Patented Jan. 15, 1952

2,582,883

UNITED STATES PATENT OFFICE

2,582,883

MODIFIED DOUBLE SOLVENT TREATMENT

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No Drawing. Application August 27, 1947, Serial No. 770,951

10 Claims. (Cl. 196—14.20)

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The present invention relates to the separation of mixtures of hydrocarbons into a paraffinic portion and a non-paraffinic portion and, more particularly, to the refining of petroleum oil and the like to a raffinate of higher paraffinicity than the charge stock.

The so-called double solvent processes of solvent treating petroleum oil employs two solvents of relatively low mutual solubilities, one of which has a high preferential solubility for the undesirable constituents of the oil, usually classified as non-paraffinic or naphthenic and aromatic hydrocarbons, and the other a high preferential solubility for the desirable constituents of the oil, usually classified as paraffinic hydrocarbons. The first solvent is usually referred to as the naphthenic solvent while the other solvent is usually referred to as the paraffinic solvent. The raffinate phase in the double-solvent treatment is a solution of the more paraffinic portion of the charge oil in the paraffinic solvent while the extract phase is a solution of undesirable constituents or non-paraffinic constituents in the naphthenic solvent.

A brief but adequate description of one modification of the double solvent method of treating petroleum oil is given in the "Process Handbook" section of Petroleum Refiner (April 1947) pages 138 and 139. The double solvent process is also described in U. S. Patents Nos. 1,912,348; 1,912,349 and 2,041,308.

The double solvent refining process which is most widely used in the petroleum industry for refining residual oils is known as the "Duo-Sol" process. The process is capable of simultaneously deasphalting and solvent refining asphaltic residua by employing a two-solvent system composed of a naphthenic solvent, "selecto," and a paraffinic solvent, liquid propane. "Selecto" is a mixture of phenol and cresylic acids usually containing 40 to 60 per cent phenol. In a Duo-Sol system, the liquid propane acts as an asphalt precipitant and diluent while "selecto" functions both as a solvent for the asphalt and an oil treating agent. A typical installation consists essentially of a three to seven stage countercurrent extraction system in which a propane-oil mixture is contacted with "selecto" plus a two stage system in which the "selecto," containing extracted material, is countercurrently washed

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with fresh liquid propane. In a seven stage unit propane would be added to the first, charge stock in the third, and "selecto" in the seventh stage. The spent solvent containing extracted material and asphalt would be drawn from the first and treated oil from the seventh stage of the unit. Temperatures of 75 to 165 degrees Fahrenheit, pressures up to 500 pounds per square inch and propane and "selecto" solvent to oil ratios up to 7:1 are usually employed.

While the double solvent treating method has been employed most widely in the treatment of petroleum fractions, it is recognized by those skilled in the art that similar mixtures of hydrocarbons, such as shale oils, synthetic oils prepared by the Fischer-Tropsch process and mixtures of hydrocarbons prepared by other methods of synthesis, likewise are amenable to this treatment.

It has now been discovered that the use of a modifier in conjunction with the paraffinic and naphthenic solvents in a typical double solvent treating process results in an increased recovery of the refined oil from the non-paraffinic materials in the charge stock. The refined oil so obtained is of a quality comparable to that produced in the conventional double solvent treating process although of somewhat higher viscosity. The rejected material, i. e. the solute of the extract phase, or tar is of higher gravity than tar from normal or conventional double solvent operations.

In general, the paraffinic solvents employed in the double solvent treatment of mixtures of paraffinic, naphthenic and aromatic hydrocarbons with or without admixed asphaltic materials are liquefied normally gaseous hydrocarbons such as the saturated and unsaturated hydrocarbons having 3 to 5 carbon atoms, lighter hydrocarbons such as methane, ethane, ethylene, acetylene, etc. mixed with hydrocarbons of 3 to 5 carbon atoms and heavier aliphatic and olefinic hydrocarbons having up to 10 or 12 carbon atoms per molecule. Other paraffinic solvents are methyl Cellosolve, Carbitol and other oxygenated compounds such as acetone, methyl, ethyl and isopropyl alcohols, etc.

The naphthenic solvents employed in the double solvent treatment of mixtures of paraf-

finic, naphthenic and aromatic hydrocarbons with or without admixed asphaltic materials are aqueous or non-aqueous liquid SO_2, liquid SO_2-benzol, furfural, dichloroethyl ether, aniline, quinoline, pyridine, nitrobenzene, benzyl alcohol, phenol, cresylic acid, ethylene diamine, di- and triethanolamines, crotonaldehyde, sulfolanes, dimethyl formamide, formic acid and acetic anhydride, etc.

