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SOLVENT EXTRACTION

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This invention relates to the separation of mixtures of hydrocarbons, and more particularly to the separation of petroleum or petroleum products into fractions of different chemical composition.

In the solvent refining of hydrocarbons such as petroleum and petroleum products, it is well known that solvents differ in their ability to separate the hydrocarbon or petroleum fraction into components of differing types. (See Ferris, Birkhimer, and Henderson, Industrial & Engineering Chemistry 23, 753-761, 1931.) It is desirable, however, that the separation of such oil components be accomplished as selectively as possible so that the maximum segregation of the components by type may be obtained.

The selective solvent extraction of petroleum and petroleum products depends upon the fact that they are mixtures of hydrocarbons, which may be roughly divided into paraffinic and naphthenic compounds, and which have different solubility characteristics. Solvents can thus be used to extract preferentially the more soluble naphthenic types of compounds from the less soluble paraffinic compounds. The more selective the solvent in its extractive action the more economical is its use or the more effective is its refining action or both. Oil fractions from different crude petroleum sources may differ considerably with respect to their composition and so may require different solvents or different operating conditions with the same solvent or both. Hence it is of material advantage to have a selective solvent whose selectivity can be varied at will to permit the most advantageous operation of a selective solvent extraction.

It is an object of the present invention to provide a solvent of variable selectivity and to provide a new and improved process for the selective refining of petroleum and petroleum products.

Other objects and advantages of this invention will be apparent by reference to the following specification.

According to the present invention mixtures of hydrocarbons, and particularly petroleum and petroleum products, are selectively separated into fractions of differing chemical compositions by treatment with a solvent containing a substituted amide and a substance or substances represented by the formula ROH in which R represents hydrogen, or an alkyl or methylol group.

Although specific disclosure will be made hereinafter of single water-soluble substituted amides, it should be understood that the invention in-

cludes the use of mixtures of as well as individual water-soluble amides.

Water-soluble substituted amides generally are suitable for use, according to this invention, it being preferred, however, to utilize the mono- and dialkyl substituted amides of acids containing from one to and including four carbon atoms, such, specifically as the mono- and di-methyl, ethyl, propyl or isobutyl formamides, acetamides, propionamides or butyramides or the like.

Although specific disclosure will be made hereinafter of water, which is my preferred hydroxyl-containing compound to be used with a substituted amide as solvent, it will be understood that the invention is not to be limited to the use of water and shall extend to the use of hydroxyl-containing compounds generally such as hereinbefore broadly described. Specifically and as illustrations of alternative hydroxyl-containing compounds, I may use mono- and polyhydric alcohols such as methanol or ethylene glycol, and the like, the only limitation on my hydroxyl-containing materials as broadly described being the necessity that they are relatively insoluble in hydrocarbon mixtures such as petroleum and petroleum products.

In applying my invention specifically to petroleum oil refining, as an example, I first mix the oil which it is desired to treat with a suitable proportion of my solvent. The mixing is accomplished at a temperature, or during elevation of the temperature to a degree, sufficiently elevated to ensure solution of the oil in the solvent. Thereafter the oil-solvent mixture is cooled, resulting in the formation of two layers which may, in turn, be separated by simple decantation.

The naphthenic hydrocarbons, being more soluble in my solvent than the paraffinic, dissolve in the greater portion of my solvent and separate into one of the two layers. The paraffinic constituents of the original oil, being less soluble in my solvent, separate into the other layer which contains a relatively small portion of the solvent.

It will be apparent that the preferential solvent characteristics of my solvent may be employed in a variety of ways for effecting selective separation. Thus, as an alternative procedure, the oil and solvent may be agitated to effect more rapid separation while heating the mixture to a temperature of more or less complete solution, or the oil and the solvent may be vigorously agitated at temperatures at which they are not wholly miscible to effect a solution. In any or all of these methods of extraction, the invention may advantageously be operated on the principle of

counter-current flow, i. e., the oil may be caused to contact the solvent which is caused to flow in the reverse direction from that of the oil.

In whatever manner the extraction step is operated, the two layers hereinbefore described are allowed to form, separated one from the other by simple decantation and thereafter I may separate the solvent from either or both of the two layers by distillation or by addition of further hydroxyl-containing material. Inasmuch as the oil fraction extracted is soluble in my solvent and relatively insoluble in the hydroxyl-containing material and inasmuch as my solvent is completely miscible with the hydroxyl-containing material, the addition of further amounts of hydroxyl-containing material to either or both of the two oil fraction-layers effects selective separation of the solvent from the oil fraction. The remaining substituted amide-hydroxyl-containing material may be separated by distillation and the recovered amide recycled if desired such, for example, as in a continuous process.

