Patented July 10, 1951 2,560,193

UNITED STATES PATENT OFFICE

2,560,193

DEHAZING HYDROCARBON OILS

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No Drawing. Application December 27, 1947, Serial No. 794,201

8 Claims. (Cl. 196—23)

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This invention relates to the refining of lubricating oils and more particularly it relates to the problem of preventing haze formation in petroleum lubricating oils when allowed to stand at moderately low temperatures. Many lubricating oils, whether from wax-free crudes or from stocks which have been dewaxed and which are satisfactory from the standpoint of pour point, nevertheless develop a haze in cool weather. Altho the presence of the haze appears to have no adverse effect on the use of the oil, nevertheless it is highly objectionable from the standpoint of marketability, particularly when encountered in motor oils which are commonly sold in glass containers and where it is desirable that the oil have a brilliant appearance in all seasons.

It is an object of this invention to eliminate haze from petroleum lubricating oils and particularly oils having viscosities in the range of SAE 20 to SAE 60. It is also an object of this invention to eliminate haze from lubricating oils which have been dewaxed at a low temperature, following the dewaxing operation with the dehazing step without the necessity for further refrigeration. Another object is to make white medicinal oils from waxy crudes which cannot now be used because of the haze problem. Still another object is to produce satisfactory transformer oils from waxy crude oils by a combination of dewaxing and dehazing steps.

The cause of haze formation in lubricating oils is not well understood. Paraffin wax has been suspected by some investigators altho the phenomenon has been observed in the case of lubricating oils from naphthenic-base crudes, such as crude from Winkler County, Texas, which require no dewaxing.

Furthermore, as indicated hereinabove, the phenomenon is also observed with oils which have been thoroughly dewaxed and which have a very low pour point. The formation of haze does not occur with all lubricating oils for some unexplained reason. The haze appears to be colloidal in nature and heretofore the problem where encountered has usually been solved by filtering the hazy oil thru clarifying filters, usually employing for this purpose an adsorbent substance or filter aid such as infusorial earth, as otherwise the haze substance passed thru the usual filter cloth unretained.

I have now discovered that the haze can be removed from lubricating oils and heavy petroleum distillates by contacting with crystalline, finely divided urea. It is preferred to activate the urea by the addition of a small amount of a

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suitable solvent such as water, methanol, ethanol and acetone. The preferred amount of activating solvent is about one-fourth mol to one mol per mol of urea employed. When water is the activating agent, not more than one-half mol should be used whereas with methanol and ethanol a larger amount can be used with less risk of slowing down the reaction by the excess. Thus one to three mols of methanol are quite effective. A chemical reaction occurs between the urea and the haze-producing substance in the oil which requires only a short time, usually about fifteen minutes to one or two hours, thirty to forty-five minutes usually being a satisfactory time of contact. One method of carrying out the operation is to filter the oil thru a bed of the urea. Another method is to agitate the urea with the oil in a suitable mixer and then separate it either by settling, centrifuging or filtering. The amount of urea required is normally about five to forty per cent of the weight of the oil. In the case of the more viscous oils it is desirable to reduce their viscosity by the use of a suitable hydrocarbon solvent which does not itself react with the urea. Highly viscous liquids react with urea very slowly. Inasmuch as urea has been found to react with straight-chain hydrocarbons having six carbon atoms or more, it is desirable to employ as the solvent only aromatic or naphthenic solvents such as toluene or cyclohexane, or branched-chain paraffinic solvents such as isooctane. Any hydrocarbon having less than six carbon atoms, however, may be used without encountering difficulty from the reaction of the solvent with the urea dehazing reagent. Examples of this type of solvent are propane, pentane and butane.

In applying my invention to wax-containing oils, the oil is first dewaxed to prevent the wax interfering with the dehazing treatment, since the straight-chain paraffin compounds, comprising the wax, also react with the urea. In the dewaxing operation, the oil is diluted with a suitable solvent such as described above, for example, using about one-half volume to five volumes of solvent per volume of oil. The diluted oil is then chilled to a low temperature, usually about 20 to —40° F., in order to crystallize the wax. The slurry of wax is then separated by filtration, for example, by forcing it thru a conventional plate filter press. The diluted oil from which the wax has been removed is next contacted with urea as described hereinabove. The temperature of contacting may suitably be about room temperature, 60–90° F., altho temperatures in the range of 30 to 150° F. may be

used. At lower temperatures, for example down to —20° F., the reaction is usually too slow for practical operation. The cold dilute oil directly from the wax-filtering operation may be passed thru a bed of the crystalline urea to remove haze-producing substances, usually after warming to near room temperature.

