

UNITED STATES PATENT OFFICE

2,428,067

TREATMENT OF HYDROCARBON OIL

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No Drawing. Application July 9, 1946,
Serial No. 682,310

9 Claims. (Cl. 196—14.35)

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The present invention relates to the solvent refining of hydrocarbon oils, and particularly petroleum lubricating oil stocks.

More specifically, this invention is concerned with a nitrobenzene extraction process wherein there is provided a novel method for avoiding emulsification difficulties and increasing the effective capacity of extraction units which employ nitrobenzene as the selective solvent.

The use of nitrobenzene in the selective solvent extraction of lubricating oils is well known in the art, and has been described in the Ferris United States Patent No. 1,788,569, and elsewhere. The nitrobenzene extraction process is applicable to all types of viscous petroleum oils, either waxy or non-waxy, be they either distillates or residuums. The extraction may be carried out batchwise, or in multi-stage countercurrent systems, or in continuous towers, usually at temperatures below 100° F., and preferably at temperatures between 40° F. and 70° F. The operation of all of these systems is well known in the art, and further detailed description thereof is here unnecessary.

In all solvent extraction processes, there must be an intimate commingling or contacting between the extraction solvent and the oil undergoing extraction. In a nitrobenzene-lubricating oil extraction system, particularly where the oil is non-waxy, there is always a tendency for the formation of emulsions of raffinate phase in the extract phase, the raffinate phase being rich in paraffinic hydrocarbons and containing a small amount of solvent, and the extract phase being rich in naphthenic hydrocarbons and containing a large quantity of solvent. In batch, and in multi-stage batch countercurrent systems sufficient settling area and settling time must be provided to permit proper stratification of the phases. In countercurrent tower systems, the velocity of flow must be such as to permit adequate separation of the phases. Thus, in all extraction systems the throughput is, to a considerable degree, limited by emulsification tendencies, usually the tendency of the raffinate phase to emulsify in the nitrobenzene extract phase. It is therefore an object of this invention to avoid emulsification, particularly during the phase separation step, and thereby substantially increase the capacity of the nitrobenzene extraction units.

We have found that when a small amount of ammonia and of an alkaline earth metal soap of a fatty acid are added to a nitrobenzene extraction system, emulsification difficulties in the extraction system may be substantially reduced and

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the throughput of the system may be greatly increased. More particularly, we have found that emulsification difficulties may be avoided by adding to the oil, an amount of ammonia equivalent to 0.005 to 0.02 gallons of 19° Bé. aqueous ammonia per barrel of oil, and from 0.0015% to 0.015% by weight of an alkaline earth metal soap of a fatty acid. Ammonia in amounts equivalent to 0.005 to 0.015 gallons of 19° Bé. aqueous ammonia per barrel of oil, and from 0.0045% to 0.006% by weight of soap (based on the oil charged) are preferred. The ammonia may be added in gaseous form or in aqueous solution, the latter being preferred, and the addition may be made prior to charging the oil to the extraction system or at any point in the extraction system where emulsification difficulties arise. It is preferred to add the alkaline earth metal soap in the form of an oil concentrate, for example, a 3% to 6% dispersion of soap in lubricating oil. The soap may be introduced directly into the viscous hydrocarbon oil charged to the system for extraction, or it may be added to the nitrobenzene or nitrobenzene extract at any point in the system. In systems where emulsification troubles develop in a particular stage or at a particular point in a tower, the ammonia and the alkaline earth metal soap may be introduced directly at that portion of the system, or into the oil or nitrobenzene entering at that portion of the system. The additives, when introduced into the system, are not recovered, but pass from the system in the raffinate phase and in the extract phase, the major portion of the soap occurring in the latter phase. Since the quantities of ammonia and of soap used are so small, they have no appreciable effect upon the properties of the raffinate or extract oils, and may be disregarded.

The alkaline earth metal soaps, such as the normal or basic soaps of calcium, barium, and strontium, may be produced by conventional methods.

For example, a fatty acid may be neutralized with the required amount of a basic compound of an alkaline earth metal to form the soap, or a fatty oil such as animal, vegetable, or marine oils may be saponified with the hydroxide or oxide of an alkaline earth metal, and the resulting soap may include small amounts of water and glycerol. Preferably the fatty acids employed to produce the soap are those containing from 12 to 20 carbon atoms, and such fatty acids may be saturated or unsaturated. Typical soaps include the calcium, barium, and strontium soaps of

oleic acid, stearic acid, palmitic acid, and mixtures of two or more thereof.

