Sept. 27, 1955 A. CHAMPAGNAT 2,719,106

EXTRACTIVE CRYSTALLIZATION PROCESSES BY MEANS OF UREA

Filed March 26, 1952 3 Sheets-Sheet 1

FIG. 1

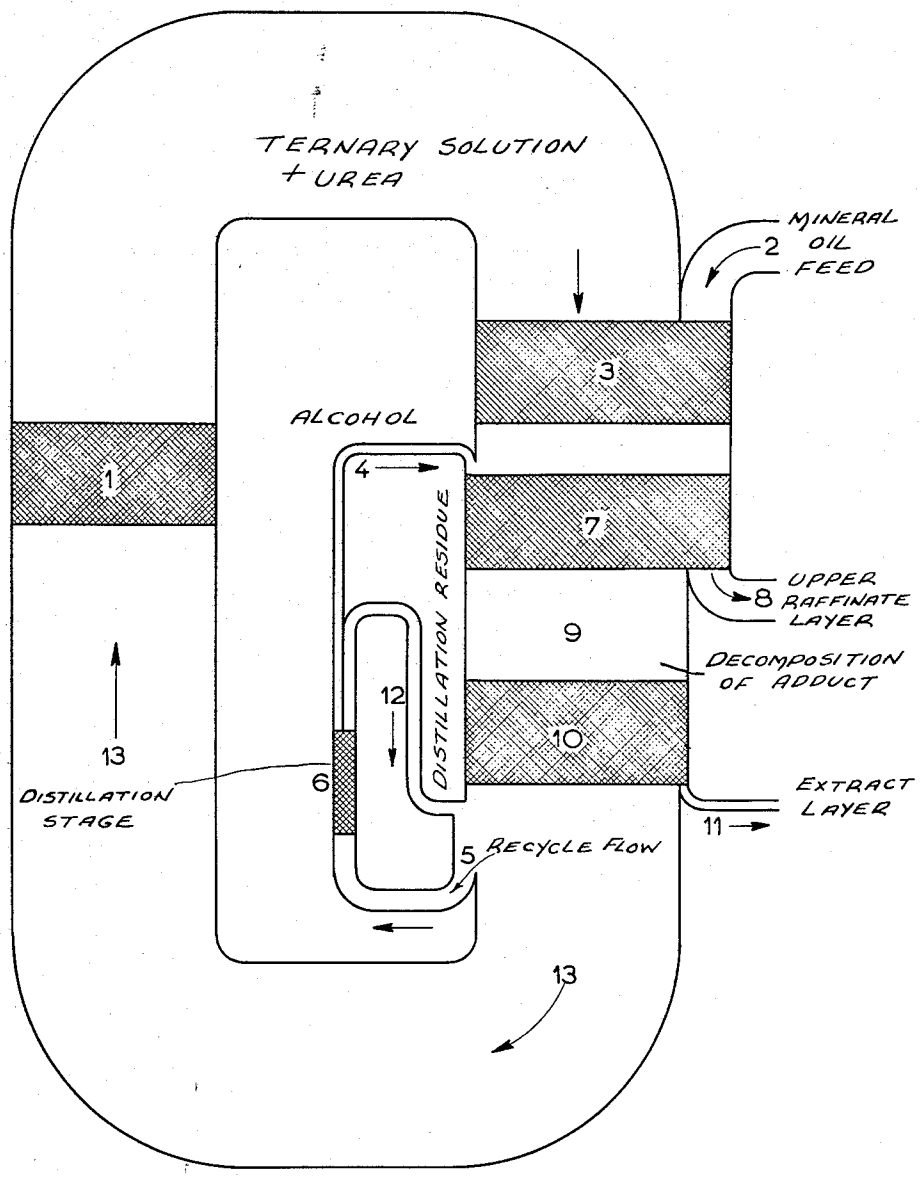

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FIG. 2

