Patented Jan. 12, 1954

2,666,020

UNITED STATES PATENT OFFICE

2,666,020

SEPARATION OF WAX-LIKE CONSTITUENTS FROM OIL WITH A COMPLEXING AGENT IN THE PRESENCE OF WATER

George B. Arnold, Glenham, Howard V. Hess, Beacon, James K. Truitt, Wappingers Falls, and James W. Fitzwilliam, Beacon, N. Y., assignors to The Texas Company, New York, N. Y., a corporation of Delaware

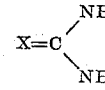
No Drawing. Application June 7, 1949, Serial No. 97,717

6 Claims. (Cl. 196—14.35)

1

This invention relates to a process for the separation of wax-like constituents from oil such as contained in hydrocarbon mixtures by treatment with an organic agent such as urea.

The invention concerns a process for separation of wax and wax-like constituents from oil by treatment with an organic complexing agent having the structure:



where X may be either oxygen, or sulfur. Examples of effective compounds or agents are urea, thiourea, and derivatives thereof which are capable of forming with waxy constituents of mineral oil, solid crystalline complex compounds readily separable from the oil. More specifically, the invention contemplates effecting contact between feed oil and the complexing agent in the presence of water and an added normally liquid paraffin hydrocarbon having about 9 to 10 carbon atoms or having in the range about 7 to 14 carbon atoms per molecule. The invention has particular application to the treatment of oils of higher molecular weight, that is, having more than about 10 or 14 carbon atoms per molecule including gas oils and lubricating oils.

The pending application Serial No. 75,542, filed February 10, 1949, now U. S. Patent 2,635,986, broadly discloses separation of wax constituents from oil by treatment with complexing agents of the foregoing character in the presence of at least a small amount of a polar solvent liquid such as the low molecular weight aliphatic alcohols. The presence of a polar substance of such character appears desirable as a means of facilitating the formation of the complex compounds.

It appears that a complexing agent such as urea enters into complex formation with paraffinic hydrocarbons in the C_7 to C_{14} range in the presence of water, forming complex compounds that are stable at temperatures in the range up to 125 to 150° F. Stable complex compounds are also formed with higher molecular weight hydrocarbons or oils of the character of gas oils or lubricating oils in the presence of small amounts of alcohol but stable complex compounds are not formed with such higher molecular weight hydrocarbons in the presence of water only.

The present invention involves the discovery that stable complex compounds are formed in the gas oil and lubricating oil range in the presence of water if there is also present some of the aforesaid paraffinic hydrocarbons having 7 to 14 carbon atoms per molecule. Thus, the invention contemplates adding a paraffinic hydrocarbon such as octanes, nonanes and decanes to feed oils of the character of gas oil and lubricating oil and using water rather than alcohol to promote complex formation.

2

Therefore, in accordance with this invention, waxy constituents are removed from gas oils and lubricating oils by treatment with the complexing agent in the presence of both water and an added low molecular weight hydrocarbon. The added hydrocarbon may be blended with the feed oil prior to, during, or both prior to and during treatment with the complexing agent. The water and the complexing agent may be added separately or in admixture.

The feed oil, complexing agent, water and added hydrocarbon are subjected to thorough mixing at a temperature in the range about 70 to 125° F. and usually not in excess of 150° F. to complete complex formation with the constituents of the feed oil which it is desired to remove therefrom. Thereafter, the mixture is subjected to settling, filtration, centrifuging or other treatment adapted to remove the complex material from the remaining liquid phase.

The oil can be washed with water, advantageously employing the well-known principle of countercurrent flow scrubbing to remove residual amounts of complexing agent. This washing may be carried out at normal room temperature or at a temperature not in excess of about 150° F.

The separated solid complex is advantageously heated to a temperature of about 180° or in the range 150 to 200° F. to effect decomposition. The heated complex breaks down into an oily or waxy layer and an aqueous or urea layer. These layers may be separated. The waxy layer can be washed with an additional quantity of water to scrub residual complexing agent therefrom. The wash water containing residual complexing agent can be distilled to form a concentrated solution of complexing agent in water. On the other hand, it may be commingled directly with the aforesaid aqueous layer and the resulting mixture concentrated to form a solution of complexing agent in water or a mixture of complexing agent in water of the desired composition effective for the treatment of fresh feed oil.

The added paraffin hydrocarbon remains in the waxy fraction and can be separated therefrom by distillation or other means as desired and thus recovered for re-use in the process.

The amount of complexing agent employed will

depend upon the wax content of the feed oil undergoing treatment and may amount to from about 3 to 4 lbs. of complexing agent per pound of waxy constituents contained in the feed oil and which it is desired to remove therefrom.

The amount of added hydrocarbon will depend upon the character of the feed oil undergoing treatment as well as the waxy constituents thereof. Usually, this added oil will amount to from about $\frac{1}{10}$ to 2 parts by weight of the waxy constituents of the feed oil which it is desired to remove.

The amount of water required to promote the complex formation usually ranges from about 1 or 2% to 5 or even 10% by weight of the feed oil although it is contemplated that either smaller or larger amounts may be used.

