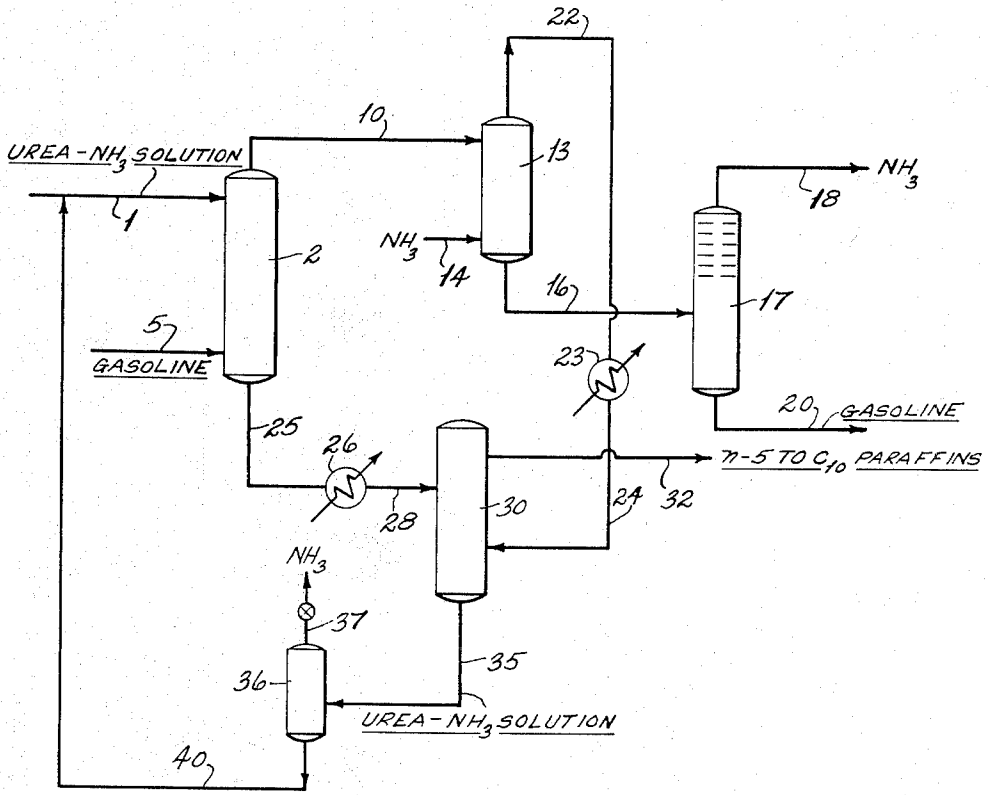
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PROCESS FOR EFFECTING COMPLEX FORMATION WITH UREA AND THIOUREA

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PROCESS FOR EFFECTING COMPLEX FORMATION WITH UREA AND THIOUREA

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This invention relates to a process for effecting complex formation between a complexing agent such as urea and the complex-forming constituents of an organic mixture. The process of the invention is particularly applicable to the separation of complex-forming constituents from hydrocarbon mixtures and can be employed in the treatment of naphtha to improve its value as motor fuel; in the preparation of low pour Diesel fuels and in the dewaxing of lubricating oil stocks.

It has recently been discovered that urea and thiourea form solid complexes with certain types of organic compounds. The class of compounds which complex with urea comprises normal aliphatic hydrocarbons containing at least six carbon atoms, terminal-substituted normal aliphatic hydrocarbons containing at least six carbon atoms, such as n-decanol and n-dodecylbenzene and some methyl-substituted n-aliphatic hydrocarbons. Thiourea forms solid complexes with some branched chain hydrocarbons and some naphthenes; triptane and 2,3-dimethylbutane are examples of branched chain aliphatic hydrocarbons that complex with thiourea; cyclopentane and cyclohexane are examples of naphthenes which complex with thiourea. The discovery of the complex-forming ability of urea and thiourea provides a very useful tool in the resolution of organic mixtures such as petroleum fractions. Urea complexing is particularly useful in the isolation of specific compounds and in the removal of undesirable components from petroleum fractions. Dewaxing of petroleum fractions such as gas oils and lubricating oils to produce low wax content products illustrates the use of urea complexing to free a petroleum fraction of undesirable constituents. The main commercial usefulness of urea complexing at the present time lies in the dewaxing of gas oils and lubricating oil fractions; low pour Diesel fuel is in demand as a jet fuel and for cold weather operation of Diesel engines; refrigerator oils characterized by low pour and Freon haze test are required in air conditioning and refrigeration equipment.

Various procedures have been proposed for effecting complex formation between complexing agents such as urea and complex-forming constituents of organic mixtures. It has been proposed that complex formation be effected by contacting an organic mixture with a saturated or super-saturated solution of urea in a polar solvent such as aliphatic alcohols, aliphatic ketones, water, etc. Complex formation is also effected

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by contacting an organic mixture with a slurry of complexing agent in a polar solvent. In addition, complex formation is effected by contacting an organic mixture with a fixed bed of urea wherein the urea is employed in conjunction with a particulate solid which is advantageously an adsorbent. In these various techniques for effecting complex formation, the presence of a polar compound such as water, an aliphatic alcohol or an aliphatic ketone expedites complex formation.

The process of this invention involves the use of anhydrous liquid ammonia as the medium for contact of the complexing agent and the organic mixture containing complex-forming constituents. In accordance with the process of this invention, contact of organic mixture with complexing agent in anhydrous liquid ammonia is effected at elevated pressure at a temperature less than 50° C. The solid complex formed on this contact is separated from the reaction mixture by filtration or decantation. Since the treated organic mixture, which will hereafter be designated the raffinate, is insoluble in liquid ammonia, its separation from the reaction medium is simply effected; residual traces of ammonia can be removed from treated mixture by flashing. Recovery of the separated complex-forming constituents is effected by decomposing the separated solid complex with anhydrous liquid ammonia at elevated pressure and at a temperature which is at least 10° C. higher than that employed for complex formation. As a general proposition temperatures of 30 to 100° C. are employed for complex decomposition. The anhydrous liquid ammonia reaction medium is advantageously modified by the presence of 1 to 10 weight per cent oxygenated hydrocarbon such as aliphatic alcohols containing 1 to 5 carbon atoms and aliphatic ketones containing 3 to 7 carbon atoms.

The process of the invention is particularly advantageous in the treatment of gasoline with urea so as to improve its octane rating. As a matter of fact, this invention makes the upgrading of gasoline by urea complexing feasible. Previously suggested procedures for improving the octane rating of gasoline by urea complexing were not effective, but the process of this invention causes substantial octane improvement of the treated gasolines. It is understood, however, that the process of the invention is also endowed with numerous advantages in the preparation of low pour Diesel fuels and in the dewaxing of lubricating oils by urea complexing.

Anhydrous liquid ammonia is a superior con-

tact medium for effecting complex formation because of its high solvent power for the complexing agent and its substantial immiscibility with most liquid hydrocarbon fractions. The extraordinary increase in urea and thiourea solubility in ammonia with increasing temperatures makes it an excellent contact medium below the prescribed temperature of 50° C. and a superior complex decomposition solvent at a temperature at least 10° C. higher than the temperature at which complex formation is effected.

An additional advantage of the use of anhydrous liquid ammonia as a contact medium for complex formation is that the raffinate is readily freed of the contact medium by flashing. The raffinate need not be subjected to a drying operation as is necessary when water or an oxygenated hydrocarbon is employed as the contact medium. Anhydrous liquid ammonia is also an excellent wash solvent for removing traces of complexing agent from the raffinate.

A further advantage of the use of liquid ammonia as the contact medium is that a ready source of cooling the complexing mixture is available at all times. This characteristic is particularly useful in upgrading gasolines by urea complexing.

The use of anhydrous liquid ammonia as a contact medium for the complexing reaction is particularly advantageous in continuous processes where complex is decomposed to recover the complex-forming materials and to yield complexing agent which is recycled to the complexing zone. Liquid ammonia is an excellent decomposition solvent for the complex because of the rapid increase of urea solubility in ammonia with increasing temperature. In addition, the use of ammonia as a complex breaker almost completely inhibits the decomposition of urea which has been found to accompany complex breaking with conventional solvents such as water and low boiling alcohols. The substantially complete inhibition of urea decomposition employing ammonia as the contact medium is a substantial advance in the field of urea and thiourea complexing since it eliminates one of the troublesome factors in adapting complexing to continuous operations.

The process of this invention can be effected with a liquid ammonia solution or slurry of complexing agent. If the complexing process of the invention is effected with an ammonia solution of complexing agent, it is necessary to employ saturated or near saturated solutions because the dilute solutions of urea and thiourea in ammonia effect substantial complex decomposition. Since the solubility of complexing agent in liquid ammonia increases markedly with an increase in temperature, it is advisable that ammonia solutions be employed that contain sufficient excess complexing agent to yield at saturated or near saturated solution at the prescribed contacting temperature.

The process of the invention is particularly suited for effecting complex formation by the saturated solution technique. The extremely rapid increase in urea solubility in ammonia with increasing temperature permits the use of a urea saturated solution at a temperature below 50° C. and the use of the same solution at temperatures 10 to 20° C. higher as a complex decomposition solvent. Other urea solvents do not exhibit this remarkable increase in urea solubility with increasing temperatures, so that their solutions are not readily employed both

for complex formation and complex decomposition by a relatively small increase in temperature.

In the slurry technique solid complexing agent is suspended in a small amount of liquid ammonia which usually constitutes 1 to 25 weight per cent of the mixtures to be treated. The slurry technique substantially reduces the size of the equipment required for complex formation.

Regardless of whether the solution or slurry technique is employed for effecting complex formation, it is necessary to effect complex formation and separation of the solid complex from the reaction mixture at a temperature below 50° C. In general, complex formation and separation of solid complex is effected at temperatures between −20 and 50° C. with temperatures of 0 to 40° C. ordinarily being employed. The optimum temperature for complexing varies with the charge stock being treated and the type of operation being employed for effecting complex formation. In general, it can be stated that temperatures in the upper part of the prescribed range are employed with higher molecular weight charge stocks and with a slurry type operation, whereas low molecular weight charge stocks such as gasoline and the saturated solution technique utilize temperatures in the lower part of the prescribed range. Maintenance of the temperature in the prescribed range is effected readily by allowing liquid ammonia to vaporize.

The successful operation of the process of this invention necessitates the use of sufficient pressure to maintain the liquid ammonia substantially in the liquid phase. It is apparent that the amount of pressure required will vary with the temperature at which the complex formation is to be effected. In general, it can be stated that pressures between 2 and 20 atmospheres are usually employed.

A particularly important advantage of the process of this invention is that the required contact time is substantially reduced over that required for complex formation with other contact media such as water, alcohols, mixtures of alcohol, ketones, etc., when compared on a basis of similar techniques. The use of liquid ammonia as the contact medium reduces the necessary contact time to effect complex formation by about 25 to 50 per cent in both the slurry and solution techniques for effecting complex formation. A time saving of this nature is particularly important in commercial installations and often spells the difference between success or failure of a particular commercial process. It is possible to produce 25 to 50 per cent more finished oil such as refrigerator oil or gasoline by the process of this invention in a given piece of equipment than can be realized by previously disclosed processes for effecting complex formation.

Similarly to temperature, the contact time varies considerably with the nature of the charge stock and with the type of treating operation employed. The slurry system requires somewhat longer contact times than does the solution technique. Complex formation with high molecular weight stock such as lube oils requires longer contact times than do lighter stocks such as gasoline. As a general proposition, the contact times required for complex formation vary between 10 minutes and 2 hours which is a significant improvement over the 30 minutes to 8 hours contact times required with other solvents such as

water, methanol, methanol-isopropanol mixtures, ketones, etc.

The amount of complexing agent employed in the process of the invention is also dependent upon the charge stock. In the production of refrigerator oils by dewaxing a lube oil the charge lube oil contains relatively small amount of materials that will complex with urea so that a large dosage of complexing agent is not required; 2 to 5 pounds of urea per barrel of lube oil treated results in production of refrigerator oils characterized by extremely low Freon haze test. When gasolines or gas oils containing a relatively large percentage of normal paraffinic material are the charge materials, it is necessary to use larger urea dosages and 5 to 20 pounds of urea per barrel of oil are required. The above figures are based on the use of a slurry type operation employing 2 to 5 per cent liquid ammonia as the slurry medium; the dosages required for the solution technique also vary with the type of oil treated but require a solution containing approximately one half the amount of solid specified for the slurry technique. In general, it can be stated that in slurry type operations 2 to 20 pounds of complexing agent per barrel of oil are required whereas in the solution technique it is necessary to employ sufficient saturated ammonia solution so that 1 to 10 pounds of complexing agent is present for every barrel of oil treated.

Decomposition of the separated complex is effected by contacting the complex with ammonia at a temperature which is at least 10° C., and preferably 20° C., higher than the temperature employed for complex formation. In general, temperatures between 30 and 100° C. are employed for complex decomposition depending on the conditions employed for complex formation. It is apparent that it is necessary to maintain elevated pressures during the decomposition of the complex in order to maintain the ammonia mainly in the liquid phase. The exceptional solubility of complexing agents and liquid ammonia and the rapid increase of solubility with increase in temperature make ammonia the ideal solvent for complex formation and complex decomposition.

The invention will be illustrated hereafter by treatment of hydrocarbon fractions with urea for the removal of complex-forming constitutents which, as described heretofore, are predominantly normal paraffinic hydrocarbons. Dewaxing of lube oils to yield refrigerator oils characterized by exceptionally low Freon haze properties, dewaxing of gas oils to produce low pour products which are useful as jet fuels, and gasoline treatment to improve its octane rating are utilizations wherein urea complexing with liquid ammonia as a contact medium shows particular advantages. It will be understood, of course, that the process of the invention is equally applicable to separation of branched chain hydrocarbons and naphthenes from mixtures by thiourea complexing in liquid ammonia.

The process of the invention is illustrated in detail in the accompanying drawing showing the upgrading of gasoline by contact with urea in liquid ammonia.

A urea-saturated ammonia solution is introduced through a pipe 1 into a tower 2 adapted for pressure operation. A heavy straight run naphtha possessing a substantial content of normal paraffins and a rating of the order of 37 is introduced into the tower 2 through a pipe 5 and is subjected to countercurrent contact with the urea-saturated ammonia solution at a temperature of about 20° C. and at a pressure of approximately 3 atmospheres. The flow of the two streams is regulated so that the average contact time in the tower is approximately 15 minutes. As a result of contact between the urea solution and gasoline at the afore-described conditions, there is formed a solid complex phase comprising C_5–C_{10} normal paraffins and urea. The solid complex phase is entrained in the ammonia solution.

There is withdrawn from the upper part of the contact tower 2 through a pipe 10 a treated gasoline fraction containing 3 to 5 weight per cent ammonia. The treated gasoline fraction is introduced into a wash tower 13 wherein it is subjected to countercurrent washing with liquid ammonia which is introduced into the tower 13 through a pipe 14. Ammonia washing of the treated gasoline fraction removes residual traces of urea and complex from the gasoline.

The ammonia-washed gasoline fraction is withdrawn from the tower 13 through a pipe 16, and is introduced into a flash tower 17 wherein ammonia is flashed from the gasoline by reducing the pressure to atmospheric. The flashed ammonia is taken off overhead from the flash tower 17 through a pipe 18. The treated gasoline fraction, whose octane rating has been improved to about 45 by removal of normal paraffinic components therefrom, is withdrawn from the tower 17 through a pipe 20 which leads to storage.

Ammonia solutions of urea and complex are withdrawn from the tower 2 through a pipe 25 and introduced into an exchanger 26 wherein the mixture of complex and ammonia solution is raised to a temperature of about 50° C. The heated mixture is then introduced through a pipe 28 into a tower 30 wherein decomposition of the complex is effected. Wash ammonia removed from the tower 13 through a pipe 22 and raised to a temperature of about 50° C. in exchanger 23 is also introduced into tower 30 through pipe 24. In the tower 30, contact of the complex with ammonia solution of urea at a temperature of about 50° C. and with wash ammonia, causes decomposition of the complex. The normal C_5–C_{10} paraffins liberated from the complex separate as a layer in the upper section of the tower 30, and are withdrawn therefrom through a pipe 22.

The ammonia solution of urea is withdrawn from the tower 30 through a pipe 35 and introduced into an evaporator 36, wherein the solution is cooled to a temperature of about 20° C. by vaporization of liquid ammonia which is withdrawn from the evaporator 36 through a pipe 37. Sufficient ammonia is flashed so that a urea-saturated ammonia solution is formed in the evaporator 36. The urea-saturated ammonia solution is withdrawn from the evaporator 36 through a pipe 40 and is recycled to the tower 2 to contact further quantities of gasoline.

The foregoing description illustrates the simplicity and efficiency of effecting complex formation with ammonia as the contact medium. An equally simple and efficient system can be employed in effecting thiourea complex formation with specific isoparaffins and naphthenes.

The following examples illustrate the many advantages which result from the use of liquid ammonia as the contact medium in urea complexing. The advantages are particularly noticeable in Example I which illustrates the upgrading of

gasoline by complexing with urea in anhydrous liquid ammonia.

Example I

360 cc. of ammonia were used as an evaporative coolant and solvent for urea complexing by vaporizing it from mixture with 1000 g. of urea and 2000 cc. of heavy straight run naphtha. The temperature was reduced from 80° F. to 20° F. by evaporative cooling. The naphtha was separated from the precipitated complex and excess urea by decanting. The naphtha initially had a CFRM clear octane of 37.5 (+3 cc. TEL 62.0) and after treating had a CFRM clear octane of 44.1 (+3 cc. TEL 67.9).

Example II

A paraffin base gas oil having a pour point of +25° F. was treated in a slurry with urea in the amount of 118 pounds per barrel of oil and 16 weight per cent (basis oil charge) of liquid ammonia saturated with urea at room temperature and under sufficient pressure to keep the ammonia in the liquid phase. The mixture was stirred for 30 minutes after which time the mixture was filtered. The gas oil, after flashing off ammonia and water washing, had a pour point of −10° F. A similar run with 175 pounds per barrel of urea and 10 weight per cent (basis oil charge) of NH_3 saturated with urea resulted in a gas oil with −20° F. pour point.

The foregoing examples illustrate the use of the process of this invention in improving the octane rating of gasoline and in producing low pour gas oil. The invention may also be employed in dewaxing lubricating oils to produce refrigerator oils characterized by exceptionally low Freon haze tests.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for effecting complex formation between complexing agents of the urea-type and compounds which form complexes with said agents which comprises contacting an organic mixture containing said complex-forming compounds with a saturated anhydrous liquid ammonia solution of said urea-type complexing agents containing 1 to 10 weight per cent oxygenated hydrocarbon selected from the group consisting of alcohols and ketones, effecting said contact at a temperature less than 50° C. and at a pressure sufficient to maintain substantially liquid phase operation with the resulting formation of a solid complex of urea and said complex-forming compounds, separating a mixture comprising said complex and said ammonia solution from said organic mixture, heating said mixture to a temperature between 30 and 100° C. and at least 10° C. higher than the temperature employed for complex formation and at a pressure sufficient to maintain substantially liquid phase operation with the resulting decomposition of said complex into complex-forming compounds and said complexing agent which dissolves in said ammonia solution and separating said complex-forming compounds from said ammonia solution.

2. A process according to claim 1 in which said oxygenated hydrocarbon is an alcohol.

3. A process according to claim 1 in which said oxygenated hydrocarbon is a ketone.

4. A process for upgrading a n-paraffin-containing gasoline which comprises contacting said gasoline fraction with a urea-saturated anhydrous liquid ammonia solution containing 1 to 10 weight per cent oxygenated hydrocarbon selected from the group consisting of alcohols and ketones, effecting said contact at a temperature less than 50° C. and at a pressure sufficient to maintain substantially liquid phase operation with the resulting formation of a complex of urea and n-paraffinic gasoline components, separating a mixture comprising said complex and said ammonia solution from said gasoline fraction, heating said mixture to a temperature between 30 and 100° C. and at least 10° C. higher than the temperature employed for complex formation with the resulting decomposition of said complex into normal paraffins and urea which dissolves in said ammonia solution, separating said normal paraffins from said ammonia solution cooling and recycling said ammonia solution to contact further quantities of n-paraffin-containing gasoline.

5. A process according to claim 4 in which said oxygenated hydrocarbon is an alcohol.

6. A process according to claim 4 in which said oxygenated hydrocarbon is a ketone.

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