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SOLVENT REFINING WITH NITROALCOHOLS

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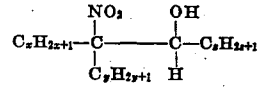
7 Claims. (Cl. 196—13)

This invention relates to refining hydrocarbon oil and, more particularly, to refining mineral oil by solvent extraction.

The invention contemplates the treatment and refining of mineral oil with a selective solvent whereby the oil is separated into fractions having desired characteristics. The invention has particular reference to the extractive treatment of mineral oil with nitroalcohols which have the following general chemical formula:



wherein x, y, and z represent zero or integers. Specific examples of nitroalcohols included in my invention are 3-nitro-4-heptanol, 5-nitro-4-octanol, 2-methyl-2-nitro-1-butanol, and 3-methyl-3-nitro-2-pentanol. These compounds may be prepared by any of the known general methods, but are most satisfactorily prepared as described in patent applications U. S. Ser. No. 146,852, filed June 7, 1937, by H. B. Hass and B. M. Vanderbilt and U. S. Ser. No. 146,855, filed June 7, 1937, by B. M. Vanderbilt which comprises reacting one mole of an aliphatic aldehyde with one mole of a primary nitro-paraffin. The invention contemplates extracting oil with any one of these compounds or their isomers, or with mixtures of any two or more of them or their isomers.

Lubricating oils, such as those produced from Mid-Continent crude, are ordinarily composed of relatively paraffinic constituents, and also relatively non-paraffinic constituents, including naphthenic, aromatic, and unsaturated hydrocarbons. A solvent of my invention is adapted to extract these relatively non-paraffinic bodies from oil for the production of lubricating oil fractions which are of relatively high paraffinic character, and therefore have relatively lower viscosity gravity constants than the untreated oil (Ferris, Birkhimer, and Henderson, Ind. and Eng. Chem., 23, pp. 753–761 (1931)).

In the application of my invention to the treatment of mineral oils, I prefer to use the general method indicated in the following: One part of the oil is mixed with from one to four parts of solvent liquid, and this mixture is then heated while agitating to a temperature somewhat above the critical solution temperature of the mixture in order to effect complete solution of the oil in the solvent. The mixture is then allowed to cool while slowly agitating to a temperature below that of the critical solution temperature. The agitation is discontinued and the two layers are allowed to settle out. The temperatures employed will depend upon the particular nitroalcohol used, the nature of the oil undergoing treatment, the degree of separation desired, and also to some extent upon whether the solvent is used alone or in combination with a modifying solvent or diluent as hereinafter mentioned.

Upon settling, the mixture separates into two layers, the bulk of the solvent liquid containing the constituents which it is desired to extract from the oil, and the oil layer containing the undissolved and relatively paraffinic oil in admixture with a relatively small amount of solvent. The two layers are then separately withdrawn and the solvent liquid recovered therefrom. If desired, the separated layers may be subjected to treatment with additional quantities of the solvent for the purpose of obtaining a series of fractions of differing characteristics. The solvent may be recovered from the oil by any suitable method such as distillation. Final traces of the solvent may be removed from the oil by finally subjecting the mixture to the action of steam for a period of time at a temperature above the boiling point of the nitroalcohol employed.

I do not wish to be in any manner limited to the above described process for effecting the extractions. The extraction may be carried out in a continuous or semi-continuous system. The process may also be carried out at a constant temperature which is somewhat lower than the critical solution temperature of the oil and the nitroalcohol employed.

The following examples are presented in order to illustrate my invention. The oil used in these examples was a Mid-Continent crude having the following properties:

Specific gravity at 60° C	0.9020
Saybolt viscosity at 100° F——sec—	307.5
Saybolt viscosity at 210° F——sec—	51
Viscosity gravity constant at 100° F—	0.846
Viscosity gravity constant at 210° F—	.840

Example I

Two parts by weight of 3-nitro-4-heptanol were mixed with one part of oil and the mixture heated until a homogeneous mixture resulted. This critical solution temperature was about 78° C. The mixture was then slowly agitated and allowed to cool to about 58° C., at which temperature the two layers were allowed to settle out. These were separately removed and each subjected to vacuum distillation in order to remove the solvent. The distillation was continued until

the liquid reached the temperature of 230° C., air being passed through at all times in order to remove completely the solvent. The oil from the solvent layer had a viscosity gravity constant equal to .870 at 100° F., and .868 at 210° F. The purified oil layer had a viscosity gravity constant equal to .830 at 100° F., and .824 at 210° F.

Example II

Two volumes of 5-nitro-4-octanol were mixed with one volume of oil and treated as in the previous example. The critical solution temperature of this mixture being about 51° C., the mixture was heated above this temperature and then cooled to about 31° C. at which temperature the liquid was separated and treated as before. The resulting oils had the following viscosity gravity constants:

	Oil from	
	Oil layer	Solvent layer
At 100° F.	.828	.865
At 210° F.	.822	.863

Example III

Two volumes of 2-methyl-2-nitro-1-butanol were mixed with one volume of oil and treated as above. In this case the critical solution temperature was about 152° C. and the separation was made at about 131° C. The resulting oils had the following viscosity gravity constants:

	Oil from	
	Oil layer	Solvent layer
At 100° F.	.823	.883
At 210° F.	.824	

Example IV

The same procedure was followed as in Example III using 2-methyl-2-nitro-1-butanol. The separation was made at 112° C., however. 80% of the oil was recovered in the raffinate which had a viscosity gravity constant of .833 at 100° F. and .828 at 210° F.