In practicing the present invention it is unnecessary to modify any of the solvent extraction systems or treating conditions, except to provide for the introduction of the ammonia and the alkaline earth metal soap at the proper point and in the desired amount.

The present invention may be further illustrated by the following examples, which, however, are not to be construed as limiting the scope thereof.

A commercial 5-stage batch countercurrent nitrobenzene solvent extraction system was operated at 40° F. using a relatively non-waxy lubricating oil stock and nitrobenzene at a charge ratio of 1 to 1 by volume. The charge oil had a S. U. viscosity of 198 seconds at 100° F., an A. P. I. gravity of 25.5°, a pour point of -10° F., an ASTM color of 2½ D, a viscosity index of 72, and a viscosity-gravity constant of 0.848. When no ammonia and alkaline earth metal soap were added, considerable difficulty was encountered in obtaining rapid and efficient stratification of the raffinate and extract phases in the settlers, due to emulsification of the finely divided raffinate droplets in the extract phase. The slow settling rate, with the resultant poorly defined interface between the phases, caused contamination of the raffinate phase with the extract, and vice versa, with simultaneous degradation of product quality and lower product yield. Furthermore, this difficulty encountered in the settlers caused overloading of the evaporators for the recovery of nitrobenzene from the oil fractions and necessitated operation at reduced charge rates. However, when small amounts of ammonia and alkaline earth metal soap were added to the charge oil, emulsification was greatly reduced and stratification and settling rate was substantially increased, with resultant increase in product quality and yield.

The specific soap employed was obtained by saponifying a mixture of hoss fat (70% oleic acid-30% stearic acid) and hog fat with lime in the presence of a small amount of water, and the resulting soap (mostly calcium oleate) was dispersed in lubricating oil to give a solution or dispersion of 6% by weight of soap in the oil. The oil-soap mixture was used to facilitate the introduction of the soap into the extraction system, although the soap could have been incorporated in the charge oil by other means.

The results obtained with and without the addition of the ammonia and the soap are given in the following table, the ammonia employed being an aqueous solution having a Bé. gravity of 19°, and the soap being given as weight percent oil-free soap.

Sample	Settling time
Oil Stock (no additive).....	13 min., 00 sec.
Oil Stock+0.006% soap.....	7 min., 00 sec.
Oil Stock+0.005 gal. NH ₄ OH.....	9 min., 45 sec.
Oil Stock+0.005 gal. NH ₄ OH+0.003% soap.....	3 min., 37 sec.
Oil Stock+0.005 gal. NH ₄ OH+0.006% soap.....	4 min., 00 sec.
Oil Stock+0.01 gal. NH ₄ OH.....	11 min., 30 sec.
Oil Stock+0.01 gal. NH ₄ OH+0.0015% soap.....	3 min., 25 sec.
Oil Stock+0.01 gal. NH ₄ OH+0.003% soap.....	4 min., 20 sec.

From the above data, it will be seen that the addition of small amounts of ammonia, per se, or of soap, per se, produce some decrease in settling time, but that the combination of both ammonia and soap results in a considerably greater decrease in settling time. While, in the above

examples, a soap comprising essentially calcium oleate was employed, similar results may be obtained using the fatty acid soaps of barium and strontium, in combination with ammonia.

The present invention is particularly adapted in the nitrobenzene extraction of non-waxy hydrocarbon oils using amounts of solvent of the order of ½ to 3 volumes per volume of charge oil. Waxy oils usually are more amenable to settling, consequently there is less occasion for the use of ammonia and the alkaline earth metal soaps in the nitrobenzene extraction of these stocks, although even in this case such additives may have a beneficial action in the settling of the raffinate and extract phases.

In the preferred mode of operation, the aqueous ammonia is added to the oil stock following its separation from the crude oil by fractionation, the oil stock at this stage usually being at a temperature between 300° F. and 800° F. After addition of the ammonia, the oil stock is cooled and the soap is added, and the mixture then further cooled to the desired temperature for selective solvent extraction with nitrobenzene. Addition of the ammonia may, of course, be made at temperatures below 300° F., but the best results appear to be obtained when the ammonia is added to the oil stock at elevated temperatures, and prior to the introduction of the stock into the extraction system. The temperature of the stock at the time of addition of the alkaline earth metal soap appears to be immaterial, and such addition may be made at ordinary or elevated temperatures.

