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3,484,368

PROCESS FOR THE PURIFICATION OF OILS
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No Drawing. Filed July 21, 1967, Ser. No. 654,981
Claims priority, application Germany, July 22, 1966,
D 50,650

Int. Cl. C10g 33/04, 31/14

U.S. Cl. 208-251

11 Claims

ABSTRACT OF THE DISCLOSURE

Purification of oils by emulsification in an aqueous medium, breaking the emulsion at boiling temperature by addition of a mixture of finely divided hydrophobic silica and calcium formate, extracting the purified oil from the residue and distilling off the solvents.

BACKGROUND OF THE INVENTION

The invention relates to an improved process for purification of oils of mineral or vegetable origin by removal of undesired impurities.

Certain crude mineral oils, residual oils and distillation fractions of crude oils contain a significant amount of heavy metals, such as, for example, vanadium, iron, nickel and copper, which can effect damage to cracking catalysts in cracking processes. In addition the vanadium is especially very harmful in residual mineral oils which are used as heating fuels as it leads to corrosion and pitting on the metal parts of the heating apparatus which can be led back to the interchange action between the metal parts and the hot ashes produced by the combustion of such fuels.

These heavy metals are bound in the form of porphyrin complexes so that the usual purification methods are not suited for the removal of these metals as the complex compounds of alkyl substituted porphyrins with vanadium and other heavy metals are oil soluble compounds which are less strongly absorbed on polar surfaces than high molecular aromatic hydrocarbons and the non-hydrocarbons in crude oils or mineral oil distillates. The porphyrin metal complexes are to a far-reaching degree thermally stable so that they sublime at higher temperatures without decomposition or also in view of their sufficient volatility distill and appear in the distillate fractions. Therefore their removal by purely thermal treatment is not possible.

It is known that these metal compounds can be removed from mineral oils by treating the oil with a sufficient amount of an alkali metal, alkaline earth metal, aluminum or other hydrides in finely divided form to effect decomposition of the complex compounds and after completion of such treatment separating the heavy metals from the oil.

It furthermore is known that lubricating oils during use undergo chemical change so that their life is limited. During use aging products are produced by oxidation, polymerization and cracking which present a complex mixture which only can be removed from the oil with great difficulty. In addition to such aging products, foreign substances from external sources as by abrasion also can contaminate used oils. As a consequence, additives, such as, metal salts of organic compounds with an acid hydrogen, have been added to improve the lubricating properties and to stabilize the oils against chemical attack in order to maintain the precipitating aging products in suspension so that no deposits occur.

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Used oils, however, still predominantly contain substances with good lubricating properties so that after removal of the foreign contaminants and the aging products could be reused or serve as starting materials for heavy duty oils if such removal could be substantially quantitative.

Fundamentally the following four procedures come into question for processing used oils of the above-mentioned crude oils, residual fuel oils and distillation fractions which are contaminated with heavy metal compounds:

- (1) Physical-mechanical processes
- (2) Extraction processes
- (3) Adsorption processes
- (4) Chemical processes

Filtration and centrifuging primarily come into consideration for the first procedure. This method which usually does not result in complete regeneration is only most seldomly successful in the case of used additive oils as the suspended particles are so finely divided by the additive colloid that they cannot be retained even by high efficiency filters. The methods used in practice usually depend upon combinations of the four procedures indicated. Neutral, basic and acidic adsorbents are used, sulfuric acid is primarily used as an extracting agent and chemical regenerating agent. Sulfuric acid regeneration is accompanied by the disadvantage of large oil losses and the characteristic odor of the oil regenerated thereby.

SUMMARY OF THE INVENTION

The object of the invention is to provide a process for the recovery of valuable purified crude or used oils which renders it possible to remove foreign substances or impurities contained in the oils whereby normal viscous, light yellow and oils are obtained which only have the odor of clean oil.

The essence of the invention resides in that the oil to be purified is emulsified with water with the aid of an emulsifying agent and the emulsion then broken at boiling temperature with a mixture of a hydrophobic silica and an alkaline earth metal formate, especially calcium formate, and recovering the purified oil from the oil containing residue by extraction and distilling off the extraction agent. The process can advantageously be carried out continuously in a cyclic process.

DETAILED DESCRIPTION OF THE INVENTION INCLUDING PREFERRED EMBODIMENT

The emulsifying agent employed in the preparation of the initial emulsions of the oil to be purified is not critical as all emulsifying agents suitable for preparing emulsions of oil and water can be used. Depending upon the oil to be purified either an oil soluble or a water soluble emulsifier may be employed. Preferably, non-ionic emulsifiers are employed as they permit a greater latitude in conditions. Suitable emulsifiers, for example, can be found among the well-known and commercially available alkyl polyglycol ethers with about 10 to 20 ethoxy groups obtained, for instance, by ethoxylation of fatty alcohols with ethylene oxide, alkyl phenyl or alkyl naphthyl polyglycol ethers, fatty acid polyglycol esters, fatty acid polyglycol amides, fatty acid polyglycol ethers produced suitably by ethoxylation of fatty acids, fatty acid amides and fatty amines, as well as similar condensation products obtained with ethylene oxide.

The hydrophobic silicas employed according to the invention can be finely divided wet precipitated silicas, pyrogenic silicas produced by pyrogenic decomposition of volatile silicon halides or electric arc silicas which have been

hydrophobized in a known manner with organohalosilanes, such as, dimethyl dichlorosilane.