Example V

Two volumes of 3-methyl-3-nitro-2-pentanol were mixed with one volume of oil and treated as above. In this case the critical solution temperature was about 111° C. and the separation was made at about 81° C. 74% of the oil was recovered in the oil layer which had a viscosity gravity constant of .828 at 100° F. and .822 at 210° F.

It will, of course, be readily recognized that certain of the nitroalcohols of this group will be more satisfactory than others for the extraction. For example, 2-nitro-1-butanol and 2-nitro-1-propanol are immiscible with the oil tested at temperatures of about 200° C. It is not generally desirable to operate the solvent extraction at such high temperatures, however, because of the tendency of the nitroalcohols to form decomposition products. Also, certain of the higher nitroalcohols have critical solution temperatures too low to permit a practical separation of the two layers by further cooling, and are consequently less desirable than those nitroalcohols containing from four to ten carbon atoms. Choice of the nitroalcohol to be employed will depend on the temperatures at which it is desired to operate, the oil being extracted, and the characteristics desired in the refined product.

In some instances it may be an advantage to carry out the extraction in the presence of a modifying solvent liquid, such as benzol or a light petroleum naphtha, or a petroleum fraction composed of propane, butane, or other similar low boiling hydrocarbons, for the purpose of facilitating the extraction and further controlling the extent thereof.

The lubricating oil distillate may be subjected to the foregoing extraction treatment either before or after dewaxing, or subsequent to treatment with other solvents or chemicals.

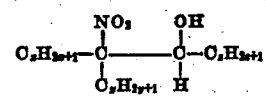
The invention is not necessarily limited to the treatment of lubricating oil fractions, since the solvent may be adapted to the refining and purification of various hydrocarbon or mineral oil fractions, including naphtha, cracked naphtha, kerosene, etc., as well as residual or distillate fractions, or products derived from petroleum or other sources.

Obviously many modifications and variations of the invention as hereinabove set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. The method of refining hydrocarbon oil containing relatively paraffinic and relatively non-paraffinic constituents, including naphthenic, aromatic, and unsaturated hydrocarbons, to remove the undesired relatively non-paraffinic constituents therefrom, which comprises extractively treating the oil with an aliphatic nitroalcohol whereby the undesired constituents are separated from the oil as an extract soluble in the solvent liquid.

2. The method of refining hydrocarbon oil containing relatively paraffinic and relatively non-paraffinic constituents, including naphthenic, aromatic, and unsaturated hydrocarbons, to remove the undesired relatively non-paraffinic constituents therefrom, which comprises extractively treating the oil with a nitroalcohol having the following general chemical formula:

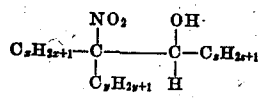


wherein x, y, and z represent zero or integers, whereby the undesired constituents are separated from the oil as an extract soluble in the solvent liquid.

3. The method of refining hydrocarbon oil containing relatively paraffinic and relatively non-paraffinic constituents, including naphthenic, aromatic, and unsaturated hydrocarbons, to remove the undesired relatively non-paraffinic constituents therefrom, which comprises extractively treating the oil with an aliphatic nitroalcohol containing less than 11 carbon atoms in the molecule, whereby the undesired constituents are separated from the oil as an extract soluble in the solvent liquid.

4. The method of refining hydrocarbon oil containing relatively paraffinic and relatively non-paraffinic constituents, including naphthenic, aromatic, and unsaturated hydrocarbons, to remove the undesired relatively non-paraffinic constituents therefrom, which comprises extractively

treating the oil with a nitroalcohol having the following general chemical formula:



wherein x, y, and z represent zero or integers and $x+y+z$ is less than nine, whereby the undesired constituents are separated from the oil as an extract soluble in the solvent liquid.

5. The method of refining hydrocarbon oil containing relatively paraffinic and relatively non-paraffinic constituents, including naphthenic, aromatic, and unsaturated hydrocarbons, to remove the undesired relatively non-paraffinic constituents therefrom, which comprises extractively treating the oil with 2-methyl-2-nitro-1-butanol, whereby the undesired constituents are separated from the oil as an extract soluble in the solvent liquid.

6. The method of refining hydrocarbon oil containing relatively paraffinic and relatively non-paraffinic constituents, including naphthenic, aromatic, and unsaturated hydrocarbons, to remove the undesired relatively non-paraffinic constituents therefrom, which comprises extractively treating the oil with 3-methyl-3-nitro-2-pentanol, whereby the undesired constituents are separated from the oil as an extract soluble in the solvent liquid.

7. The method of refining hydrocarbon oil containing relatively paraffinic and relatively non-paraffinic constituents, including naphthenic, aromatic, and unsaturated hydrocarbons, to remove the undesired relatively non-paraffinic constituents therefrom, which comprises extractively treating the oil with 3-nitro-4-heptanol, whereby the undesired constituents are separated from the oil as an extract soluble in the solvent liquid.

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