In the examples given below, the selective removal of non-paraffinic constituents from a mineral oil has been measured by following the change in viscosity-gravity constant of the oil. The constant has been described by J. B. Hill and H. B. Coats in Industrial and Engineering Chemistry, volume 20, page 641, et seq., in an article entitled "The viscosity-gravity constant of petro-

decantation. The solvent and oil were separated by distillation. In this example pure dimethyl formamide and a dimethyl formamide solution containing 10% water by volume respectively were used as solvents. The data in the table below demonstrate the increase in solvent selectivity brought about by the addition of hydroxyl containing material to the substituted amide.

Example II

A Pennsylvania distillate was extracted with an equal volume of solvent consisting of pure dimethyl formamide and with additions of 5 volume per cent of water and methanol, respectively. When using pure dimethyl formamide the oil-solvent mixture was heated to miscibility with agitation, cooled to 80° C. and maintained at that temperature for ½ hour with agitation, allowed to settle and the two resultant layers decanted. When using dimethyl formamide-water and dimethyl formamide-methanol as the solvents the extraction was made by agitating oil and solvent 2 hours at about 90° C., cooling to 80° C. with agitation, settling, and separating the raffinate and extract layers by decantation. In each case the oil was then freed from solvent by distillation. The data below on the oils so obtained show an increase in selectivity and in miscibility temperature on the addition of hydroxyl containing material to the substituted amide.

Solvent	Temperature			Gravity degrees API	Saybolt Universal viscosity sec. at 100° F.	Field	Viscosity gravity constant	Selectivity
	Miscibility	Separation						
	° C.	° C.						
Example I			Gulf Coast distillate	20.2	577		0.872	
DMF (dimethyl formamide)	115-120	85	{ Raffinate	24.5	539	71.3	0.847	.103
90% DMF			{ Extract	11.2	2,074	22.2	0.950	
10% water		85	{ Raffinate	22.0	573	90.8	0.864	.128
Example II			{ Extract	6.8	5,124	8.8	0.992	
DMF	130	80	Penna. distillate	30.2	178.4		0.820	
95% DMF			{ Raffinate	31.3	163.7	89.0	0.814	0.071
5% water	173	80	{ Extract	19.9	*51.8	8.6	0.885	
95% DMF			{ Raffinate	30.8	169.5	96.0	0.817	0.105
5% methanol	134	80	{ Extract	15.0	*56.5	4.1	0.922	
			{ Raffinate	31.4	165.6	90.5	0.813	0.075
			{ Extract	19.5	*51.6	9.2	0.888	

*Viscosity at 210° F.

leum lubricating oils." If a given crude petroleum be distilled into successive fractions and the specific gravities and viscosities of the several fractions determined, it will be found that they conform to the general relationship:

$$G = a + \frac{1.0752 - a}{10} \log (V - 38)$$

in which G is the specific gravity at 60° F., V is Saybolt Universal viscosity at 100° F., and a is the viscosity-gravity constant. This viscosity-gravity constant is lower for fractions of paraffinic crudes than for fractions of naphthenic crudes. This constant is, therefore, an index of the paraffinicity of an oil, and a decrease in the value of this constant for a given fraction of oil indicates an increase in paraffinic hydrocarbon content. Moreover the difference in the values of the constant for the paraffinic and naphthenic fractions obtained in a solvent extraction is a measure of the selectivity of the solvent.

Example I

A Gulf Coast distillate was extracted with an equal volume of solvent by heating with agitation to 125-128° C., cooling with agitation to about 85° C., agitating at 85° C. for 30 minutes, settling for ten minutes and separating the two layers by

The use of dimethyl formamide-water solvent has been specifically disclosed by Examples I and II. However, as indicated previously, water-soluble substituted amides generally are suitable for use according to this invention, the only restriction being my preference for employing one to four carbon atom amides such as previously specifically mentioned. Any of these substituted amides may almost equally as well be substituted for dimethyl formamide without sacrificing advantages of this invention.

Other variations may also be made in the methods of operation while utilizing the principles of this invention, without departing therefrom or sacrificing the advantages thereof.

Although I have indicated by Example I that 10% by volume of water in the amide-water solution is an effective solvent, it should be understood that this is an illustration only and not a limitation. The selectivity of the substituted amide-ROH solution is increased as the concentration of the amide is decreased and thus the solvent's selectivity may be varied by changing its composition. Thus, for example, if it is desired to vary the selectiveness of my hydroxyl-containing compound-amide solvent, the content of hydroxyl-containing compound may be considerably raised or lowered to give solvents containing

from 99% by volume amide and 1% by volume of hydroxyl-containing compound to solvents containing 1% amide and 99% by volume of hydroxyl-containing compound.

