

ALIEN PROPERTY CUSTODIAN

RAFFINATION OF MINERAL OILS AND TARS

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The present invention relates to the raffination of mineral oils and tars with selective solvents and has for its object to provide improved methods for this purpose.

It is known that the term selective solvents designates such solvents as more readily dissolve the less saturated components of the oils including the O and S compounds resin and asphaltic substances and the like than the more saturated components. A great variety of solvents of inorganic and organic nature have been found to be suitable, and the phenols, and in particular the lower homologues such as phenol, cresols, and mixtures thereof and also technical mixtures such as crude phenol, crude cresol and creosotes have obtained particular importance as selective solvents.

It is known to extract mineral oils and tars by selective dissolving agents free from water, for instance by phenols free from water, and it is also known to effect the decomposition of mineral oils by phenols to which 5-15% of water or alcohol has been added. Finally it has already been proposed to decompose mineral oils in a first step with phenol to which little water, e. g. 5% has been mixed, into a raffinate and an extract, and to dilute the extract in a second step with water whereby a portion of the extract is precipitated as insoluble. This method has been evolved after it had been found that in the usual treatment with selective solvents a certain amount of valuable components of the oil passes into the extract, and it has been endeavoured by the proposed way to recover the same from the extract. However, this endeavour is not successful or anyhow leads to an incomplete success only, because, when water is added to the extract layer, the paraffinic components which are still present in small quantities, and which are less readily soluble, are not separated in a pure condition, but at the same time unsaturated hydrocarbons and impurities are separated so that in the best case a raffinate of the same condition as the initial oil is obtained, which must be treated again.

According to the invention, the treatment of the mineral oils and tars by selective solvents is carried out in the first step with the addition of an agent which counteracts the dissolving action of the solvent. This method has been found to give better results than the inverse way of first dissolving the main quantity of the oil with the exception of a relatively unimportant residue of highly saturated oil by means of concentrated solvent and subsequently endeavouring gradually

to separate by the addition of water the oils which have passed into the solution. In a preferred form of the present invention the additional agent is a diluting substance for the respective selective solvent. In a modification of the invention, an antisolvent which is more readily soluble in the oil or the tar, respectively, than in the respective selective solvent and which therefore reduces the solubility of the substances under treatment by the selective solvent, is used as the additional agent.

According to the invention, the mineral oils or tars are thus first treated with a selective solvent, while the solubility of the selective solvent is decreased in this step by the addition of an agent performing this effect. The preliminary raffinate is then separated and is subsequently treated in one or more further steps until the desired qualities are obtained. In these further steps the treatment is effected by a selective solvent as in the first step, using, however, less of the additional agent or none at all.

In carrying out the invention according to the first-mentioned of the two main forms, i. e. with the addition of an agent acting as a diluting means for the selective solvent, a diluting agent is employed which is readily soluble in the selective solvent, and less readily soluble or not at all soluble in the oils and tars to be treated. Water, mono- and polybasic alcohols, acetic acid, or the like, may, for instance, be used as diluting agents.

When carrying out the invention in the second modified form, use is made in the first step, in addition to the selective solvent, of an agent which is more readily soluble in the substance under treatment than in the respective selective solvent. In the second step, the treatment with the selective solvent is then carried out without addition, or with an addition of a substantially lower amount only, of an additional agent. The treatment in the first step may, for instance, be effected by a rather concentrated phenol with an addition of gasoline. The treatment in the second step may then be carried out with phenol of the same degree of concentration as in the first step, however without addition of gasoline. Other substances may be used instead of gasoline, provided that the respective substance fulfills the condition of being more readily soluble in the oil under treatment than in the selective solvent. In the first instance, paraffinic hydrocarbons have proved to be suitable for this purpose.

In some cases it is recommendable to employ the selective solvent and the additional agent in the same proportion for a number of successive

treatments, i. e. to repeat the treatment in one step before continuing the process with a reduced amount of the additional agent. Oftentimes, better results are obtained by this method than by at once subjecting the substance under treatment in the respective step to the action of the total amount of selective solvent plus additional agent.

The raffination may be carried out at constant temperature although it is generally of advantage to maintain different temperatures in the individual steps in order to obtain the optimum separation effect. Preferably temperatures increasing from step to step are employed; however, with oils and tars having a high solidifying point one may also in a first step extract the material at a relatively high temperature and afterwards treat the raffinate obtained, in a given case after deparaffination, at a lower temperature, which may if desired subsequently be increased.

It is possible to operate in one or all steps according to the counter-stream system; it is also possible to use in one or all steps only a single treatment in mixers or mixing pumps and subsequent separation of layers in settling tanks or centrifuges.

Naphtenic solvents, such as SO₂, furfural, pyridine, aniline, nitrobenzene, oxybenzaldehyde and phenols may, for instance, be used as selective solvents.

In the individual steps of the process either the same or different kinds of phenol may be used as desired, e. g. diluted phenol C₆H₅OH may be used in the first step and crude cresol or the like in the second; however it will generally be advisable to maintain the same solvent in view of the greater simplicity.

The process according to the present invention leads relative to the treatment with phenol free from water, or with aqueous phenol of an unchanged degree of concentration, to an increase in output and/or an improvement of the qualities (height of pole, density), in particular with asphaltic oils. In certain cases a successful raffination with phenol has for the first time been made possible by the method proposed, as for example, the treatment of oils obtained from oil chalk.

It is of course necessary that the temperature, the quantity of solvent applied, and the number of the steps or stages should be adapted to the initial material used in each particular case. When the conditions are suitably adjusted, it is possible to keep the percentage of solvent in the raffinate so low that it is not necessary to effect blowing-off between the individual steps.

Example I

50 parts of the residue of a naphthenic crude

are treated with a mixture of 40 parts of phenol and 10 parts of glycol. The layers formed by this treatment are then separated, the upper raffinate layer is then freed from the solvent by distillation.

100 parts of this raffinate are then treated with 80 parts of phenol free from water, whereby again layers are formed. The upper layer after separation and evaporation of the solvent gives a good lubricating oil. The temperature in the first step may be 50° C, and in the second step 70° C.

Example II

100 parts of a lubricating oil fraction from Heider oil chalk are in the first step treated first with a mixture of 45 parts of phenol and 5 parts of water. The upper layer formed is then separated and once more subjected to the same treatment.

Then the newly formed raffinate layer is separated, and 100 parts of this layer are in the second step treated with 80 parts of concentrated phenol. Of the two layers formed by this treatment the upper raffinate layer is separated, freed from the solvent by distillation, and is then subjected to an after-treatment with 3% of bleaching earth.

The whole process may be carried out at a temperature of 40° C. The following table shows the qualities of the starting material as compared with those of the raffinate produced.

	Starting material	Raffinate
Density.....	0,970	0,925
Viscosity (degrees Engler at 50° C)	18,3	11,3
Viscosity-index.....	-18	+50
Conradson.....	2,35	0,7

Example III

100 parts of a lubricating oil distillate derived from a German asphaltic basic crude oil from the district of Nienhagen (15° Engler at 50° C) are diluted with 50 parts of gasoline, and the oil-gasoline mixture is then treated with 100 parts of pure cresol at 20° C. The layers are separated, and the raffinate layer is freed from the added gasoline by fractional distillation and is then subjected to an extraction with pure cresol (100% concentrated) at 30° C. The resultant raffinate is freed from the solvent by distillation.

By the process a lubricating oil for engines of good ageing stability has been produced, the viscosity of which is 11° Engler at 50° C.

It is to be understood that the invention is not limited to the working conditions stated in the above examples.

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