After contacting with the urea, the oil is separated and the diluent is separated from the oil by distillation in the customary manner. The resulting oil is then found to be free of haze even when maintained at a low temperature.

As an example of dehazing an oil from a wax-free crude, a quantity of transformer oil from Winkler crude having a pour point of —60° F. and a haze point of —10° F. was treated with 35 per cent by weight of urea activated with an equimolar amount of methanol. The yield of contacted oil obtained was about 98 per cent. After drying the oil to remove the methanol dissolved therein, it was tested for haze by chilling to —65° F.. No visible haze was detectable. The pour point was unchanged by the treatment.

After a period of use in dehazing, the urea loses its effectiveness and can then be regenerated by dissolving it in a solvent or melting it and separating the haze substance and hydrocarbon material which has been extracted from the oil. The urea is then recrystallized and used again. If a urea solvent is used in the regeneration step, for example water, methanol, ethanol, acetone, etc., it is usually necessary to evaporate at least a part of the solvent before the urea is ready for re-use, as it is desirable to control the amount of urea solvent present when contacting the hazy oil as indicated hereinabove. Thus, if too large an amount of solvent is present, the effectiveness in removing the haze is greatly reduced.

Having thus described my invention what I claim is:

1. In a process for refining a substantially wax-free petroleum oil of satisfactorily low pour point which develops a visible haze on being cooled to a low temperature, the improvement which comprises intimately contacting said oil with urea for a period of time sufficient to react the organic haze-forming substances in said oil with said urea, and separating the resulting urea reaction product from said oil, whereby a haze-free oil is obtained.

2. The process of claim 1 wherein the urea is employed as a finely divided crystalline solid activated with about one-fourth to one mol of a urea solvent per mol of said urea.

3. The process of claim 2 wherein the solvent employed is water.

4. The process of claim 2 wherein the solvent employed is methanol.

5. The process of claim 1 wherein said contacting is effected by percolating said oil through a filter bed of finely divided crystalline urea.

6. In a process for refining a hydrocarbon oil which is substantially free from wax removable therefrom by solvent-dewaxing but which develops a visible haze on being cooled to a low temperature, the improvement which comprises intimately contacting said oil with urea for a period of time sufficient to react the organic haze-forming substances in said oil with said urea, and separating the resulting urea reaction product from said oil, whereby a haze-free oil is obtained.

7. In a process for refining a substantially wax-free lubricating oil of satisfactorily low pour point which develops an objectionable haze on being cooled to a low temperature, the improvement which comprises reducing the viscosity of said oil by dilution with a solvent of low viscosity, unreactive with urea, intimately contacting said oil with urea at a temperature within the range of about 30 to 150° F. for a period of time sufficient to react the organic haze-forming substances in said oil with said urea, and separating the resulting urea reaction product from said oil, whereby a haze-free lubricating oil is obtained.

8. A process for refining a wax-containing lubricating oil which comprises reducing the viscosity of said oil by dilution with a relatively low-boiling hydrocarbon solvent substantially free from straight-chain hydrocarbons containing more than five carbon atoms in the molecule, chilling the diluted oil to a temperature sufficiently low to crystallize the wax content therein, separating said wax from the oil at said low temperature, contacting the resulting wav-depleted oil with urea in the presence of said hydrocarbon solvent, whereby said urea reacts with the organic haze-forming constituents of said oil, separating said urea and combined organic haze-forming constituents, and recovering a haze-free lubricating oil from said hydrocarbon solvent.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,166,891	Gee	July 18, 1939
2,221,301	Kipper	Nov. 12, 1940
2,411,959	Dietrich et al.	Dec. 3, 1946

OTHER REFERENCES

From Technical Oil Mission, Reel 143, translated by Shell Bureau of Mines, Dept. of Interior, May 22, 1946, (5 pages), depos. Lib. of Congress.

Morrell et al.: "Stability of Pure Hydrocarbons to Light," Indus. and Eng. Chem., vol. 28 (1936), pages 448–452.