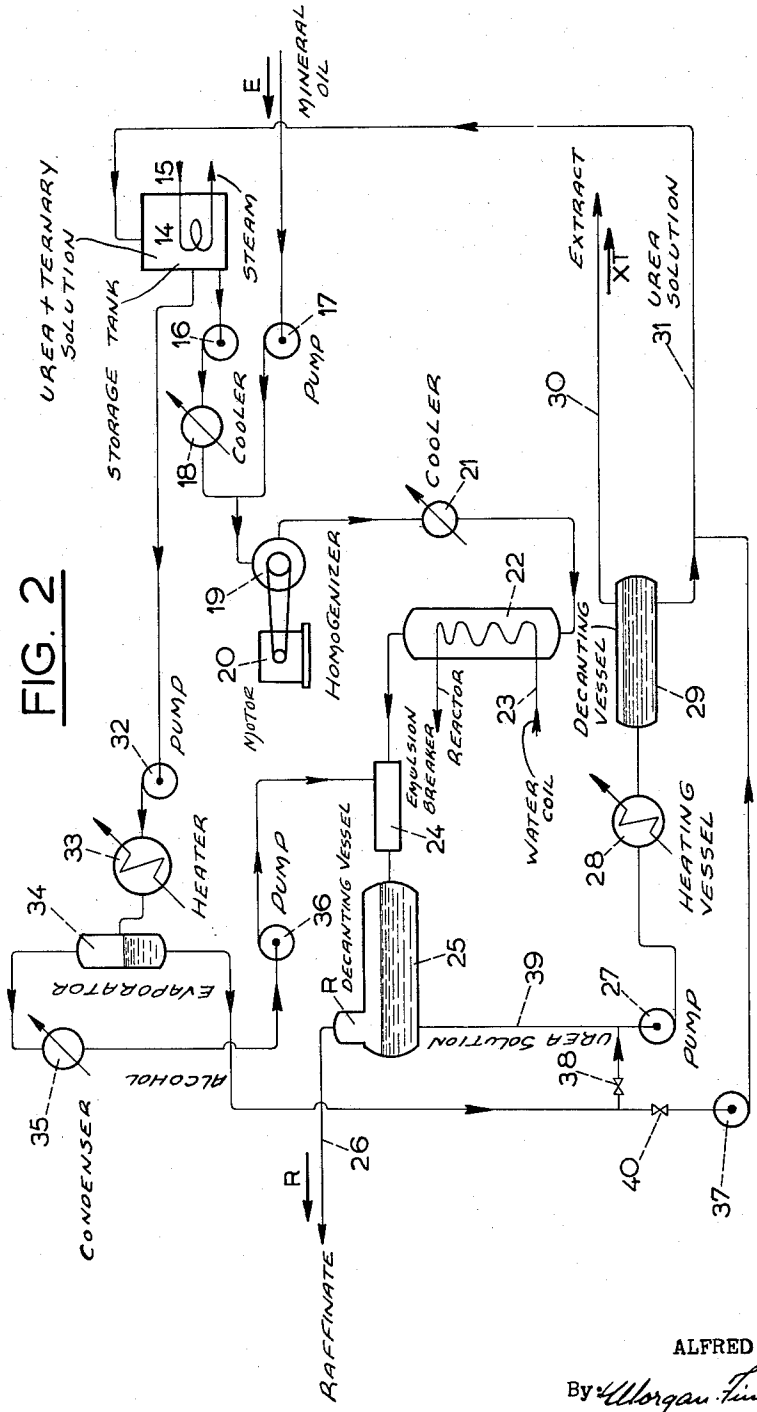

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FIG. 3

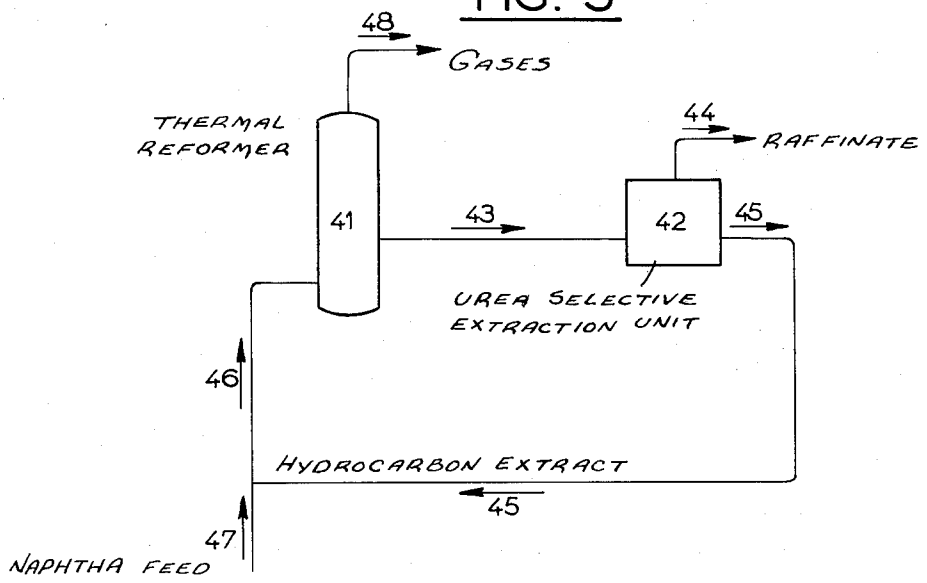
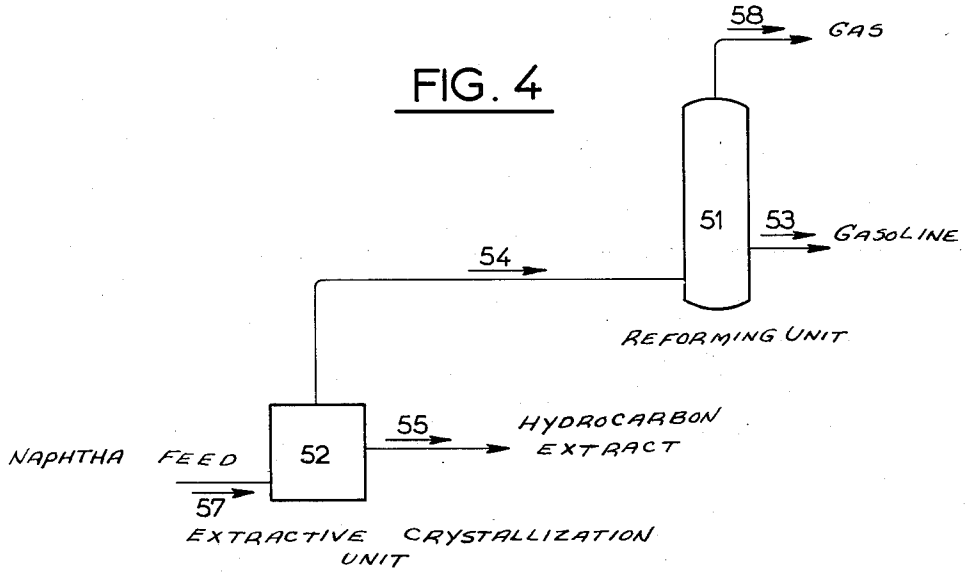


