United States Patent Office
3,044,949
Patented July 17, 1962

3,044,949

PROCESS FOR LOWERING THE POUR POINT OF HIGH BOILING POINT HYDROCARBON MIXTURES, ESPECIALLY LUBRICATING OILS

Wilhelm Schlenk, Ludwigshafen (Rhine), Germany, assignor to Badische Anilin- & Soda-Fabrik Aktiengesellschaft, Ludwigshafen (Rhine), Germany

No Drawing. Filed Apr. 14, 1959, Ser. No. 806,247
Claims priority, application Germany Apr. 17, 1958
1 Claim. (Cl. 208—25)

This invention relates to a process for lowering the pour point of high boiling point hydrocarbon mixtures, especially lubricating oils, by the separation therefrom of substances which raise the pour point.

It is known that linear hydrocarbons can be separated from organic mixtures containing the same by treating the mixtures with urea. The linear compounds thereby form crystallized addition compounds and are separated from the mixtures in this form. The process is suitable inter alia for the removal of paraffin hydrocarbons from diesel oil or lubricating oil. In the working up of lubricating oil it is preferable, for the dilution of the reaction mixture, to work in the presence of a liquid which dissolves the mixture to be separated, but not urea.

The removal of linear compounds from the oils has the consequence, among others, that the pour point of the oil is lowered. In the case of fractions of the boiling range of the diesel oils, for example, the pour point can be lowered without difficulty by the said measures to values of −25° C. and less. The process has therefore been adopted by industry for the removal of paraffin hydrocarbons from diesel fuels. It has been found, however, that in the case of certain high boiling point hydrocarbon mixtures, for example, in the case of many lubricating oils, the pour points obtainable by the known methods do not fulfill practical requirements. Thus, in the case of a paraffin-base machine oil, which has a viscosity of about 10° E. at 50° C., it is only possible by treatment with urea to lower the pour point to values of about 0° C. (between about +3° C. and −60° C., depending on the origin) even when working with an excess of urea or repeating the urea treatment several times.

It was therefore dsirable to find a simple but nevertheless effective method by which the pour point could be lowered to the necessary extent even in cases of the said kind.

I have now found that the pour point of a high boiling point hydrocarbon mixture, especially a lubricating oil, which cannot be lowered or can only be lowered with difficulty to the desired extent by treatment with urea, can be lowered considerably by adding to the mixture urea and one or more substances which readily form addition compounds with urea. The compounds contained in the initial materials and which raise the pour point form urea adducts at different speeds. By additional substances which "readily" form addition compounds with urea I mean those of which the adduct-forming speed is greater than the mean adduct-forming speed of the compounds to be removed. It is easy to decide by a preliminary test whether a substance fulfils this requirement.

The additives may belong to a great variety of chemical classes. Hydrocarbons having a carbon number of at least 12, advantageously 12 to 20, and alcohols with carbon numbers of at least 10, preferably between 10 and 20, are suitable. Suitable esters are those derived from mono or di-carboxylic acids and from mono- or dihydric alcohols. Their carbon number should be more than 8, preferably between 10 and 20. The components from which the esters are built up may contribute to a very different extent to the total carbon number. Thus it is possible for the acid radical to be large and the alcohol radical small, for the acid radical to be small and the alcohol radical large, or for both to be of about the same size. Ketones used for the process may be symmetrical or unsymmetrical and their carbon number advantageously amounts to at least 9, preferably 9 to 20. Symmetrical or unsymmetrical ethers with carbon numbers of at least 8, preferably between 12 and 20, are also suitable as additives. In general, the additives preferably should contain between 8 and 45 carbon atoms and should as far as possible be linear or in any case only slightly branched or should consist mainly of such compounds. The following additives may be enumerated by way of example and not by way of limitation: hydrocarbon mixtures rich in unbranched paraffin hydrocarbons with carbon numbers between about 14 and 17 such as are obtained from many petroleums or also synthetically; soft paraffin wax with mainly linear constituents with carbon numbers between about 18 and 26 and melting points between about 28 and 40° C. (obtainable for example by the Fischer-Tropsch process); hard paraffin wax with mainly unbranched constituents with carbon numbers between about 24 and 45 and with melting points between about 50 and 90° C.; and also chemically unitary compounds such as normal-dodecane, normal-pentadecane, cetane, eicosane, dodecanol-(1), tetradecanol-(1), cetyl alcohol, eicosanol-(1), pentadecanol-(8), myricyl alcohol, ethyl caproate, methyl caprylate, methyl caprate, ethyl laurate, normal-amyl caprylate, methyl myristate, ethyl palmitate, ethyl oleate, methyl stearate, normal-amyl caproate, normal-octyl caproate, normal-nonyl myristate, cetyl stearate, myricyl pelargonate, di-normal-amyl glutarate, diethyl adipate, dibutyl adipate, dibutyl suberate, dipropyl sebacate, dicetyl suberate, dihexyl suberate, diamyl sebacate, nonanone-(5), undecanone-(2), undecanone-(6), pentadecanone-(8), nonadecanone-(10), di-normal-amyl ether, di-normal-heptyl ether, di-normal-decyl ether, dicetyl ether, amyl heptyl ether and methyl dodecyl ether.

