United States Patent [19]

Brasher et al.

[11] **3,719,585**

[45] **March 6, 1973**

[54] **SOLVENT DEWAXING WITH SEPARATION OF SOLVENT BY LIQUID-LIQUID EXTRACTION**

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[22] Filed: **Dec. 28, 1970**

[21] Appl. No.: **101,735**

[52] **U.S. Cl.** **208/33**

[51] **Int. Cl.** **C10g 43/08**

[58] **Field of Search** 208/33

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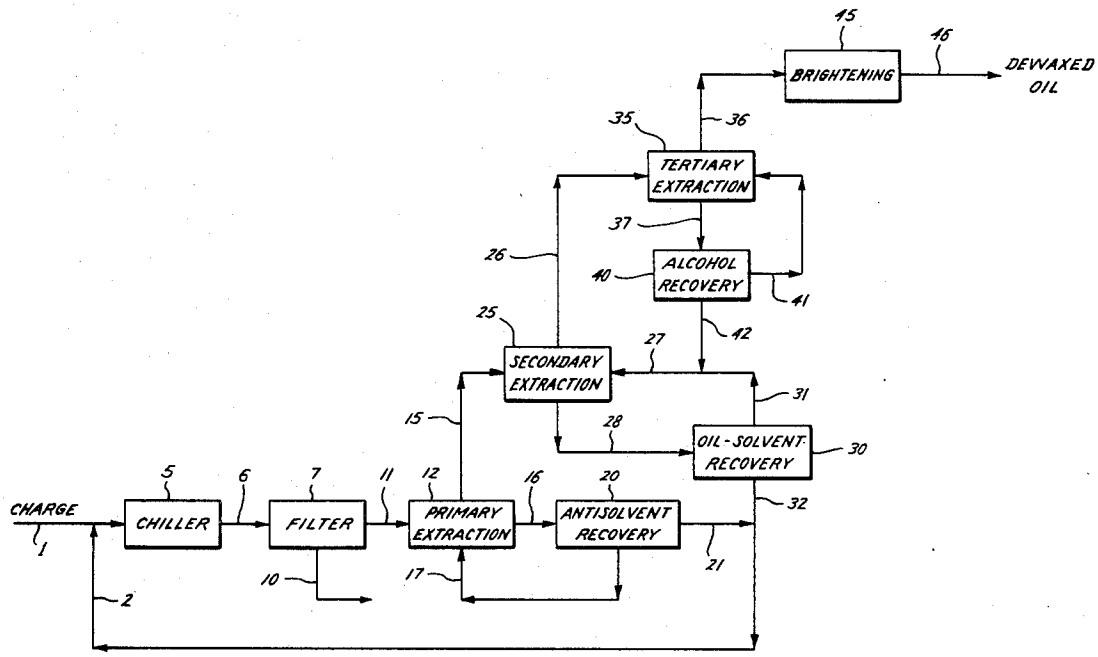
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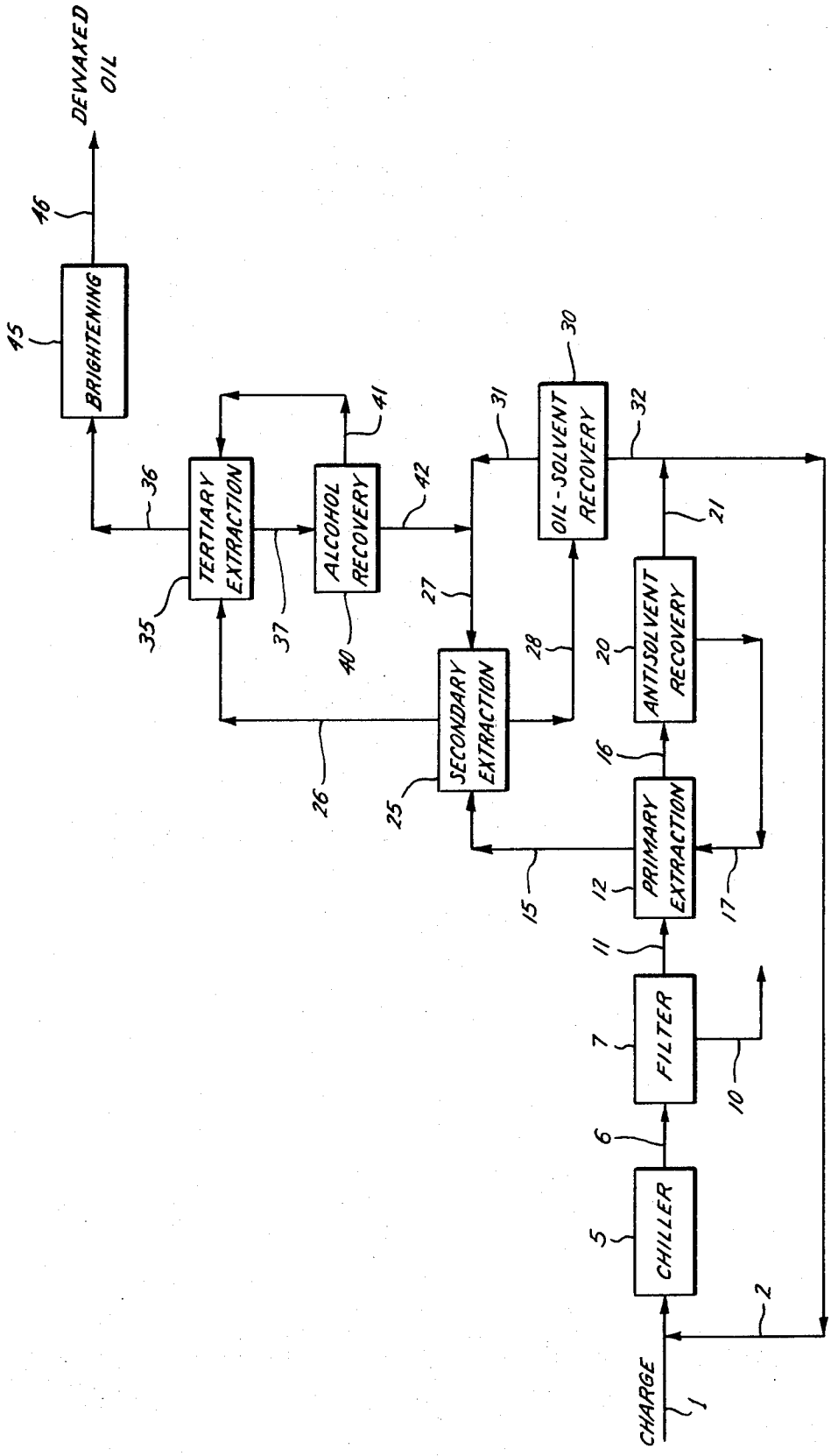
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[57] **ABSTRACT**

