., unrefined distillates of paraffin base oils, such as Pennsylvanian oils with unrefined distillates of mixed-base or asphaltic crudes, such as German oils. One of the two oils to be mixed, suitably the paraffin base oil, which is rich in saturated hydrocarbons and requiring only small quantities of refining agent, may be pre-refined, whereafter the produced mixture is treated with a further refining or precipitating means, particularly with sulphuric acid. It has also turned out well to pre-treat with bleaching earth one of said oils to be mixed. For this purpose, too, the paraffin base oils are particularly suitable. Similarly, mixtures of lubricating distillates with residual oils may be produced in a condition satisfying all requirements of a first class oil for motor cars. In this latter case it is often to advantage to free the residual oil of at least part of its asphalt content by treating it with a precipitating agent such as propane, alcohols and the like, before mixing or blending said residual oil with the other component.

The process has proved of special value for manufacturing mixed lubricating oils which are unobjectionable in use, from crude distillates or residual oils, e. g., such of German origin, with synthetic oils such as for instance obtained by the process of Fischer and Tropsch.

In many cases when selectively refining certain residual oils, particularly those of high asphalt content, by means of phenol, furfurol, sulphurous acid, or the like, a comparatively dark raffinate is obtained not suitable as a lubricating oil. An after-treatment with sulphuric acid or bleaching earth is of no use in this case. If, however, a lubricating oil distillate from the same or any other crude is mixed according to the present invention to such a residual oil, by subsequent refining with sulphuric acid a test-proof bright lubricating oil may be produced with only a slight loss of oil.

The present process is principally intended for the manufacture of lubricating oils. As usual the quantity of the required refining agent, e. g., sulphuric acid, also in this case depends on the nature of the oil used and is ascertainable in each case by preliminary trial.

The present process, however, is of considerable importance also for the manufacture of mixed motor fuel oils. It is already known to free tar oils from asphalt and other sediment forming components by mixing same with gas oil from petroleum or with the product known under the trade-mark "Kogasin" (a synthetic motor fuel from the Fischer process), and distilling the obtained mixture, if necessary under pressure. But in a distillation process it is unavoidable, especially as the conditions of solubility in the heat differ from those in the cold, that part of the components to be separated is carried over into the distillate mechanically or in the form of azeotropic mixtures and afterwards causes inconveniences during use. On the other hand oils mostly undergo a chemical change during their distillation, causing the formation of much polymerized material or even coke. Since, however, it is rarely, if ever, possible to obtain all the suitable oil as a distillate, with the known process a larger or smaller production of poor residual oil must be accounted for. All these disadvantages are avoided by the treatment according to the present invention. For instance highly saturated petroleum-gas-oils, hydrogenated products or synthetic gas-oils may be treated in mixture with light lignite-tar-oils, cracking products and the like. In this case regularly less than 1% of sulphuric acid, e. g., 0.1 to 0.2% is sufficient. If convenient, other refining agents may be employed; also in this case very slight quantities are sufficient. If the oils show a strong tendency for the formation of sediments, it is advisable to distil the motor fuel mixture after refining, e. g., after treatment with acid.

The possibility to operate without artificial heat supply when using the new process affords simultaneously the advantage that any detrimental actions of such heating on the oils are prevented.

The present process has nothing to do with the known methods of de-asphalting crudes or fractions thereof with precipitating agents such as low boiling hydrocarbons, alcohol mixtures and

so on. The latter act chiefly on the asphalts and asphaltic resins readily separable, whereas considerable quantities of tar- and sludge-forming substances remain in the oil in a state of a more or less stable distribution. The new process, on the contrary, is specially intended for the removal of these components particularly detrimental to the use of the oil. These may be diminished, it is true, by the usual refining methods but they cannot be eliminated completely by them without injury to the oil or at least without losses of valuable oil components.

Since flocculation generally occurs spontaneously no long periods of settling are required in the new process. The oils, consequently, can be mixed with each other and with the refining agent for instance in a quick mixing apparatus and then at once may be freed by means of centrifuges, filters or the like from the components separated out, or they may be treated with the refining agent in countercurrent. Oil mixtures showing a strong tendency to separation may to advantage be subjected to a preliminary purification by settling or centrifuging before the refining agent is added.

