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DEWAXING MINERAL HYDROCARBON OILS

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This invention relates to a process for separating from mineral oils various waxy substances occurring therein. More particularly it pertains to a diluent for decreasing the viscosity of the oil and the solubility of the wax, whereby the wax and oil may be readily separated when the oil-solvent mixture is chilled to solidify the wax.

Mineral oils, such as petroleum hydrocarbon products and tars, naturally contain varying amounts of waxy paraffins or petrolatum, for convenience hereinafter designated as waxes, which at normal temperatures are dissolved in the oil or in a liquid state, but which tend to solidify or become very viscous at low temperatures, causing the oil to resist flow or to have a cloudy appearance.

The removal of wax from oil, and more particularly the removal of mineral wax from mineral oil, has heretofore been accomplished by diluting the waxy oil with a suitable diluent or diluent mixture, chilling the solution so formed to precipitate the wax, and separating the precipitated wax by some suitable means, such as filter pressing. The function of the diluent was to reduce the viscosity of the chilled mixture, whereby the separation of the wax was facilitated.

More recently it was proposed to improve the separation by employing diluents or diluent mixtures which exercise a selective solvent action between the solid wax and the oil. For example, it is known to effect the separation of these waxes from hydrocarbon oils by diluting the oil with mixtures of two liquids, one of which is a good solvent for hydrocarbons, and the other a poor solvent for paraffin wax. For example, a mixture of benzol and acetone has been used for dewaxing lubricating oils.

According to the present invention it was found that excellent results are obtained by using a dewaxing mixture containing $\beta\beta'$ dichloroethyl ether ("Chlorex") as the selective solvent, sometimes known as the "poor solvent" and any mutual solvent for Chlorex and for hydrocarbons as the secondary solvent, sometimes known as the "solubility enhancing solvent" or the "good solvent". As secondary solvents we may use, for example, benzene, carbon tetrachloride, toluene, trichloroethylene, and the like or mixtures of these or similar compounds. The aromatic portion of kerosene, known as "kerosene extract", which is obtained by extracting kerosene with selective solvents for aromatics, such as sulfur dioxide, phenol, etc., may also be used as the secondary solvent. We have found that the combinations Chlorex-trichloroethylene and Chlorex-benzene give excellent results, and these combinations constitute the preferred embodiments of our invention.

Sometimes it is advantageous to use mixtures of secondary solvents. For instance in the combination Chlorex-benzene-toluene, the toluene serves to decrease the melting point of the benzene, which is about +6° C.

The process may be operated by dissolving the wax-bearing oil such as paraffinous petroleum residues, paraffinous lubricating oils, lignite tar, shale oils and low temperature tar in the mixture while slightly heating the latter, after which the paraffin wax is caused to separate out in a crystalline state at a lower temperature, such as, for example, 0° C., depending on the desired pour point. We have found that our dewaxing mixture is effective to cause the removal of sufficient wax to cause the pour point of the dewaxed oil to be somewhat below the temperature at which the wax is separated. After the separation of the wax the solvents may be removed from the oil and from the wax by distillation, or by any other method, such as washing with a suitable selective solvent, such as ethyl alcohol, to dissolve the Chlorex and then distilling the oil or wax to recover the benzene and/or other solvent remaining therein.

The dewaxing may be conducted either according to a batch or a continuous method. It is sometimes desirable to precipitate the wax in several stages, whereby a number of waxes of different melting points may be produced. In this operation each precipitation and separation of wax is effected at a lower temperature than the preceding separation. The quantity of the solvent mixture in the oil may be varied at each stage so as to be present in the correct quantity to dissolve substantially all of the oil at the particular temperature of separation, while not causing substantial amounts of wax to be dissolved. Thus, it is often necessary to add more dewaxing solvent mixture at each successive stage, which solvent mixture need not contain the two solvents in the same ratio as in the solvent mixture which was added at an earlier stage.

The quantity of solvent mixture to be employed depends upon the viscosity of the oil and the temperature to which it is to be chilled. We have found that in most cases a quantity of the solvent mixture equal to between 100% and 500% of the oil is suitable, although in certain cases different quantities may be used. For any given

dilution ratio, i. e., ratio of combined solvent mixture to oil, the use of larger amounts of Chlorex causes larger amounts of oil to be precipitated; and the use of larger amounts of the secondary solvent causes more wax to be dissolved in the solvent mixture. The proper ratios of Chlorex to secondary solvents is determined by the consideration that the mixture should have a high solvent power for the liquid hydrocarbons, and a low solvent power for the solid hydrocarbons, at the temperature at which the separation occurs. In general, we have found that mixtures containing between 30% and 80% of Chlorex and between 70% and 20% of the secondary solvent are suitable for dewaxing oils.

The invention may be further understood from the following examples which are not, however, understood to limit the scope of this patent:

Example I.—A distillate derived from a paraffinous Mid-Continent oil, having a pour point between +27° C. and +20° C. was mixed with 300% by volume of a solvent mixture consisting of 50% by volume of Chlorex, and 50% by volume of benzene. The resulting solution was chilled to −20° C. and the liquid removed from the solidified wax by filtration. The solvent was removed from the filtrate, whereby an oil was produced having a pour point of −23° C. and amounting to 70% of the original oil. The melting point of the separated wax was 41° C.

Example II.—A similar oil, having a pour point of about +20° C. was mixed with 300% by volume of a solvent mixture consisting of 40% by volume of trichloro-ethylene and 60% by volume of Chlorex. The resulting mixture was chilled to −20° C. and the liquid removed from the solidified wax by vacuum filtration. The filtrate yielded an oil having a pour point of −21° C. and the yield was 71% of the original oil. The separated wax had a melting point of 42° C.

It will be understood that our invention is not restricted to the use of binary solvent mixtures, inasmuch as we may use mixtures containing other selective solvents together with our dewaxing mixtures, particularly substances having an intermediate solvent power, such as ether. The additional component should, preferably, have some selective solvent properties.

Moreover, it is not necessary to mix all of the components of the solvent mixture before dissolving them in the oil. Thus, the secondary solvent may be added first, either in a pure state or with small amounts of the Chlorex, followed by the addition of the requisite amount of Chlorex or a solution containing large amounts of Chlorex.

We claim as our invention:

1. A process for dewaxing oil by mixing a liquid dewaxing agent having a high solvent power for the oily components of the wax-bearing oil but low solubility for its waxy components, chilling the resulting mixture to precipitate waxy components and separating the precipitated material from the oil containing solution, characterized by the use as the dewaxing agent of a mixture of trichloroethylene and $\beta\beta'$ dichloroethyl ether.

2. A process for dewaxing oil by mixing a liquid dewaxing agent having a high solvent power for the oily components of the wax-bearing oil but low solubility for its waxy components, chilling the resulting mixture to precipitate waxy components and separating the precipitated material from the oil containing solution, characterized by the use as the dewaxing agent of a mixture consisting of between 30% and 80% of $\beta\beta'$ dichloroethyl ether and between 70% and 20% of trichloroethylene.

3. A process of dewaxing oils, which comprises incorporating with the oil $\beta\beta'$ dichloroethyl ether and trichloroethylene, chilling, and separating the wax.

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