FIG. 4



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EXTRACTIVE CRYSTALLIZATION PROCESSES BY MEANS OF UREA

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Application March 26, 1952, Serial No. 278,627

Claims priority, application France April 4, 1951

11 Claims. (Cl. 196—14.12)

This invention relates to an improved process for the refining of mineral oils. More particularly, the invention relates to a process for the extractive fractionation of petroleum oils, by means of urea.

It is well-known that urea forms crystalline solid adducts with straight chain and slightly branched chain hydrocarbons but does not form solid compounds with naphthenes, highly branched compounds or aromatics. By the use of urea a method has been developed for refining petroleum fractions by resolution of the fractions into chemical types by forming the above solid compounds, removing the remaining liquid phase (known as the "urea adduction raffinate"), decomposing the solid compounds and recovering from the product the liberated hydrocarbons (known as the "urea adduction extract").

It is also known that the presence of methanol or other lower alcohols in admixture with urea and petroleum fractions undergoing treatment accelerates the rate of formation of the solid derivatives. It has also been stated in the prior art that mixtures of methanol and water may be employed as the activating agent.

In general the methods previously described have been based on the formation of the adducts by the use of urea in solid form. Such methods usually have the disadvantage that the adduct is obtained in the form of an agglomerated mass from which the raffinate can only be freed by expensive filtration operations with considerable washing of the filtered adduct.

It is an object of the present invention to provide a process for the extractive fractionation of mineral oils, particularly petroleum oils and, more particularly of petroleum oil distillate fractions, by the method of urea adduction wherein the urea adduction raffinate is separable from the solid phase in a more efficient manner than has been possible by the prior art methods hereinbefore described.

It has now been found that, by the application of urea to the urea adduction process as a solution in the solvent material hereinafter described, the urea adduct may be formed, under the conditions of an emulsion, more rapidly than hitherto and with the formation of a solid phase in a form which is more readily separable from the liquid phase than has been the case hitherto.

According to the present invention, the above object is accomplished by a process which comprises treating a mineral oil with a solution of urea in a ternary solvent comprising, in admixture, water, a water-soluble monohydric alcohol or water-soluble ketone, and an organic compound having in the molecule at least one alcohol group and, in addition, one amine group or at least one other alcohol group, to form an emulsion of the oil-in-water type, thereafter maintaining said emulsion under conditions such that a solid urea adduct is formed with components of the mineral oil and thereafter separating the solid urea adduct from the liquid phase.

The solvent according to the invention essentially contains three components as aforementioned, but it is not a matter of consequence if the "ternary" solvent contains minor amounts of other materials as, in fact, would be inevitable when using commercial grade constituents. Clearly also it is not of consequence that there is used, instead of a monohydric alcohol or ketone, a mixture of compounds of these chemical types, since such a mixture would be serving the same function as either constituent alone without departing from the scope of the invention.

By the process of the invention the urea adduct is formed as a suspension in a liquid phase comprising a solution of urea in the ternary solvent, the raffinate being present as an emulsion in the urea solution.

Preferably the density of the solution of urea in the ternary solvent is adjusted to be greater than that of the hydrocarbons and less than that of the adducts. On subjecting the urea adduction product to conditions for breaking the emulsion, said product is then converted to a two layer system consisting of an upper raffinate layer and a lower layer comprising a suspension of the solid urea adduct in the urea solution.

The preferred method of breaking the emulsion comprises adding thereto an aqueous solution of a water soluble monohydric alcohol or ketone. Preferably the aqueous solution so added comprises the alcohol or ketone employed in forming the urea solution. Suitably the emulsion is broken by the addition of aqueous alcohol or of aqueous ketone, preferably containing 75–90% of said alcohol or ketone based on the weight of aqueous alcohol or aqueous ketone. Preferably the aqueous alcohol or aqueous ketone constitutes 2–50% of the weight of the urea solution employed for adduct formation. In the recovery of the urea adduct from the two layer system, the layers of said system are separated and the lower layer subsequently heated to decompose the urea adduct, whereby a two phase system is formed, thereafter separating a phase, consisting essentially of the adduction extract, from a phase consisting of a solution of urea.