When the effects of the foregoing combinations of "paraffinic" solvent and "naphthenic" solvent are modified by the use of a third component, hereinafter termed a modifier, the oily constituents of high viscosity present in the charge stock are retained in the raffinate phase instead of being rejected in extract phase as in conventional double solvent treatment. As a result the process yield is higher and the raffinate is of higher viscosity. By modification of other variables a much higher yield of oil of comparable quality is obtained using the modified solvent combinations than is obtained with conventional solvent combinations.

The solvent combinations are advantageously modified by the use of a modifier selected from the group consisting of carbonates of aliphatic, cycloaliphatic, and aromatic hydrocarbons and heterocyclic compounds, of which group diethyl carbonate is preferred.

While the use of one of the afore-enumerated modifiers in conjunction with one of the conventional combinations of "paraffinic" solvent and "naphthenic" solvent brings about the advantages enumerated hereinbefore, a more selective action in the presence of smaller amounts of modifier can be obtained by incorporating small amounts of water, say up to 25 weight per cent in the "naphthenic" solvent.

The modified double solvent refining operation with or without aqueous "naphthenic" solvent is conducted in about the same manner as conventional double solvent refining operations with provision for adding modifier or modifier and water at any point or points in the unit. However, improved results are obtained by washing the extract phase with fresh "paraffinic" solvent-modifier mixture. Thus, for example, in a nine stage system paraffinic solvent and modifier are added in the first stage, charge oil in the third stage, and aqueous or non-aqueous naphthenic solvent in the ninth stage while the treated mixture of hydrocarbons, i. e. mixture of hydrocarbons of increased paraffinicity, is withdrawn from the ninth and the rejected extract from the first stage of the unit. The raffinate and extract are separately treated in any suitable manner, say by distillation, to remove the "paraffinic" solvent and the "naphthenic" solvent respectively. The ratio of paraffinic solvent and naphthenic solvent to charge stock may be varied from 1:1 to 7:1, while the modifier ratio (based on the charge stock) may vary from 0.15 to 1.5:1. The temperatures employed may vary from 75 to 206 degrees Fahrenheit.

Those skilled in the art will understand that although the use of modifiers in conjunction with the solvents in a double solvent treatment of a mixture of paraffinic and non-paraffinic hydrocarbons has been discussed hereinbefore and will be described hereinafter in conjunction with treatment in isolated zones known as stages, nevertheless the treatment can be carried out in a tower or towers or in equipment employing centrifugal force to accelerate the separation of the raffinate phase from the extract phase. Furthermore, the solvent treatment of charge stock with a naphthenic solvent and particularly with aqueous "naphthenic" solvents in the absence of a "paraffinic" solvent is improved by the use of the novel modifiers enumerated hereinbefore.

Thus, for example, a mixture of paraffinic and non-paraffinic hydrocarbons can be treated in the manner described in the "Process Handbook" section of Petroleum Refiner (April 1947) pages 122 and 123, using dichloroethyl ether, phenol or, in general, any "naphthenic" solvent containing up to 10 per cent of water (aqueous naphthenic solvent) together with one or more of the modifiers enumerated hereinbefore.

Typical of the treatment of charge stocks containing paraffinic and non-paraffinic hydrocarbons are the following non-limiting examples.

EXAMPLE I

A residual stock of 187 seconds Saybolt Universal viscosity at 210 degrees Fahrenheit was processed in double solvent treating unit having seven extraction and two extract wash stages employing about 300 weight per cent of "naphthenic" solvent of 50 per cent phenol content ("selecto"), about 500 weight per cent of propane and about 50 weight per cent of the preferred modifier, diethyl carbonate, at a temperature of about 100 degrees Fahrenheit.

EXAMPLE II

In order to provide a standard whereby the effect of the modifiers can be evaluated, a portion of the same stock was treated at the same temperature with about 300 weight per cent of "naphthenic" solvent of 50 percent phenol content ("selecto") and about 500 weight per cent of propane.

EXAMPLE III

In order to show the effect produced by using a "naphthenic" solvent containing water in conjunction with a "paraffinic" solvent and a modifier, diethyl carbonate, a charge stock of 458 seconds Saybolt Universal viscosity at 210 degrees Fahrenheit was processed in the same equipment employing about 350 weight per cent "naphthenic" solvent of 50 per cent phenol content ("selecto") containing about 1.5 per cent of water, about 450 weight per cent of propane and about 25 weight per cent of diethyl modifier at a temperature of about 120 degrees Fahrenheit.

EXAMPLE IV

To provide a standard of comparison for the results obtained in Example III, a portion of the same charge stock was treated with the same amounts of the same "naphthenic" and "paraffinic" solvents in the absence of a modifier.

EXAMPLE V

The results obtained in this operation establish that increasing the phenol content of the "naphthenic" solvent is not a means of obtaining a yield of raffinate similar in amount and quality to that obtained employing a modifier. A portion of the oil of 458 seconds Saybolt Universal viscosity at 210 degrees Fahrenheit, used in Examples III and IV was treated with about 350 weight per cent of a "naphthenic" solvent ("selecto") having an 80 per cent phenol content and about 450 weight per cent of propane at a temperature of about 120 degrees Fahrenheit.