Wet precipitated hydrophobized silicas can, for instance, have a BET surface area of about 20 to 200 m.²/g., preferably, about 100–150 m.²/g., such as, for example, in a hydrophobized precipitated silica containing 98.3–99.0% of silica and about 0.9 to 1.1% of carbon derived from chemically bound methyl groups which cause the hydrophobicity, and having a primary particle size of 20–300 m μ , a secondary particle size of 0.7–9 μ , a BET surface area of 20 $\pm$ 3 m.²/g. and a pH of 3.4–4.9 (4% in water:acetone) and a hydrophobized wet precipitated silica containing 2.80 $\pm$ 0.20% of carbon derived from bound methyl groups having a BET surface area between 110 and 150 m.²/g. and a pH of 6–7 (for instance, Degussa hydrophobized silicas TK70, D17 and D500).

Pyrogenic silicas, for instance, have a surface area between about 100 to 200 m.²/g. and an average primary particle size of about 10 to 50 m μ , such as, for example, in the hydrophobized pyrogenic silica Aerosil R972 (produced as described in *Chemische Zeitung*, 89, pp. 437–400) which is a pure pyrogenic silica which has hydrophobic properties by virtue of chemically bound methyl groups and has a SiO₂—CH₃ content >99.8%, a carbon content 1.1 $\pm$ 0.2% (corresponding to about 0.6 millimol of (—CH₃) per square meter), a BET surface area of 120 $\pm$ 30 m.²/g., an average primary particle size of about 20 m μ and a pH of 3.6–4.0 (4% dispersion in 1:1 methanol:water).

The quantities of the mixture of hydrophobized silica and alkaline earth metal formate employed can, for instance, be between 20 and 100 parts by weight per 100 parts by weight of oil and the proportion of alkaline earth metal formate being about 2 to 50 parts by weight per 100 parts by weight of hydrophobized silica.

If desired, a small quantity of sulfuric acid can be used to acidify the emulsion which is first produced to assist in the removal of any basic impurities which, for instance, may give rise to pyridine like odors.

The purified oils obtained according to the invention are odorless, have little color, leave practically no ash on combustion and are marked by good stability with respect to color and oxidation. The dissolved additives and their decomposition products are completely removed. The process according to the invention is not limited to the treatment of impure mineral oils, such as, for example, used crankcase oils, but also can be applied to the purification of vegetable oils.

The following example will serve to illustrate the effectiveness of the process according to the invention with reference to the treatment of a strongly contaminated almost black colored used crankcase oil with an unpleasant odor which could no longer be regenerated by known methods.

EXAMPLE

12 g. of the used crankcase oil were first emulsified with 200 ml. of water and 4 g. of a non-ionic polyglycol ether emulsifying agent (trimethylol propyl oleate ethoxylated with ethylene oxide to provide 6 ethoxy groups) and then acidified with a small quantity of sulfuric acid.

The emulsification effected dissolving out of the water soluble impurities and the acidification with the small quantity of sulfuric acid served to remove the basic impurities which smelled similar to pyridine.

The emulsion was then broken at boiling temperature within a few minutes by addition of 3 g. of a mixture of

85 weight parts of the finely divided hydrophobized wet precipitated silica described above having a C content of about 2.80% and 15 weight parts of calcium formate, whereby the oil phase was adsorbed on the silica. The oil containing adsorbate was collected by filtering and dried and then was extracted in a Soxhlet extractor with petroleum ether. After the petroleum ether was distilled off, 14 g. of a light yellow oil of normal viscosity which only had the odor of clean mineral oil were obtained. A portion of the oil soluble emulsifier was also adsorbed on the silica and caused the 2 g. average in the weight of the product.

What is claimed is:

1. A method of purifying impure oils which comprises emulsifying the oil to be purified with water and an emulsifying agent adapted to form an emulsion of oil and water and subsequently breaking the emulsion at boiling temperature by addition of an amount of from 20 to 100 weight parts per 100 weight parts of the oil treated of a finely divided hydrophobic silica admixed with from 2 to 50 weight parts of an alkaline earth metal formate per 100 weight parts of the oil, extracting the purified oil from the oil-containing silica and distilling off the extraction agent.

2. The method of claim 1 comprising in addition slightly acidifying the emulsion with a small quantity of sulfuric acid before breaking the emulsion.

3. The method of claim 1 in which said alkaline earth metal formate is calcium formate.

4. The method of claim 1 wherein the hydrophobic silica is a wet precipitated silica having a BET surface area of about 20 to 200 m.²/g.

5. The method of claim 4 wherein the wet precipitated silica has a primary particle size of between 20 and 300 m μ .

6. The method of claim 1 wherein the hydrophobic silica is a pyrogenic silica having a surface area between about 100 and 200 m.²/g.

7. The method of claim 6 wherein the pyrogenic silica has a primary particle size of about 10 to 50 m μ .

8. The method of claim 6 wherein the pyrogenic silica is obtained by pyrogenic decomposition of volatile silicon halides.

9. The method of claim 1 wherein the hydrophobic silica is an electric arc silica.

10. The method of claim 1 wherein the emulsifying agent is a non-ionic emulsifier.

11. The method of claim 10 wherein the emulsifier is an alkyl polyglycol ether with about 10 to 20 ethoxy groups, an alkyl phenyl or alkyl naphthyl polyglycol ether, a fatty acid polyglycol ester, a fatty acid polyglycol amide, a fatty acid polyglycol ether or a condensation product of a fatty acid with ethylene oxide.

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U.S. Cl. X.R.

208—188