Examples

(1) 50 kilos of a machine oil from German crude refined with 5% of concentrated sulphuric acid (density=0.930; viscosity $E°_{50}$=15.7; Indiana-test=101.8 milligrams/45 hours) are mixed with 50 kilos of a raffinate from the selective phenol treatment of an oil of same origin (density=0.908; viscosity $E°_{50}$=11.0; Indiana-test=4.5 milligrams/45 hours). The mixture has an Indiana-test of 79.2 milligrams/45 hours. By refining the mixture once more with 1% of concentrated sulphuric acid, the ageing tendency is reduced markedly. The Indiana-test only shows 23.8 milligrams of sedimentation within 45 hours.

(2) A mixture of 30 kilos of a so-called Bayonne-oil (Pennsylvanian; density=0.900/20° C.; viscosity $E°_{50}$=12.6) with 70 kilos of a machine oil distillate refined with 5% of sulphuric acid (German crude; density=0.932/20° C.; viscosity $E°_{50}$=16.02) gives a sedimentation of 120.1 milligrams/45 hours in the Indiana-test. If the mixture is refined with 1% of sulphuric acid, only 65.7 milligrams/45 hours are observed. Refining the components, each, with 1% of sulphuric acid before mixing gave no improvement at all regarding the ageing test compared with the untreated mixture.

(3) If 90 parts of a gas-oil (density=0.846; viscosity $E°_{20}$=1.33; boiling index=302° C.) are mixed with 10 parts of a creosote containing lignite-tar-oil (density=0.929; viscosity $E°_{20}$=2.04; boiling index=273° C.) at once very heavy precipitates are formed. If both oils are refined before mixing, each, with 1% of concentrated sulphuric acid and 1% of bleaching earth, also heavy precipitates appear after mixing. If, however, the mixture of the untreated components is refined with only 0.5% of concentrated sulphuric acid, the mixture remains clear even when stored for weeks. Even yet smaller amounts of acid may be sufficient.

In a corresponding manner one may stabilise mixtures of lignite-tar light oils, if desired after having previously decreosotized them, with synthetic gas-oil or of marine fuel oil from lignite tar with petroleum gas-oil, and so on.

Having now particularly described and ascertained the nature of my said invention, I declare that what I claim is:

1. Method of manufacturing oils of high stability which comprises blending a hydrocarbon oil of predominately aliphatic character and relatively rich in saturated hydrocarbon components with at least 10% of a hydrocarbon oil of predominately aliphatic character and containing a substantially smaller amount of saturated hydrocarbons, said two oils having similar boiling ranges and being members of the group consisting of Diesel fuel oils and lubricating oils, at least one of said oils containing a substance which renders the mixture unstable, and subjecting the mixture to a treatment by contact with a relatively small amount of a chemical precipitating agent.

2. Process as defined in claim 1 in which the chemical precipitating agent is an acid.

3. Process as defined in claim 1 in which the chemical precipitating agent is a strong mineral acid.

4. Process as defined in claim 1 in which the chemical precipitating agent is sulfuric acid and is used in quantity not exceeding about 1% of the mixture.

5. Process as defined in claim 1 in which the hydrocarbon oils are Diesel fuel oils.

6. Process as defined in claim 1 in which the hydrocarbon oils are lubricating oils.

7. Process as defined in claim 1 in which the hydrocarbon oils are Diesel fuel oils and in which the precipitating agent is sulfuric acid and is used in quantity not exceeding about 1% of the mixture.

8. Process as defined in claim 1 in which the hydrocarbon oils are lubricating oils and in which the precipitating agent is sulfuric acid and is used in quantity not exceeding about 1% of the mixture.

9. Process as defined in claim 1 in which the hydrocarbon oils are a lignite tar oil and a saturated petroleum Diesel fuel oil and in which the mixture is treated with about 0.5% of concentrated sulfuric acid.

FRIEDRICH SCHICK.