The process may be carried out by first subjecting the mixture to a conventional urea treatment, then adding to the resultant raffinate one of the said additives and treating the mixture with urea. The treatment as a rule consists of a thorough mixing of the components. This operation may, if desired, be repeated one or more times. In some cases it is advantageous to separate a part of the high pour point constituents of the initial mixture before the treatment with urea and additives, by mechanical means, for example by filtration or pressing out, if desired with the addition of solvents. However, the initial mixture, even when it has a relatively high pour point, for example +47° C., may have the additives added directly thereto and then be treated with urea.

The amount of urea to be used in all in one or more stages depends on the amount of adduct-forming substances to be removed from the mixture, i.e. the adduct-forming substances originally present and those added. As a general rule about 4 parts by weight of urea are necessary for the separation of 1 part by weight of adduct-forming substance. It is preferable to use a certain excess of urea, for example up to 6 parts by weight per part by weight of adduct-forming substance, in order that the reaction may proceed sufficiently rapidly and completely.

The amount of adduct-forming substance to be added as the additive may amount to about 10 to 60% by weight with reference to the oil to be freed from paraffin hydrocarbons, depending on the nature of the oil and the pour point and cloud point which are to be achieved. The amount can easily be ascertained in each case by preliminary tests.

The amount of liquid necessary for dilution depends above all on the amount of urea which is to be used in the reaction or in the reaction stage in question. In general, it is suitable to keep the density of the substance, i.e. the ratio of solid phase (in grams) to liquid phase (in ccs.), at a value of 1:4 or less. As diluents there may be used especially lower chlorohydrocarbons with up to about 3 carbon atoms, such as methylene chloride, ethylene chloride, chloroform, carbon tetrachloride, trichlorethylene, trichlorethane and tetrachlorethane, and also low molecular weight carboxylic acid esters with up to about 5 carbon atoms, such as methyl acetate, ethyl acetate, ethyl propionate and methyl butyrate, and low molecular weight ketones with up to about 6 carbon atoms, such as acetone, butanone, diethyl ketone and methyl-isobutyl ketone. Oils which have been partly or wholly freed from paraffin hydrocarbons and which originate from the process itself may also serve as diluents. The process may be carried out with or without the addition of solvents for urea, such as methanol or ethanol.

The adducts may be split up in known manner by treatment with liquids which dissolve the urea (for example with water or methanol) or with liquids which dissolve the enclosed organic compounds. The urea is used again for the deparaffination. The raffinate is freed in known manner from the solvent by distillation and the latter can be used again.

The raffinates obtained by the said process exhibit considerably lower pour points and cloud points than oils which have been obtained by urea-deparaffination without the use of additives. The process is suitable above all for the deparaffination of lubricating oils, such as spindle oils, turbine oils, oils for automobile and aircraft engines, diesel motor oils, gear oils and cylinder oils, but may if necessary be used for diesel oils or other relatively high boiling oils, for example oils boiling above about 200° C.

The following examples will further illustrate this invention but the invention is not restricted to these examples. The parts specified in the examples are parts by weight.