We claim:

1. The method of avoiding emulsification difficulties and promoting the separation of the raffinate phase from the extract phase in the selective solvent extraction of viscous hydrocarbon oil employing nitrobenzene as the extraction solvent, which comprises adding to the extraction system a small amount of ammonia and of an alkaline earth metal soap of a fatty acid sufficient to promote phase separation.

2. The method of avoiding emulsification difficulties and promoting the separation of the raffinate phase from the extract phase in the selective solvent extraction of viscous hydrocarbon oil employing nitrobenzene as the extraction solvent, which comprises adding to the extraction system ammonia in an amount equivalent to 0.005 to 0.02 gallon of 19° Bé. aqueous ammonia per barrel of oil and from 0.0015% to 0.015% of an alkaline earth metal soap of a fatty acid.

3. The method of avoiding emulsification difficulties and promoting the separation of the raffinate phase from the extract phase in the selective solvent extraction of viscous hydrocarbon oil employing nitrobenzene as the extraction solvent, which comprises adding to the extraction system ammonia in an amount equivalent to 0.005 to 0.015 gallon of 19° Bé. aqueous ammonia per barrel of oil and from 0.0045% to 0.006% of an alkaline earth metal soap of a fatty acid.

4. The method of avoiding emulsification difficulties and promoting the separation of the raffinate phase from the extract phase in the selective solvent extraction of viscous hydrocarbon oil employing nitrobenzene as the extraction solvent, which comprises adding to the extraction system ammonia in an amount equivalent to 0.005 to 0.02 gallon of 19° Bé. aqueous ammonia per barrel of oil and from 0.0015% to 0.015% of calcium oleate.

5. The method of avoiding emulsification difficulties and promoting the separation of the raf-

finiate phase from the extract phase in the selective solvent extraction of viscous hydrocarbon oil employing nitrobenzene as the extraction solvent, which comprises adding to the extraction system ammonia in an amount equivalent to 0.005 to 0.02 gallons of 19° Bé. aqueous ammonia per barrel of oil and from 0.0015% to 0.015% of barium oleate.

6. The method of avoiding emulsification difficulties and promoting the separation of the raffinate phase from the extract phase in the selective solvent extraction of viscous hydrocarbon oil employing nitrobenzene as the extraction solvent, which comprises adding to the extraction system ammonia in an amount equivalent to 0.005 to 0.02 gallons of 19° Bé. aqueous ammonia per barrel of oil and from 0.0015% to 0.015% of strontium oleate.

7. In the extraction of lubricating oil stock with nitrobenzene at a temperature between 40° F. and 70° F. to separate the oil into a raffinate phase rich in paraffinic hydrocarbons and an extract phase rich in naphthenic hydrocarbons, the character of the oil being such that substantial emulsification occurs during extraction, the method of accelerating separation of the phases which comprises incorporating in the oil a small amount of ammonia and of an alkaline earth metal salt of a fatty acid, and effecting separation of the phases in the presence of said agents at the aforesaid temperature.

8. The method of avoiding emulsification difficulties and promoting the separation of the raffinate phase from the extract phase in the selective solvent extraction of viscous hydrocarbon oil employing nitrobenzene as the extraction sol-

vent, which comprises incorporating in the oil at an elevated temperature a small amount of ammonia, cooling the mixture, adding a small amount of an alkaline earth metal salt of a fatty acid, contacting the oil containing the additives with nitrobenzene, and separating the resulting raffinate and extract phases.

9. The method of avoiding emulsification difficulties and promoting the separation of the raffinate phase from the extract phase in the selective solvent extraction of viscous hydrocarbon oil employing nitrobenzene as the extraction solvent, which comprises incorporating in the oil at a temperature between 300° F. and 800° F. a small amount of ammonia, cooling the mixture, adding a small amount of an alkaline earth metal salt of a fatty acid, contacting the oil containing the additives with nitrobenzenes, and separating the resulting raffinate and extract phases.

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