A summary of the results obtained in each of the Examples I to V is provided in the following table:

Table I

COMPARATIVE DUO-SOL REFINING DATA ON RESIDUAL STOCKS EMPLOYING AS THE NAPHTHENIC SOLVENT SELECTO, SELECTO-WATER WITH LIQUID PROPANE DIETHYL CARBONATE

Processing Conditions:							
Duo-Sol Refining—							
Oil-Selecto-Propane Ratio by Wt.	1-3-5						
Temperature, °F.	100						
Diethyl Carbonate Ratio Based on Oil		0.50					
Phenol Content of Selecto, Per Cent Wt.		50				50	
Water Content of Selecto, Per Cent Wt.							
Run Number		1032				862	
Percolation, Oil/Clay Ratio by Wt.		0.8:1				1.4:1	
Yields, Per Cent Vol.:							
On Process—							
Extraction		84.1				78.9	
Dewaxing, Ultimate		75.8				75.2	
Overall—							
On Residuum		58.9				54.8	
On Crude	23.4	13.8				12.8	
Processing Step:	Raw Resid.	Waxy Raff.	Dewaxed Raff.	Finished Oil	Waxy Raff.	Dewaxed Raff.	Finished Oil
Inspections—							
Gravity, °A. P. I.	23.4	27.8	26.4	28.5	29.2	28.2	28.6
Gravity, Specific @ 60° F. (Pyc @ 77° F.)							
Pour Point, °F.	110		15	20		20	20
Flash Point, °F. (COC)	515		490	495		495	485
Fire Point, °F. (COC)	570		560	555		555	545
K. V. @ 100° F. (Centistokes)			343.2	247.4		246	221
@ 210° F. (Centistokes)	40.0	23.82	24.84	20.42	20.46	20.66	18.96
S. U. V. @ 100° F., Seconds			1588	1143		1137	1021
@ 210° F., Seconds	187	114.6	119.1	99.9	100.1	101	93.8
Viscosity Index			101	103		105	103
Viscosity Gravity Constant @ 210° F.	0.823	0.803	0.813	0.801	0.796	0.803	0.802
Color, Lovibond, ¼" Cell	>750	>750	>750	80	750	550	75
Carbon Residue, Per Cent Wt.	4.5						
Sulfur, Per Cent Wt.	0.71						
Tar—							
Specific Gr. @ 60° F. (Pyc @ 77° F.)		1.0460			1.0380		
S. U. V. @ 210° F., Seconds		>10,000			>10,000		

Processing Conditions:										
Duo-Sol Refining—										
Oil-Selecto-Propane Ratio by Wt.	1-3.5-4.5									
Temperature, °F.	120									
Diethyl Carbonate Ratio Based on Oil		0.25								
Phenol Content of Selecto, Per Cent Wt.		47				47			80	
Water Content of Selecto, Per Cent Wt.		1.5				1.5				
Run Number		1177				1182			1164	
Percolation, Oil/Clay Ratio by Wt.		20:1				19:1			10:1	
Yields, Per Cent Vol.:										
On Process—										
Extraction		56.3				51.6			56.4	
Dewaxing, Ultimate		83.0				84.0			85.7	
Overall—										
On Residuum		44.6				41.4			46.5	
On Crude	36.3	16.2				15.1			16.9	
Processing Step:	Raw Resid.	Waxy Raff.	De-waxed Raff.	Finished Oil	Waxy Raff.	De-waxed Raff.	Finished Oil	Waxy Raff.	De-waxed Raff.	Finished Oil
Inspections—										
Gravity, °A. P. I.	16.5	28.7	27.9	28.1	29.3	28.5	28.4	28.2	27.5	27.6
Gravity, Specific @ 60° F. (Pyc @ 77° F.)	0.9609	0.8880			0.8851			0.8943		
Pour Point, °F.	75		15	15		15	15		15	20
Flash Point, °F. (COC)	520		500	500		480	480		505	500
Fire Point, °F. (COC)	595		565	575		545	545		565	565
K. V. @ 100° F. (Centistokes)			242.6	241.4		192	194.7		272.5	268.7
@ 210° F. (Centistokes)	98.3	17.46	18.92	18.85	15.59	16.35	16.37	19.37	20.13	20.01
S. U. V. @ 100° F., Seconds			1121	1115		887	900		1259	1241
@ 210° F., Seconds	458	87.6	93.6	93.3	80.1	83.1	83.2	95.5	98.6	98.2
Viscosity Index			95	96		96	95		93	94
Viscosity Gravity Constant @ 210° F.	0.872	0.802	0.807	0.805	0.800	0.805	0.805	0.804	0.809	0.807
Color, Lovibond, ¼" Cell	>750	83	82	60	48	54	24	190	170	78
Carbon Residue, Per Cent Wt.	12.0			0.20			0.15			0.35
Sulfur, Per Cent Wt.	1.7			0.47			0.32			0.57
Tar—										
Specific Gr. @ 60° F. (Pyc @ 77° F.)		1.0550			1.0415			1.0469		
S. U. V. @ 210° F., Seconds		>10,000			>10,000			>10,000		

The solvent refined oils obtained as described hereinbefore, particularly when liquid SO_2 or liquid SO_2-benzol or "selecto" are used as naphthenic solvents, can be dewaxed merely by removing a portion of the propane to chill the oil and adjust the propane concentration to that desirable for dewaxing. In other words, the concentration of propane and organic carbonate in the raffinate is adjusted, preferably by vaporization of the propane, to provide a ratio of propane to organic carbonate from about 3:1 to about 1:3 by volume. The vaporization of the propane serves to chill the raffinate to dewaxing temperatures although the raffinate can be chilled by other suitable means. When adjusting the ratio of propane to organic carbonate in the raffinate to provide a dewaxing mixture, it is also preferred to adjust the ratio of solvent refined oil to dewaxing mixture in the raffinate to 1:0.2 to 1:8 with a ratio of 1 to 3 preferred.

I claim:

1. In the treatment of a mixture of paraffinic and non-paraffinic hydrocarbons contaminated with asphaltic materials which comprises con-

tacting a charge stock containing paraffinic hydrocarbons, non-paraffinic hydrocarbons and asphaltic material with two substantially mutually immiscible solvents comprising a solvent for paraffinic hydrocarbons and a solvent for non-paraffinic hydrocarbons and separating a raffinate fraction more paraffinic than said charge stock from an extract fraction more non-paraffinic than said charge stock, the improvement which comprises employing a solvent for non-paraffinic hydrocarbons consisting essentially of phenol and cresols and at least 1.5 weight per cent added water and a solvent for paraffinic hydrocarbons consisting essentially of propane and about 1 to about 20 per cent of an organic carbonate.

2. In the treatment of a mixture of paraffinic and non-paraffinic hydrocarbons contaminated with asphaltic material which comprises contacting a charge stock with propane and a mixture of phenol and cresols in the proportion of 1:1–3.5:1–4.5 by weight, and separating a raffinate fraction more paraffinic than said charge stock from an extract fraction more non-paraffinic than said charge stock, the improvement which comprises employing a mixture of phenol and cresols to which about 1.5 to about 25 per cent water has been added and propane to which about 1 to about 20 per cent of an organic carbonate has been added.

3. The process as set forth and described in claim 1 wherein the organic carbonate is diethyl carbonate.

4. The process as set forth and described in claim 2 wherein the organic carbonate is diethyl carbonate.

5. In the treatment of a mixture of paraffinic and non-paraffinic hydrocarbons contaminated with asphaltic material which comprises contacting a charge stock with propane and cresylic acids in the proportion by weight of 1:1–3.5:1–4.5, and separating a raffinate fraction more paraffinic than said charge stock from an extract fraction more non-paraffinic than said charge stock the improvement which comprises carrying out the separation in the presence of 1.5 to about 25 per cent added water and about 1 to about 20 per cent of an organic carbonate.

6. The process described and set forth in claim 5 wherein the added organic carbonate is diethyl carbonate.

7. The method of treating a mixture of hydrocarbons admixed with asphaltic material and subsequently dewaxing said mixture of hydrocarbons which comprises contacting a waxy mixture of paraffinic and non-paraffinic hydrocarbons admixed with asphaltic material with liquid, normally gaseous hydrocarbon, a mixture of phenol and cresols and an organic carbonate in the ratio of 1 part of oil to 1–3 parts of propane to 1–3 parts of said mixture of phenol and cresols to 0.15 to 1.5 parts of organic carbonate all by weight, separating a raffinate phase comprising wax, paraffinic hydrocarbons, propane and organic carbonate from an extract phase comprising non-paraffinic hydrocarbons, asphalt and mixture of phenol and cresols, adjusting the ratio of propane to organic carbonate in said raffinate phase from 1 to 3:0.15 to 1.5 by weight to 3:1.5 to 1:5, chilling said raffinate to dewaxing temperature and separating high molecular weight paraffinic hydrocarbons from said raffinate phase to provide a solvent treated dewaxed oil.

8. The invention as set forth and described in claim 7 wherein the liquid, normally gaseous hydrocarbon is propane.

9. The invention as set forth and described in claim 7 wherein the organic carbonate is diethyl carbonate.

10. The invention as set forth and described in claim 7 wherein the liquid, normally gaseous hydrocarbon is propane and the organic carbonate is diethyl carbonate.

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