Example 1

133 parts of lubricating oil (machine oil raffinate 10° to 11° E./50° C., pour point +47° C.), 625 parts of ethylene chloride, 200 parts of urea, 20 parts of a solution of urea in methanol which is saturated at room temperature and 40 parts of methyl myristate are ground in a ball mill for 6 hours. The reaction mixture is filtered. The resultant filter cake (266 parts) yields, when split up, a mixture of 40 parts of myristic acid ester and 26 parts of hydrocarbon which can be split up into its constituents by distillation. The filtrate obtained by the filtration of the reaction mixture leaves behind, when the ethylene chloride has been distilled off, 107 parts of deparaffinated oil. This has a pour point of −14° C. and does not cloud upon solidification. After adding 1% of the pour point depressant known under the registered trademark Fluxan N, the pour point is −16° C. and the cloud point is −16° C.

If 133 parts of the same lubricating oil are treated in the same way but without the myristic acid ester, 115 parts of deparaffinated oil are obtained which has a pour point and a cloud point of −3° C.

Example 2

100 parts of the preliminarily deparaffinated oil (pour point −3° C.) obtained according to paragraph 2 of Example 1 are mixed with 500 parts of ethylene chloride and 10 parts of a solution of urea in methanol which is saturated at room temperature and while in a Retsch mill 28 parts of cetane and 200 parts of urea are gradually added in the course of 2 hours. After a grinding period of 2½ hours in all, the reaction mixture is worked up as in Example 1. From the filtrate there are obtained 97 parts of an oil with the pour point −16° C. After adding 2.5% of Fluxan N, the product has a pour point and cloud point of −20° C.

Example 3

133 parts of lubricating oil (pour point +47° C.) such as is used in Example 1, 500 parts of ethylene chloride, 150 parts of urea, 20 parts of a solution of urea in methanol which is saturated at room temperature and 40 parts of soft paraffin wax are ground for 6 hours in a ball mill. By working up according to Example 1, 108 parts of deparaffinated oil are obtained of which the pour point is −11° C. Addition of 1% of Fluxan N depresses the setting point to −16° C. The cloud point is −14° C.

Example 4

133 parts of lubricating oil (machine oil raffinate, 10° to 11° E./50° C., pour point +47° C.), 800 parts of symmetrical tetrachlorethane, 200 parts of urea, 20 parts of a solution of urea in methanol which is saturated at room temperature and 40 parts of normal-pentadecane are ground for 2 hours in a Retsch mill. The reaction mixture is filtered. The filtrate, when the tetrachlorethane has been distilled off, leaves behind 109 parts of deparaffinated oil which has a pour point of −14° C. and a cloud point of −12° C. The filter cake (264 parts) is washed with tetrachlorethane and heated with 2000 parts of tetrachlorethane for 15 minutes at 90° C. The reaction mixture is filtered while hot. As a filter cake there remain 200 parts of urea, which can be used again. The filtrate leaves behind by evaporation 64 parts of a hydrocarbon mixture from which by distillation there are separated as the low boiling point fraction 40 parts of normal-pentadecane which can also be used again as an additive.

Example 5

133 parts of lubricating oil (machine oil raffinate, d_4^{20} 0.916; 7.7° E./50° C.; pour point +35° C.), 700 parts of trichlorethylene, 200 parts of urea and 10 parts of methanol are ground for 6 hours in a ball mill. During this period, a total of 40 parts of hard paraffin wax (melting point 50° to 52° C., average chain length of the paraffin C_{26}) is added a little at a time to the mixture. The reaction mixture is then filtered. The filtrate leaves behind, after the trichlorethylene has been distilled off, 110 parts of deparaffinated oil with a pour point of −13° C. (no previous clouding). From the filter cake, by heating with trichlorethylene as in Example 4, 200 parts of urea are recovered.

Example 6

133 parts of lubricating oil (machine oil raffinate, 10° to 11° E./50° C.; pour point +47° C.), 450 parts of ethyl acetate, 200 parts of urea, 40 parts of normal dodecyl alcohol and 20 parts of a solution of urea in methanol which is saturated at room temperature are ground in a ball mill for 6 hours. The mixture is centrifuged, the solution freed from ethyl acetate by distillation and again filtered. There remain behind 109 parts of deparaffinated oil having a pour point of −17° C.