I claim:

5 1. In a process for separating normally liquid hydrocarbon mixtures into fractions of different compositions the step which comprises bringing the mixtures into contact with a solvent contain-
10 ing a substituted aliphatic amide of an acid of from 1 to 4 carbon atoms and a compound represented by the formula ROH in which R represents a substance from the group; hydrogen, alkyl and methylol groups, separating the resultant layer containing the major portion of the solvent
15 and the major portion of the hydrocarbons, and separating the hydrocarbons from the solvent.

2. In a process for separating normally liquid hydrocarbon mixtures into fractions of different compositions the step which comprises bringing
20 the mixtures into contact with a solvent containing a substituted aliphatic amide of an acid of from 1 to 4 carbon atoms and water, separating the resultant layer containing the major portion of the solvent and the major portion of the hydrocarbons, and separating the hydrocarbons
25 from the solvent.

3. In a process for separating normally liquid hydrocarbon mixtures into fractions of different compositions the step which comprises bringing
30 the mixtures into contact with a solvent containing a substituted aliphatic amide of an acid of from 1 to 4 carbon atoms and methanol, separating the resultant layer containing the major portion of the solvent and the major portion of the hydrocarbons, and separating the hydrocarbons
35 from the solvent.

4. A process for separating mineral oils containing liquid paraffinic and naphthenic hydrocarbons into fractions which comprises the steps
40 of bringing the oil into contact with a dimethyl formamide-water solvent, separating the resultant layer containing the major portion of the solvent and the major portion of the naphthenic hydrocarbons by decantation from the remainder
45 of the oil, and treating both portions of the oil to remove the solvent from the oil.

5. A process for separating mineral oils containing liquid paraffinic and naphthenic hydrocarbons into fractions which comprises the steps
50 of bringing the oil into contact with a dimethyl formamide-methanol solvent, separating the resultant layer containing the major portion of the solvent and the major portion of the naphthenic hydrocarbons by decantation from the remainder
55 of the oil, and treating both portions of the oil to remove the solvent from the oil.

6. A process for separating mineral oils containing liquid paraffinic and naphthenic hydrocarbons into fractions which comprises the steps
60 of bringing the oil into contact with a solvent containing about 90% by volume of dimethyl formamide and 10% water, separating the resultant layer containing the major portion of

the solvent and the major portion of the naphthenic hydrocarbons by decantation from the remainder of the oil, and treating both portions of the oil to remove the solvent from the oil.

7. A process for separating petroleum oils containing liquid paraffinic and naphthenic hydrocarbons into fractions which comprises bringing
5 the oil into contact with a substituted aliphatic amide of 1 to 4 carbon atoms and water, heating, while agitating, the mixture until complete
10 solution of the oil and the solvent, cooling the solution until separation into two layers, one rich in paraffinic and one rich in naphthenic hydrocarbons, occurs, separating the two layers by decantation and removing the solvent from the
15 oil in the two layers

8. A process for separating petroleum oils containing liquid paraffinic and naphthenic hydrocarbons into fractions which comprises bringing
20 the oil into contact with a substituted aliphatic amide of 1 to 4 carbon atoms and methanol, heating, while agitating, the mixture until complete solution of the oil and the solvent, cooling the solution until separation into two layers, one
25 rich in paraffinic and one rich in naphthenic hydrocarbons, occurs, separating the two layers by decantation and removing the solvent from the oil in the two layers.

9. A process for separating petroleum oils containing liquid paraffinic and naphthenic hydrocarbons into fractions which comprises bringing
30 the oil into contact with a dimethyl formamide-water solvent, heating, while agitating, the mixture until complete solution of the oil and the solvent, cooling the solution until separation into
35 two layers, one rich in paraffinic and one rich in naphthenic hydrocarbons, occurs, separating the two layers by decantation and removing the solvent from the oil in the two layers.

10. A process for separating petroleum oils containing liquid paraffinic and naphthenic hydrocarbons into fractions which comprises bringing
40 the oil into contact with a dimethyl formamide-methanol solvent, heating, while agitating, the mixture until complete solution of the oil and the solvent, cooling the solution until
45 separation into two layers, one rich in paraffinic and one rich in naphthenic hydrocarbons, occurs, separating the two layers by decantation and removing the solvent from the oil in the two
50 layers.

11. A process for separating petroleum oils containing liquid paraffinic and naphthenic hydrocarbons into fractions which comprises bringing
55 the oil into contact with a solvent containing about 90% by volume dimethyl formamide and 10% water, heating, while agitating, the mixture until complete solution of the oil and the solvent, cooling the solution until separation into
60 two layers, one rich in paraffinic and one rich in naphthenic hydrocarbons, occurs, separating the two layers by decantation and removing the solvent from the oil in the two layers.

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