When operating under the preferred conditions of emulsion breaking hereinbefore described whereby the emulsion is broken by addition of an aqueous solution of the alcohol or ketone employed in the ternary solvent, the solution of urea recovered after urea adduction comprises the same components as that employed for the urea adduction, the components being present, however, in different proportions. According to a preferred embodiment of the invention, for recycle operation, part of the recovered urea solution is distilled to take overhead a fraction comprising an aqueous alcohol or ketone, which is employed again as emulsion breaking agent, and to recover as bottoms a urea solution which is added to the remainder of the recovered urea solution. Alternatively, if desired, the distillation bottoms may be returned to the system after separation of the adduction raffinate but prior to the adduct deposition stage. With allowance for process losses, the urea solution so obtained is of the composition of the urea solution employed for adduct formation and is thus suitable, after addition of make-up materials, for recycle to the urea adduct forming stage.

The ternary solvent should comprise 10–90% by weight of the aqueous monohydric alcohol or ketone, and preferably contains 50–80% by weight of the aqueous monohydric alcohol or ketone, the balance being made up of the third component. If desired, of course, a mixture of monohydric alcohols and/or ketones may be employed in the ternary solvent. It is preferred that 2–30% of water be employed, based on the combined weight of water, monohydric alcohol and ketone in the ternary solvent. Suitable alcohols include methanol, n-propanol, isopropanol and 2-methyl propanol. Suitable ketones

include acetone and methyl ethyl ketone. The preferred material is methanol.

The third component of the ternary solvent is preferably a dihydric glycol, a trihydric glycol or an ethanolamine. Suitable materials are ethylene glycol, glycerol, diethylene glycol, propylene glycols, butylene glycols, monoethanol amine, diethanolamine and triethanolamine. The preferred material is ethylene glycol.

A particularly preferred ternary solvent for use in the process of the invention has the composition:

60 parts by weight of methanol
15 parts by weight of water
25 parts by weight of ethylene glycol

It has been established that starting with a saturated solution of urea in a ternary solvent according to the invention and rapidly cooling this solution by about 15° C. with vigorous agitation, a super-saturated solution is formed from which are obtained urea crystals which could be termed "nascent" and which are of very small dimensions.

It has also been established that the presence of these "nascent" crystals of urea facilitates the formation of an oil-in-water type emulsion in the presence of hydrocarbons and makes it possible to obtain a very finely dispersed emulsion and hence a rapid reaction.

Thus according to a particularly preferred manner of operating according to the process of the invention, the urea adducts are formed while the urea solution is in a super-saturated state. In practice this may be achieved by cooling a saturated solution of urea in a ternary solvent so as to obtain nascent urea crystals, then bringing into contact these two phases and forming an emulsion, preferably in a colloid mill, from the supersaturated solution of urea and the hydrocarbon fraction. It is also possible to bring into contact the hydrocarbon fraction and the saturated urea solution and then to cause the nascent crystallization of urea by cooling. This may be effected in practice by delivering the urea solution to the contacting zone at a temperature above that of the mineral oil, while containing an excess of urea over that necessary to saturate the solution at the temperature of adduct formation. This method allows the crystals to react from the time of their formation with the hydrocarbon fraction. Accordingly, there is attained an improved heat economy. Since the cooling of the urea solution is effected by the fresh charge of cool hydrocarbons, said hydrocarbons become heated when in contact with said urea.

The use of the ternary solvent according to the invention achieves the following advantages:

The saturated solutions of urea in these solvents are not miscible with the hydrocarbons and promote the formation of an oil-in-water type emulsion as well as the formation of the adduct. According to the invention, adduct crystals are obtained which are very fine and remain in suspension for long periods, without agglomerating, thus facilitating the separation of the unreacted hydrocarbons. There is the further advantage that fine crystals which do not agglomerate have less tendency to absorb the raffinate.

Further, as hereinbefore described, the density of the solution of urea in the ternary solvent is readily adjusted to be greater than that of the hydrocarbons and less than that of the adducts which can consequently pass into the urea solution phase upon the decantation of the raffinate.

A third advantage of the urea solutions is that their wetting power with respect to the adduct crystals is higher than that of the hydrocarbons with respect to these crystals. It is for that reason that the adduct crystals do not remain in suspension in the decanted raffinate and do not absorb it to any appreciable extent.

The process of the present invention, using the urea solutions hereinbefore described, may thus be operated without the use of cumbersome technical processes such as filtration, drying, or distillation of large quantities of products, and may rely to the fullest extent on the use of decantation as the actual means of separation.

The process of the present invention is particularly suitable for the separation of hydrocarbons contained in petroleum products, such as gasoline, kerosine, or gas oil, into a raffinate practically free from normal aliphatic hydrocarbons and an extract essentially consisting of normal aliphatic hydrocarbons.

The process of the invention is illustrated but in no way limited with reference to the accompanying drawings, wherein:

Figure 1 is a diagrammatic representative of the essential stages of the process, and

Figure 2 is a flow diagram of an apparatus suitable for use in the continuous treatment of petroleum distillation fractions, for example a petroleum naphtha.

With reference to Figure 1:

A saturated urea solution in the ternary solvent is cooled at stage **1** and passed with the mineral oil feed, introduced by line **2**, to stage **3** where an emulsion containing the urea adduct is formed. Aqueous methanol introduced by line **4** is mixed with the product to form a two layer system in stage **7**. The upper raffinate layer is removed by line **8**, the lower layer being heated in stage **9** to decompose the adduct. In stage **10** a two layer system is formed, the extract layer being removed by line **11**. To the unsaturated urea solution removed from stage **10** is added, by line **12**, a distillation residue, having a high urea content, whereby a saturated urea solution is reformed. The necessary distillation feed for providing the aqueous methanol used in stage **7** is withdrawn from the main recycle flow or urea solution by line **5** and passed to the distillation stage **6** from which overhead aqueous methanol is withdrawn by line **4** and bottoms by line **12**. The remaining saturated urea solution is recycled to stage **1**.

Apparatus and conditions for effecting the process of the invention on a commercial scale are illustrated with reference to Figure 2:

A urea solution, in the ternary solvent, at near saturation point is maintained at slightly elevated temperature, for example 40° C. in intermediate storage tank **14** by means of steam coils **15**. A pump **16** draws the urea solution and delivers it to a cooler **18** wherein said solution is cooled to a temperature comprised between 20 and 30° C.

Mineral oil, preferably dried in a drier not represented on the diagram, is drawn by pump **17** into homogenizer **19**. This also receives the cooled urea solution coming from cooler **18**. The streams of urea solution and of mineral oil are sent in a constant ratio into the homogenizer **19** which is served by motor **20**.

In homogenizer **19** a finely dispersed emulsion is formed due to the presence of crystals of nascent urea. The emulsion is cooled (for example to 15° C.) in a cooler **21**. The reaction between the emulsified products takes place in reactor **22**, cooled by a water coil **23** which serves to keep the temperature constant. (The temperature would otherwise tend to rise due to the exothermic reaction by which the adduct is formed.) The emulsion is broken in vessel **24** by the addition of the required quantity of aqueous methanol supplied by pump **36** (this aqueous methanol is obtained by distilling part of the urea solution contained in **14** as will be set forth in the course of the description).

In decanting vessel **25** the separation of the two layers resulting from breaking the emulsion in vessel **24** takes place. Raffinate which forms the top layer is removed by pipe **26** and transferred to a storage vessel.

The urea solution which holds the crystals of the adduct in suspension forms the lower layer in decanting vessel **25**. It is removed by means of pump **27**. The urea solution is then heated to 40° C. in the steam heated vessel **28**. As a result the adduct is decomposed into its constituents, which separate into two layers in the de-

canting vessel 29. The upper layer comprises extract and is conveyed to a storage vessel by pipe 30 while the lower layer comprising a urea solution at 40° C. is sent to the intermediate storage vessel 14 by pipe 31.

The auxiliary circuit, for distilling a fraction of the initial urea solution held in the tank 14, comprises a pump 32 conveying this urea solution into heater 33 which is preferably at a temperature of about 115° C. The separation of the aqueous methanol vapors takes place in evaporator 34 which may be without a reflux condenser. The aqueous methanol vapors condense in condenser 35. The liquid aqueous methanol is sent by pump 36 into the mixer 24 where it is used to break the emulsion. The warm residue from distillation vessel 34 is conveyed by pump 37 into pipe 31 in which it serves to reconstitute in amount and composition the initial urea solution prior to its being returned to reservoir 14. In a variation of this process the hot residue from 34 can be delivered wholly or partially by valve 38 (valve 40 being wholly or partially closed) into pipe 39 in order to reheat the urea solution containing the suspended adduct. The residue is employed to heat the urea solution prior to its being passed on to heater 28.

It is advantageous to heat with steam all the pipes and all the equipment in which the urea solution circulates in order to avoid blockages when the operation of the plant is stopped.

The industrial plant which has been described with reference to Figure 2 is very suitable for the treatment of reforming distillates according to the manner of operation described in Example 1 hereinafter. In this example it is shown that the octane number may be raised by four units by refining with urea according to the invention. This increase in octane number is due to the fact that in the reforming of naphtha, the normal aliphatic hydrocarbons are left unchanged or are produced and it is the removal of these hydrocarbons by urea solution according to the invention which makes it possible to raise the octane number.

The normal aliphatic hydrocarbons which have been separated as extract according to the invention are available for cracking and it is well known from the cracking of hydrocarbons that they are an excellent starting material giving, by cracking, gases with a high content of unsaturated hydrocarbons. These are in increasing demand for the manufacture of chemicals of great economic importance.

In the treatment of a thermally reformed distillate by the process of the invention, one may also return the extract to the reforming step together with further amounts of fresh reforming charge. The extract, which has a very low octane number, gives, on reforming, highly valuable unsaturated gases.

In Figures 3 and 4 accompanying this specification there is illustrated schematically and without any intention of limiting the process, two preferred combinations of a thermal reforming unit with a unit for the selective extraction by means of urea in accordance with the invention.

It is advantageous, as previously stated, to combine, as represented in diagram 3, a thermal reforming unit 41 and a urea selective extraction unit 42 of the type represented in diagram 2. The reformed spirit 43 from the reforming unit 41 is treated in 42 by extractive crystallization with urea according to the invention and gives a raffinate 44 with a high octane number and an extract 45 consisting essentially of normal aliphatic hydrocarbons. The extract 45 is returned in feed 46 of the reforming unit 41 together with naphtha 47 that is the fresh feed. With this combination, there is produced a refined reforming spirit 44, of a high octane number and gases 48 issuing from the reforming which are much richer in commercially valuable unsaturated hydrocarbons than if the reforming feed had consisted solely of naphtha. But on the other hand the recycling of the extract decreases the capacity of the reforming unit with regard to the reforming of fresh feed.

According to another method of combination (Diagram 4) which does not have this drawback there is treated directly in the extractive crystallization unit 52 of the type represented in Figure 2, a naphtha 57, for example of boiling range 160–260° C. as illustrated in Example 3, hereinafter, to obtain an extract 55 of normal aliphatics, distilling at 160–260° C., which is a highly valuable material for chemical synthesis or for a special cracking unit (not shown) for the purpose of producing liquid and gaseous normal aliphatic hydrocarbons, particularly unsaturated ones, which are of great interest for the chemical industry. The raffinate 54, which is free of normal aliphatic hydrocarbons is fed into the reforming unit 51 which is then completely used to produce gas 58 and a gasoline 53 of a high octane number.

In fact the cracking reactions show that naphtha boiling at 160–260° C. and free from normal aliphatic hydrocarbons does not give on reforming straight chain aliphatic hydrocarbons with more than 6 carbon atoms in the molecule, which hydrocarbons are just the constituents with low octane number. In consequence the octane number of reformed spirit 53 is improved by the process.

The invention is further illustrated but in no way limited with reference to the following examples.

Example 1

A ternary solution was prepared consisting of:

75 parts by weight of 85% aqueous commercial methanol

25 parts by weight of commercial ethylene glycol

A solution was prepared of urea in this solvent, saturated at 38° C., it contains 37% by weight of urea.

With further reference to Figure 1, 230 parts by weight of the urea solution was cooled (stage 1) to 20° C., with vigorous stirring. At this temperature the saturation concentration in the solvent is 29% by weight and very fine "nascent" urea crystals were formed.

100 parts of a thermally reformed distillate boiling over the range 40–200° C. was added (line 2), and vigorously stirred at 15° C. (stage 3) whereby an oil in water type emulsion, stabilized by the "nascent" urea crystals, was formed. As the reaction is slightly exothermic it was necessary to cool in order to maintain the temperature constant.

On examining the emulsion under the microscope it was ascertained that it comprised a continuous phase, consisting of a saturated urea solution which held droplets of raffinate (thermal reforming spirit deprived of normal aliphatic hydrocarbons) in suspension. The adduct crystals (urea-normal aliphatic hydrocarbons) were very abundant when the reaction was complete and enclosed droplets of raffinate. The excess urea crystals form a kind of lattice which makes the emulsion thixotropic and prevents the droplets of raffinate from collecting together and from forming a continuous phase which is capable of being separated by decantation.

To ascertain whether the reaction is complete, a sample of emulsion was withdrawn, the raffinate removed therefrom by centrifuging and several drops of it introduced into an excess of a saturated solution of urea in anhydrous methanol. If the reaction is complete no precipitate of adduct is formed thus proving the absence of normal aliphatic hydrocarbons in the raffinate.

On a laboratory scale, using a turbo-emulsifier to maintain the emulsion, the reaction was complete in an hour.

Twenty-seven parts by weight of the initial urea solution was distilled (stage 6) so as to collect 10 parts of a distillate (line 4) at 88° C. consisting of 90% aqueous methanol.

To break the emulsion and cause it to loose its thixotropy the solution of aqueous methanol prepared as described above was added.

The product was settled to form two layers (stage 7) and the upper layer decanted (line 8). Thus there was

separately obtained an upper layer containing the raffinate phase which is free of normal aliphatic hydrocarbons and a lower consisting of urea solution holding in suspension very fine adduct crystals of straight chain hydrocarbons with urea.

The addition of 90% methanol was controlled so that the urea solution was practically free from excess urea crystals to avoid impairing the efficiency of the separation by decantation.

The lower layer was heated to 40° C. (stage **9**). This resulted in the decompositon of the complex since there was no longer a supersaturated solution of urea, the complex in consequence being unstable. The product was settled to form two layers (stage **10**) viz. an upper layer consisting of the extract phase **11** and containing the straight chain hydrocarbons decanted (line **11**) and a lower layer consisting of an unsaturated solution of urea in the ternary solvent. The solution was unsaturated because on the one hand the temperature exceeded 38° C., and, on the other hand, the aqueous methanol has been added (by line **4**).

Thus urea solution was reconstituted in composition and volume by the addition (line **12**) of the residue from the distillation of stage **6**, consisting of 17 parts by weight of a mixture of ethylene glycol and urea still containing a small amount of methanol and water.

27 parts by weight of the reconstituted urea solution, thus reconstituted, were withdrawn (line **5**) the remainder of the urea solution being returned to stage **1** and the cycle of operations restarted.

In the experiments carried out the yield of raffinate was 87% by weight. The thermal reforming distillate and raffinate obtained had the following characteristics:

	S. G. at 15°	Octane Number (Motor Method)		Octane Number (Research Method)	
		No Addition	+2.3 cc. TEL/gallon	No Addition	+2.3 cc. TEL/gallon
Thermal Reforming Distillate.	0.7672	71.4	77.6	81.5	89.5
Raffinate	0.7735	75.4	81.5	85.4	93.5

It thus has been found that according to the invention the octane number can be raised by four units by the motor method as well as by the Research Method, retaining the tetraethyl lead susceptibility and the higher rating by the Research Method compared with results obtained by the Motor Method. This example shows that thermal reforming leaves untouched or forms normal aliphatic hydrocarbons which are found in the reformed spirit. It is by the extraction of these hydrocarbons that the octane number may be raised by four degrees.

Example 2

This example illustrates the application of the process of the invention to the treatment of a straight run motor spirit.

The same urea solvent was employed as used in Example 1 and at the same time initial concentration (saturation concentration at 38° C., 37% of urea).

330 parts of this urea solution were rapidly chilled from 38° C. to 20° C. and 100 parts of spirit boiling over the range 60–180° C. from the direct distillation of crude Middle East petroleum were added. The whole was cooled to 15° C. with vigorous mechanical stirring. A finely dispersed and stable emulsion was formed. After stirring this stable emulsion for one hour it was ascertained from the qualitative test described in Example 1 that the reaction was complete.

The splitting of the emulsion was carried out by the method used in Example 1 but in the present example there was added 20 parts of 90% aqueous methanol obtained by distillation of a further 54 parts of the initial urea solution. The 34 parts of hot residue were kept for further use.

The emulsion having been broken, the raffinate was separated by decantation. The urea solution with the addition of aqueous methanol and containing the adduct, was heated to 40° C. The extract layer was decanted and recovered and the urea solution reconstituted by the addition of 34 parts of the hot residue from the preliminary distillation.

54 parts of the reconstituted urea solution were withdrawn for distillation and the remaining urea solution cooled to 20° C., for treatment of further stocks.

The yield of raffinate, free from straight chain hydrocarbons, was 85% by weight of the treated spirit.

The results obtained by the treatment were as follows:

	S.G. at 15° C.	Octane Number (Motor Method)	
		No Addition	+2.3 cc. TEL/gallon
Straight Run Spirit	0.7297	45	59.8
Raffinate	0.7380	49.5	64

Example 3

This example illustrates the application of the process of the invention to the treatment of a straight run naphtha.

330 parts of a urea solution saturated at 38° in the same solvent as that used in Example 1 were cooled and the solution stirred vigorously at 25° with 100 parts of naphtha having a distillation range of 160–260° C. and from the distillation products of a Middle East crude. The mixture was led into a homogenizer. The reaction took less than 10 minutes according to the qualitative test for the determination of straight chain hydrocarbons mentioned in Example 1.

The emulsion was broken by the addition of 10 parts of 90% by weight aqueous methanol obtained by the distillation of a further 27 parts of the initial urea solution. The distillation residue was kept hot for further use in the process.

The raffinate was separated by decantation.

The urea, together with the aqueous methanol carrying the adduct in suspension, was heated to 48° C. whereby the adduct was decomposed, setting free the extract which was separated by decantation.

The urea solution was reconstituted by the addition of 17 parts of the hot distillation residue.

27 parts of the reconstituted urea solution were withdrawn for distillation and the remaining solution used for a further treatment of 100 parts of naphtha. The yield of raffinate obtained was 85% by weight of naphtha treated. In the following table are shown the characteristics of the naphtha, prior to treatment, and of the raffinate obtained:

	S.G. at 15°	Octane Number, Motor Method
Original naphtha	0.790	23
Raffinate	0.7973	35

Such raffinate free from straight chain hydrocarbons will give, on reforming, a reformed spirit free from straight chain hydrocarbons and, therefore, of an octane number much greater than that of a spirit obtained by reforming the same naphtha not treated with urea.

What we claim is:

1. A process for the extractive fractionation of mineral oils which comprises treating a mineral oil with a solution of urea in a ternary solvent consisting essentially of, in admixture, about 2% to about 30% water, a water-

soluble oxygen-containing organic compound selected from the group consisting of ketones, mono-hydric alcohols, and mixtures of the foregoing, and an alcoholic organic compound selected from the group consisting of poly-hydric alcohols and mono-amino-alcohols, forming an emulsion of the oil-in-water type, maintaining said emulsion under conditions such that a solid urea adduct is formed with components of said mineral oil, separating said solid urea adduct from the remaining components of said mineral oil, decomposing said urea adduct and recovering the liberated components of said mineral oil.

2. A process for the extractive fractionation of mineral oils which comprises treating a mineral oil with a solution of urea in a ternary solvent consisting essentially of, in admixture, about 2% to about 30% water, a water-soluble oxygen-containing organic compound selected from the group consisting of ketones, monohydric alcohols, and mixtures of the foregoing, and an alcoholic organic compound selected from the group consisting of polyhydric alcohols and mono-amino-alcohols, forming an emulsion of the oil-in-water type, maintaining said emulsion under conditions such that a solid urea adduct is formed with components of said mineral oil, breaking said emulsion to form a two-layer system consisting of an upper layer comprising the urea adduction raffinate and a lower layer comprising a suspension of said solid urea adduct in said urea solution, separating said raffinate from said lower layer, separating said urea adduct from said urea solution, decomposing said urea adduct and recovering the liberated components of said mineral oil.

3. A process as claimed in claim 2 in which said emulsion comprising said urea adduct is broken by addition thereto of an emulsion-breaking agent comprising an aqueous solution of a water-soluble monohydric alcohol.

4. A process as claimed in claim 2 in which said emulsion is broken by addition thereto of an emulsion-breaking agent obtained as an overhead fraction by distillation of part of said urea solution recovered after decomposition of said adduct.

5. A process for the extractive fractionation of mineral oils which comprises treating a mineral oil with a supersaturated solution of urea in a ternary solvent consisting essentially of, in admixture about 2% to about 30% water, a water-soluble oxygen-containing organic compound, selected from the group consisting of ketones, monohydric alcohols, and mixtures of the foregoing, and an alcohol organic compound selected from the group consisting of polyhydric alcohols and monoamino alcohols, forming an emulsion of the oil-in-water type, maintaining said emulsion under conditions such that a solid urea adduct is formed with components of said mineral oil, adding thereto an emulsion-breaking agent comprising an aqueous solution of a water-soluble monohydric alcohol to form a two-layer system consisting of an upper layer comprising the urea adduction raffinate and a lower layer comprising a suspension of said solid urea adduct in said urea solution, separating said raffinate from said lower layer, subjecting the separated lower layer to conditions under which the urea adduct is decomposed, with formation of an urea adduction extract phase and an urea solution phase, and separating the phases.

6. A process as claimed in claim 5 in which said ternary solvent consists of methanol, water and an alcoholic organic compound selected from the group consisting of polyhydric alcohols, mono-amino-alcohols and mixtures of polyhydric alcohols and mono-amino-alcohols.

7. A process as claimed in claim 5 in which said ternary solvent consists of ethylene glycol, water and a water-soluble oxygen-containing organic compound selected from the group consisting of ketones, monohydric alcohols and mixtures of the foregoing.

8. A process for the extractive fractionation of petroleum naphtha which comprises treating a petroleum naphtha with a supersaturated solution of urea in a ternary solvent consisting essentially of, in admixture, about 2% to about 30% water, a water-soluble oxygen-containing organic compound selected from the group consisting of ketones, monohydric alcohols, and mixtures of the foregoing, and an alcoholic organic compound selected from the group consisting of mixtures of polyhydric alcohols and mono-amino-alcohols, forming an emulsion of the oil-in-water type, maintaining said emulsion under conditions such that a solid urea adduct is formed with components of said petroleum naphtha, adding thereto an emulsion-breaking agent comprising an aqueous solution of a water-soluble mono-hydric alcohol to form a two-layer system consisting of an upper layer comprising the urea adduction raffinate and a lower layer comprising a suspension of said solid urea adduct in said urea solution, separating said raffinate from said lower layer, subjecting the separated lower layer to conditions under which the urea adduct is decomposed, with formation of an urea adduction extract phase and an urea solution phase, and separating the phases.

9. A continuous process for the production of a high octane gasoline wherein a petroleum naphtha is subjected to thermal reforming with recovery of a reformed gasoline, wherein said reformed gasoline is treated by the process claimed in claim 8 with recovery of a raffinate of high octane number and of an extract of low octane number and wherein said extract is recycled to the naphtha feed stream to undergo further thermal reforming.

10. A process for the production of straight chain hydrocarbons and high octane gasoline which comprises treating a petroleum naphtha by the process claimed in claim 8 with recovery of an extract comprising straight chain hydrocarbons and a raffinate comprising highly branched chain hydrocarbons and aromatics, wherein said raffinate is thereafter subjected to thermal reforming with recovery of a high octane gasoline.

11. A process as specified in claim 5 in which the oxygen containing organic compound is a mixture of a monohydric alcohol and a ketone, and in which the combined weight of the water, monohydric alcohol and ketone in the ternary solvent employed in said urea solution for the formation of said adduct constitutes 50–80% by weight of said ternary solvent.

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