Example 7

133 parts of lubricating oil raffinate (d_4^{20}=0.93; 10° E./50° C.; pour point +52° C.), 600 parts of ethylene chloride, 200 parts of urea, 40 parts of normal-tetradecyl alcohol and 25 parts of a solution of urea in methanol which is saturated at room temperature are mixed in a turbomixer for 15 minutes. The reaction mixture is filtered. When the ethylene chloride is distilled off from the filtrate there remain 109 parts of deparaffinated oil of the pour point −14° C.

Example 8

133 parts of lubricating oil raffinate (d_4^{20}=0.92; 10° to 11° E./50° C.; pour point +47° C.), 625 parts of ethylene chloride, 200 parts of urea, 40 parts of di-normal-heptyl ether and 20 parts of methanol are ground for 6 hours in a ball mill. The reaction mixture is filtered.

The filter cake (268 parts) yields upon separation a mixture of 40 parts of di-normal-heptyl ether and 28 parts of hydrocarbon which by distillation is separated into its constituents. The filtrate leaves behind, when the ethylene chloride is distilled off, 105 parts of deparaffinated oil with a pour point of −17° C. The recovered urea and the di-normal-heptal ether can be used again for deparaffination.

Example 9

133 parts of lubricating oil raffinate ($d_4^{20}=0.92$; 11° E./50° C.; pour point +47° C.), 625 parts of ethylene chloride, 200 parts of urea, 40 parts of nonanone-(5) and 20 parts of methanol are ground in a ball mill for 6 hours. The reaction mixture is filtered. The filter cake (265 parts) yields, when separated, a mixture of 40 parts of nonanone-(5) and 25 parts of hydrocarbon which is separated into its constituents by distillation. The filtrate, when the ethylene chloride is distilled off, leaves behind 108 parts of deparaffinated oil which has the pour point −12° C.

Example 10

133 parts of lubricating oil raffinate ($d_4^{20}=0.92$; 10° to 11° E./50° C.; pour point +47° C.), 450 parts of methyl acetate, 200 parts of urea, 40 parts of undecanone-(2) and 20 parts of a solution of urea in methanol which is saturated at room temperature are grounded for 6 hours in a ball mill. The reaction mixture is filtered. The filter cake obtained (265 parts) yields, when separated, a mixture of 40 parts of undecanone-(2) and 25 parts of hydrocarbon which is separated into its constituents by distillation. The filtrate, after the methyl acetate has been distilled off, leaves behind 108 parts of deparaffinated oil with a pour point of −12° C.

Example 11

133 parts of lubricating oil raffinate ($d_4^{20}=0.92$; 11° E./50° C.; pour point +47° C.), 625 parts of ethylene chloride, 200 parts of urea, 40 parts of undecanone-(6) and 25 parts of a solution of urea in methanol which is saturated at room temperature are ground for 6 hours in a ball mill. The reaction mixture is filtered. The filter cake (269 parts) yields, when separated, a mixture of 40 parts of undecanone-(6) and 29 parts of hydrocarbon which is separated into its constituents by distillation. The filtrate leaves behind, when the ethylene chloride has been distilled off, 104 parts of deparaffinated oil which has a pour point of −16° C.

Example 12

133 parts of lubricating oil raffinate ($d_4^{20}=0.92$; 10° to 11° E./50° C.; pour point +47° C.), 625 parts of ethylene chloride in which 40 parts of pentadecanone-(8) have previously been dissolved, 200 parts of urea and 25 parts of a solution of urea in methanol which is saturated at room temperature are ground for 6 hours in a ball mill. The reaction mixture is filtered. The filter cake (265 parts) yields, when separated, a mixture of 40 parts of pentadecanone-(8) and 25 parts of hydrocarbon. The filtrate, after distilling off the ethylene chloride, leaves behind 108 parts of deparaffinated oil having a pour point of −10° C.