By way of example, a lubricating oil distillate having a Saybolt Universal viscosity of about 300 seconds at 100° F. containing about 1% wax by volume and having a "Freon haze" temperature of around minus 20° F. was treated with urea amounting to about 4 lbs. per lb. of wax contained in the oil in the presence of a small amount of water, namely, about 10% by volume of the oil. The mixture was subjected to agitation at a temperature of about 75° F. for a period of 75 minutes. However, formation of a solid complex did not occur to any appreciable extent so that upon settling it was possible to separate only substantially pure urea as the solid material.

By contrast, when another sample of this lubricating distillate was mixed with 2% by volume of n-tetradecane and treated with the same amount of urea plus the urea required to complex the n-tetradecane and in the presence of water as before at the same temperature, formation of a stable solid complex occurred. This complex was withdrawn and the so-treated oil was found to have a "Freon haze" temperature of about minus 75 to minus 80° F.

The "Freon haze" temperature is determined by mixing the oil with "Freon 12" (dichlorodifluoromethane) in the proportion of about 90% "Freon 12" and 10% oil by volume, chilling the mixture and observing the temperature at which haze appears.

The action of the added hydrocarbon n-tetradecane appears to be that of a complex stabilizer or promoter so that the resulting complex of urea and haze-forming constituents of the aforementioned lubricating oil distillate is sufficiently stable to remain in solid crystalline form during settling and separation from the settling vessel.

An important advantage of the invention resides in the use of water rather than alcohol or some other solvent liquid to promote complex formation. The water can be readily separated from the treated oil, whereas a liquid such as alcohol, due to its miscibility with oil, requires provision for solvent recovery. Thus, the present invention eliminates the need for such solvent recovery and, therefore, provides a more simple and economical process.

While the treatment of relatively low viscosity oils has been indicated nevertheless it is contemplated that the invention may have application to the treatment of more viscous oils and oils of relatively high wax content. The treatment of the more viscous type of oil may be facilitated by the use of petroleum hydrocarbon type diluents such as naphtha and liquefied normally gaseous hydrocarbons. In this way, the process may be applied to the treatment of waxy concentrates to effect separation of desired wax fractions.

The process may have application to the treatment of oils derived from animal, vegetable or marine sources and to oils which have been subjected to other types of refining such as hydrogenation.

The process may be used in conjunction with other types of dewaxing operations either to effect a preliminary removal of wax or to effect removal of residual wax constituents from previously dewaxed oil. It may also be used for deoiling wax concentrates and for the fractionation of wax according to molecular or melting point.

The process may be used to effect separation of normal paraffins from non-paraffinic hydrocarbons such as aromatics and naphthene hydrocarbons and thus provide a means for manufacturing transformer oil. On the other hand, certain aromatic and naphthenic hydrocarbons having long aliphatic side chains enter into complex formation with urea and thus such constituents may be separated from hydrocarbon mixtures containing them by the procedure of this invention. It may be used for the removal of oxygen-containing compounds from mineral oils which have been subjected to previous treatment with oxidizing agents.

The invention is particularly effective for the treatment of oils of the character of gas oils and relatively low viscosity lubricating oil distillates useful in the manufacture of lubricants for refrigerator service and turbines or for the manufacture of oils useful as diesel fuels and jet fuels, etc.

While urea has been specifically mentioned, it is contemplated that substituted derivatives thereof such as ethanol urea, diethyl urea, butyl urea, may be used as well as other derivatives containing various di, tri and/or tetra valent inorganic and/or organic compounds.

Obviously many modifications and variations of the invention, as hereinbefore 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.

We claim:

1. In the separation from a lube oil of constituents which form crystalline complexes with urea, the method which comprises subjecting said lube oil to contact with urea in the presence of water and an added normal paraffin hydrocarbon containing about 7 to 14 carbon atoms per molecule with the result that the complex-forming constituents in the lube oil enter into crystalline complex formation with urea, and separating resulting crystalline complex from the oil.

2. The method according to claim 1 in which contact of the lube oil with urea is effected at a temperature not in excess of about 150° F.

3. The method according to claim 1 in which the added C_7 to C_{14} normal paraffin hydrocarbon amounts to 0.1 to 2 parts by weight of the complex-forming constituents of the lube oil.

4. In the separation from a lube oil of constituents which form crystalline complexes with a complexing agent selected from the group consisting of urea and thiourea, a method which comprises subjecting said lube oil to contact with said agent in the presence of water and an added paraffin hydrocarbon containing between 7 and 14 carbon atoms which readily forms com-

plexes with said complexing agent with the result that complex-forming constituents of said lube oil enter into crystalline complex formation with urea and separating the resulting crystalline complex from said lube oil.

5. The method according to claim 4 in which contact of said lube oil with said complexing agent is effected at a temperature not in excess of about 150° F.

6. The method according to claim 4 in which the added C_7 to C_{14} hydrocarbon amounts to from about 0.1 to 2 parts by weight of the complex-forming constituents of said lube oil.

GEORGE B. ARNOLD.
HOWARD V. HESS.
JAMES K. TRUITT.
JAMES W. FITZWILLIAM.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,499,820	Fetterly	Mar. 7, 1950
2,549,372	Fetterly	Apr. 17, 1951

OTHER REFERENCES

Bengen, German patent application O. Z. 12,438 (March 18, 1940). U. S. publication date May 22, 1946, 5 pages.