In a dewaxing process wherein a wax-bearing mineral oil is diluted with a solvent mixture comprising an oil-solvent and a wax-antisolvent, the resultant oil-solvent mixture is cooled effecting separation of wax and the solvent mixture is separated from wax free oil by re-extraction. Re-extraction is effected by contacting the oil and solvent mixture with solvents for the wax-antisolvent and for the oil-solvent. The dewaxed oil is subjected to a final brightening.

10 Claims, 1 Drawing Figure




CHARGE
1
2
CHILLER
5
6
FILTER
7
10
11
PRIMARY EXTRACTION
12
15
17
ANTISOLVENT RECOVERY
16
20
21
OIL-SOLVENT RECOVERY
30
31
32
SECONDARY EXTRACTION
25
26
27
28
ALCOHOL RECOVERY
40
41
42
TERTIARY EXTRACTION
35
36
37
BRIGHTENING
15
16
DEWAXED OIL

SOLVENT DEWAXING WITH SEPARATION OF SOLVENT BY LIQUID-LIQUID EXTRACTION

BACKGROUND OF THE INVENTION

Most types of petroleum crude oil, particularly paraffinic crudes contain at least small quantities of waxes. Upon distillation, for example, these waxes are carried into the distillate fractions. When a petroleum fraction containing wax is used as a lubricant base, the waxes present in the oil fraction crystallize out at low temperatures, and therefore interfere with the flow or circulation of the oil. Many applications, therefore, require that the wax content of the oil be reduced to a minimum or be substantially eliminated.

The conventional practice of dewaxing a mineral oil fraction involves chilling the oil in admixture with a selective solvent which shows a preferential solubility for oil over wax at a low temperature to crystallize the wax which is then separated by filtration, centrifuging or the like. The pour point of the oil produced by this process may be as low as −15°F. or lower.

The selective solvents used in dewaxing are those which are miscible with the components other than solidified wax, that is, the oil or liquid fraction of the mixture, but which have low solvent action on the solidified wax, that is, the higher melting point wax or solid fraction, at temperatures within the range of about +10° to −30°F. The selective solvent used may advantageously comprise a mixture of an oil-solvent, for example benzene, toluene, and their mixtures, and a wax-antisolvent, for example an aliphatic ketone such as acetone, methyl ethyl ketone, methyl isobutyl ketone, and the like. Other wax-antisolvents may be employed, for example, sulfur dioxide, furfural, phenol, benzaldehyde, formates, acetates, and the like. Similarly other oil-solvents may be used, for example, low boiling aliphatic ethers such as isopropyl ether, halogenated aliphatic hydrocarbons such as dichloroethane, methylene chloride, and propylene dichloride, and chlorinated aromatic hydrocarbon such as chlorobenzene.

After separation of wax from the remaining oil-solvent mixture, the solvent mixture is separated from the dewaxed oil. Heretofore, the usual method of solvent separation has been by distillation. The distillative separation of solvent from dewaxed oil is effected at temperatures sufficiently high to remove all of the solvent as distillate from the remaining lubricating oil. When employing a preferred solvent, a methyl ethyl ketone-toluene mixture, it is necessary to employ distillation temperatures typically of about 445°F. or higher to effect complete separation of the solvent. We have observed that color degradation may occur in the course of the dewaxing process, that is, the color of the dewaxed oil is inferior to the color of the waxy oil charge. We have now determined that this color degradation occurs in the course of separation of the solvent from the dewaxed oil by distillation and steam stripping. Accordingly, it is an objective of the present invention to provide a solvent dewaxing process wherein color degradation is prevented. In another aspect, it is an objective of this invention to prevent color degradation in the course of dewaxing by separating solvent from dewaxed filtrate by re-extraction with a liquid which exhibits selective solvent action on a dewaxing solvent mixture comprising a wax-antisolvent and an oil-solvent.

SUMMARY OF THE INVENTION

In accordance with the process of this invention, low pour test lubricating oil is manufactured from wax-bearing mineral oil by the steps of mixing the mineral oil with a solvent mixture comprising an alcohol soluble oil-solvent and a water soluble wax-antisolvent, chilling the resulting mixture to a dewaxing temperature to crystallize the wax, separating the crystallized wax from the remaining mixture of dewaxed oil, oil-solvent and wax-antisolvent, and recovering dewaxed oil, oil-solvent and wax-antisolvent separately from the remaining mixture by liquid-liquid extraction. In the liquid-liquid extraction, the remaining mixture after wax separation is contacted with water in a first extraction zone effecting extraction of the wax-antisolvent from the mixture forming a first raffinate comprising oil and oil-solvent. The first raffinate is then contacted with an alcohol in a second extraction zone effecting extraction of oil-solvent from said first raffinate forming a second raffinate comprising oil and dissolved alcohol. The second raffinate is then contacted with water in a third extraction zone effecting extraction of alcohol from said second raffinate forming a third raffinate which comprises said low pour test lubricating oil stock. Liquid-liquid contact is effected in each of the extraction zones at a temperature within the range of about 60° to 160°F. Advantageously, after extraction of solvent mixture from the lubricating oil stock, the lubricating oil stock is brightened at a temperature of about 180°F. The alcohol, employed in the second extraction zone may be an alcohol selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol and normal propyl alcohol. A preferred oil-solvent is an aromatic hydrocarbon selected from the group consisting of benzene, toluene, and mixtures thereof. The preferred wax-antisolvent is a ketone selected from the group consisting of acetone, methyl ethyl ketone, methyl isobutyl ketone, and mixtures thereof. The preferred solvent mixture comprises methyl ethyl ketone and toluene.

DESCRIPTION OF THE DRAWING

Wax-bearing oil charge in line **1** is admixed with solvent mixture in line **2** and passed to chiller **5**. The solvent mixture in line **2** may comprise for example about 30 to 70 volume percent methyl ethyl ketone, wax-antisolvent and about 70 to 30 volume percent toluene oil-solvent. Preferably about 40 to 60 volume percent antisolvent and 60 to 40 volume percent oil-solvent, respectively, are employed. The ratio of solvent mixture to waxy oil charge may be for example 1:1 to about 5:1. The waxy oil charge and solvent mixture are combined or heated to a temperature at least the temperature of complete miscibility of the oil, wax, and solvent prior to chilling by means not shown. In chiller **5**, the temperature of the wax and oil solvent mixture is reduced to a temperature within the range of about +10° to −30°F. AT these temperatures the wax crystallizes as a slurry in the oil and solvent mixture. The slurry of wax crystals is passed through line **6** to filter **7**. In filter **7** the wax is separated from the oil and solvent mixture and discharged through line **10**. Filtrate comprising dewaxed oil and solvent mixture is discharged through line **11**. Wax in line **10** is processed for recovery of the occluded and dissolved solvent by conventional means not shown.

The filtrated in line 11 is passed to primary extraction 12. Primary extraction 12 may comprise a liquid-liquid contacting device such as a packed column, a centrifugal contactor, or a rotating disc contactor. In extraction zone 12 the oil and solvent mixture is countercurrently contacted with water introduced through line 17 effecting extraction of the wax-antisolvent constituent of the solvent mixture. The ratio of water to oil and solvent mixture may be within the range of about 0.5:1 to 10:1 and preferably within the range of about 1:1 to 5:1. Raffinate comprising dewaxed oil and oil-solvent is discharged through line 15 to secondary extraction 25. Extract comprising wax-antisolvent dissolved in water is passed through line 16 to wax-antisolvent recovery facility 20. Facility 20 may comprise, for example, distillation means wherein the wax-antisolvent is distilled and separated as a distillate discharged through line 21 for recycle through line 2. Water separated in recovery facility 20 is recycled through line 17 to primary extraction zone 12.

In secondary extraction facility 25, the primary raffinate is contacted with an alcohol, for example, ethyl alcohol, in liquid-liquid contacting apparatus. This apparatus may be of the same type as that employed in extraction zone 12. The ratio of alcohol to primary extract may be within the range of about 0.5:1 to 10:1 and preferably within a range of about 1:1 to 5:1. In secondary extraction zone 25, the oil-solvent constituent of the primary raffinate is extracted and some alcohol becomes dissolved in the remaining dewaxed oil because of mutual miscibility of the oil, alcohol and oil-solvent. The raffinate comprising dewaxed oil and alcohol is discharged through line 26 to tertiary extraction zone 35. Extract comprising oil-solvent dissolved in alcohol is discharged through line 28 to oil-solvent recovery facility 30. Oil-solvent recovery facility 30 may be a distillation zone in which the alcohol is separated as distillate through line 21 and returned to secondary extraction zone 25 through line 27. Recovered oil-solvent is discharged through line 3 and combined with wax-antisolvent in line 21 to comprises the solvent mixture passed through line 2 to charge line 1.

Secondary raffinate is contacted with water from line 41 in tertiary extraction zone 35. Tertiary extraction zone 35 may be facility of the same type as extraction zones 25 and 12. The ratio of water of secondary raffinate may be within the range of about 0.1:1 to 5:1 and preferably within the range of about 0.25:1 to 1:1. In tertiary extraction zone 35 the oil and alcohol mixture is countercurrently contacted with water effecting extraction of the alcohol. Extract is discharged through line 37 to alcohol recovery facility 40. Recovered alcohol is discharged through line 32 for return to secondary extraction zone 25 through line 27. Recovered water is discharged through line 41 to provide the water employed in tertiary extraction zone 35.

Dewaxed oil, washed free of alcohol is discharged through line 36 to brightening facility 45. Brightening facility 45 is employed to remove any cloud or haze resulting from the contacting with alcohol and water. Such brightening may be effected by blowing with nitrogen or air at temperature of about 150° to 180°F. or by vacuum dehydration employing the application of a vacuum of about 29 inches mercury. Brightening is preferably effected at temperatures within the range of about 150° to 200°F. and preferably at a temperature of about 180°F. Brightened dewaxed oil is discharged through line 46 to provide the low pour test lubricating oil stock product.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In an example of the process of this invention, a lubricating oil stock having a dewaxed oil viscosity of 100 Saybolt Universal seconds viscosity at 100°F. was dewaxed employing methyl ethyl ketone as wax-antisolvent and toluene as oil-solvent. After separation of the wax, the resulting filtrate had a composition of 25 volume percent dewaxed oil, 37.5 volume percent methyl ethyl ketone and 37.5 percent toluene. The oil solvent mixture was then water washed at 70°F. effecting separation of methyl ethyl ketone and then washed with formula 30 denature ethyl alcohol at 70°F. effecting extraction of toluene. The composition of formula 30 denatured ethyl alcohol is about 86 volume percent ethyl alcohol, 9 volume percent methyl alcohol and 5 volume percent water. After extraction of the solvent mixture with water and alcohol, the color of the dewaxed oil was 22 on the Lovibond 6 inch colorimeter. In comparison, a sample of the same filtrate was stripped at 238° F. and 27 inches vacuum producing a dewaxed oil after solvent separation having a 60 color on the Lovibond 6 inch scale.

In another example of the process of this invention, a waxy charge oil having a dewaxed viscosity of 178 Saybolt Universal seconds at 100°F. and a Lovibond 6 inch color of 105 was dewaxed with a methyl ethyl ketone-toluene solvent mixture. Upon water-alcohol washing of the solvent mixture from the dewaxed oil, the resulting product had a Lovibond 6 inch color of 150. In comparison, upon stripping another portion of the oil and solvent mixture by stripping at 238°F. and 27 inch vacuum, the resulting dewaxed oil had a color on the 6 inch Lovibond scale of 190 in one test and 210 in a check test.

In another example of the process of this invention, a waxy lubricating oil having a 265 Saybolt Universal seconds viscosity at 100°F. and a 20 Lovibond 6 inch color was dewaxed with a methyl ethyl ketone-toluene solvent mixture. A sample of the resulting oil and solvent mixture was washed with water, washed with formula 30 alcohol, water washed separating dissolved alcohol, and brightened at 180°F. producing a dewaxed oil having a Lovibond 6 inch color of 16. A second sample of the oil and solvent mixture was stripped employing conventional distillation and steam stripping to separate the solvent mixture. The resulting dewaxed oil had a Lovibond 6 inch color of 30.

WE CLAIM:

1. In the production of a low pour test lubricating oil stock from a wax-bearing mineral oil by the steps comprising mixing said mineral oil with a solvent mixture comprising an alcohol soluble oil-solvent and a water soluble wax-antisolvent, chilling the resulting mixture to a dewaxing temperature to crystallize the wax, separating the crystallized wax from the remaining mixture comprising oil, oil-solvent, and wax-antisolvent, and recovering oil, oil-solvent and wax-antisolvent separately from said remaining mixture, the improvement which comprises:

contacting said remaining with water in a first extraction zone effecting extraction of said wax-antisolvent from said remaining mixture forming a first raffinate comprising oil and said oil-solvent,

contacting said first raffinate with an alcohol in a second extraction zone effecting extraction of said oil-solvent from said first raffinate forming a second raffinate comprising oil and dissolved alcohol, and

contacting said second raffinate with water in a third extraction zone effecting extraction of alcohol from said second raffinate forming a third raffinate comprising said low pour test lubricating oil stock.

2. The process of claim 1 wherein said remaining mixture is contacted with water at a temperature within the range of about 60 to 160°F.

3. The process of claim 1 wherein said first raffinate is contacted with alcohol at a temperature within the range of about 60 to 160°F.

4. The process of claim 1 wherein said second raffinate is contacted with water at a temperature within the range of about 60 to 160°F.

5. The process of claim 1 wherein said third raffinate is brightened at a temperature of about 180°F.

6. The process of claim 1 wherein said alcohol is selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol, and normal propyl alcohol.

7. The process of claim 1 wherein said oil-solvent is selected from the group consisting of benzene and toluene.

8. The process of claim 1 wherein said wax-antisolvent is an aliphatic ketone selected from the group consisting of acetone, methyl ethyl ketone and methyl isobutyl ketone.

9. The process of claim 1 wherein said solvent mixture comprises methyl ethyl ketone and toluene.

10. The process of claim 1 in which the remaining mixture is contacted with water at a temperature between 60 to 160°F., the first raffinate is contacted with an alcohol selected from the group consisting of methyl alcohol, ethyl alcohol, isopropyl alcohol and normal propyl alcohol at a temperature between 60 to 160°F., the second raffinate is contacted with water at a temperature between 60 to 160°F. and the third raffinate is brightened at a temperature between 150 and 200°F.

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