Example 13

133 parts of lubricating oil raffinate ($d_4^{20}=0.92$; 10° to 11° E./50° C.; pour point +47° C.), 625 parts of ethylene chloride, 200 parts of urea, 40 parts of methyl caprate and 25 parts of a solution of urea in methanol which is saturated at room temperature are ground for 6 hours in a ball mill. The filter cake (264 parts) obtained after filtration is worked up as in the foregoing examples. The filtrate, after distilling off the ethylene chloride, leaves behind 109 parts of deparaffinated oil having a pour point of −18° C.

Example 14

133 parts of lubricating oil raffinate ($d_4^{20}=0.92$; 10° to 11° E./50° C.; pour point +47° C.), 625 parts of ethylene chloride, 200 parts of urea, 40 parts of di-normal-amyl glutarate and 20 parts of methanol are ground in a ball mill for 6 hours. The mixture is filtered and the filter cake treated in the usual way. The filtrate, after distilling off the ethylene chloride, leaves behind 113 parts of deparaffinated oil having the pour point −10° C.

Example 15

133 parts of lubricating oil raffinate ($d_4^{20}=0.92$; 10° to 11° E./50° C.; pour point +47° C.), 625 parts of ethylene chloride, 200 parts of urea, 40 parts of normal-amyl caproate, and 20 parts of methanol are ground in a ball mill for 6 hours. The mixture is filtered and the filter cake (262 parts) worked up as usual. The filtrate leaves behind, when the ethylene chloride has been distilled off, 113 parts of deparaffinated oil of which the pour point is −11° C.

Example 16

133 parts of lubricating oil (machine oil raffinate; $d_4^{20}=0.916$; 7.7° E./50° C.; pour point +35° C.), 650 parts of methylene chloride, 200 parts of urea, 40 parts of normal-nonyl acetate and 20 parts of methanol are ground for 6 hours in a ball mill. The mixture is filtered and the filter cake (264 parts) separated into its components in the usual way. The filtrate, after distilling off the methylene chloride, leaves behind 109 parts of deparaffinated oil of which the pour point is −15° C.

Example 17

133 parts of lubricating oil raffinate ($d_4^{20}=0.92$; 10° to 11° E./50° C.; pour point +47° C.), 600 parts of methyl isobutyl ketone, 200 parts of urea, 40 parts of normal-hexadecane and 10 parts of methanol are ground for 6 hours in a ball mill. The mixture is filtered and the filter cake (264 parts) worked up in the usual way. The filtrate leaves behind, when the methyl isobutyl ketone has been distilled off, 109 parts of deparaffinated oil of which the pour point is −11° C.

What I claim is:

A process for lowering the pour point of lubricating oils, diesel oils, and oils boiling above about 200° C. which comprises contacting said oils with urea in the presence of from about 10% to about 60% by weight based on the weight of the oil of an added substance having an adduct-forming speed greater than the mean adduct-forming speed of the paraffin hydrocarbons in said oil, said substance being selected from the group consisting of substantially linear aliphatic hydrocarbons having from 12 to 45 carbon atoms, soft paraffin waxes with substantially linear constituents having from about 18 to 26 carbon atoms and having melting points between about 28° C. and 40° C., hard paraffin waxes with substantially linear constituents having from about 24 to 45 carbon atoms and having melting points between about 50° C. and 90° C., linear alcohols having from 10 to 20 carbon atoms, linear carboxylic acid esters having from 10 to 20 carbon atoms, linear carboxylic acid esters derived from monocarboxylic acids and dihydric alcohols, said esters having from 10 to 20 carbon atoms, linear carboxylic acid esters derived from dicarboxylic acids and monohydric alcohols, such esters having 10 to 20 carbon atoms, linear ketones with 9 to 20 carbon atoms, linear ethers with 12 to 20 carbon atoms, and thereafter separating the urea paraffin addition compounds from said lubricating oil.

References Cited in the file of this patent

UNITED STATES PATENTS

2,658,887	Arnold et al.	Nov. 10, 1953
2,666,020	Arnold et al.	Jan. 12, 1954
2,890,161	Brown et al.	June 9, 1959

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,044,949 July 17, 1962

Wilhelm Schlenk

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 5, line 27, for "grounded" read -- ground --; column 6, line 35, for "11° L./50° C." read -- 11° E./50° C. --.

Signed and sealed this 20th day of November 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents