United States Patent Office 2,731,455 Patented Jan. 17, 1956

2,731,455

POUR POINT REDUCTION OF PETROLEUM OIL FRACTIONS WITH ACTIVATED UREA-WAX COMPLEX

Leo Salzmann, Petrolia, Pa., Lucian J. Leta, Boulder City, Nev., and Leslie C. Borell, Franklin, Pa., assignors to L. Sonneborn Sons, Inc., a corporation of Delaware

No Drawing. Application September 19, 1950, Serial No. 185,692

8 Claims. (Cl. 260—96.5)

This invention relates to new and useful improvements in the pour point reduction of petroleum oil fractions.

Wax-bearing oils, such as lubricating oil fractions, possess a so-called pour point, i. e., that temperature at which the oil loses fluidity. The pour point is conventionally determined by the well known ASTM tests such as the one designated as G97–39.

The reduction of the at times relatively high pour point of a wax-bearing lubricating oil fraction may be obtained either by the use of suitable additives such as, for example, aluminum stearate or other material, or by physical removal of the wax. In the former at least a portion of the wax remains largely in the oil and the additive performs the function of a crystallization modifier to thereby influence the pour point. In the mechanical wax separation for the reduction of pour point, a large amount of wax is physically removed from the oil. Though the use of additives may reduce the pour point of an oil to a satisfactory low point to meet relatively rigid temperature conditions it is, in many instances, not desired to retain in the oil appreciable quantities of wax. Alternatively, removal of wax from the oil by mechanical operations, such as centrifuging, will not ordinarily remove a sufficient quantity of the wax to give a satisfactory low pour point.

Co-pending application, Serial No. 185,691 filed September 19, 1950, discloses the lowering of the relatively high pour point of a lubricating oil fraction permitting the obtaining of appreciably lowered pour points and preferably pour points lowered by at least 10° F.

In accordance with this disclosure petroleum oil fractions and, preferably, lubricating oil fractions having a relatively high pour point for instance due to the wax contained therein, are intimately contacted at a temperature of about 60–110° F. and preferably 70–90° F. with urea, in amount sufficient to appreciably lower the normal pour point of said fractions, preferably at least 10° F.

Such urea treatments may be conducted either as a single batch operation or as a multiple stage treatment. In most cases, and particularly when using a single batch treatment, up to about 50% by weight of urea calculated on the amount of oil fraction present, and preferably 15–35% by weight of urea, give satisfactory results reducing the pour point in most cases appreciably more than by 10° F. When using the multiple stage treatment it is possible to use lesser amounts of urea and obtain a more economical operation with substantially the same pour point reducing efficiency.

It is in most cases necessary to add a suitable activator while the urea treatment of the oil fraction is proceeding. Such activator is preferably a lower alcohol not exceeding three carbon atoms in the aliphatic chain. Satisfactory activators are, for instance, methanol, ethanol, propyl and isopropyl alcohol. Methanol, however, gives particularly good results and is the preferred activator material. It is also of advantage to continuously stir the mix of urea and petroleum oil fraction. For best results

the mixing should be adequate for efficient contact purposes.

The activator used in accordance with the practice of the invention disclosed in co-pending application Serial No. 185,691 should be preferably at least 0.5% by volume of the total volume of liquid present. Best results are obtained by an amount of activator of about 2% by volume. Amounts of activator appreciably higher than about 2% do not further increase the efficiency of the activator. Though 2% by volume of activator material gives maximum results, it has been disclosed that 1–1.5% of activator material is most practical for use in large scale operation.

As shown in said co-pending application the dewaxing capacity of the urea is partly or completely exhausted in the treatment of oil fractions, the extent of exhaustion depending upon the type, duration, number of contacts or other conditions of such treatment.

One object of this invention comprises the regeneration of partially or completely exhausted urea obtained in the cloud or pour point reduction of a wax-bearing petroleum oil fraction.

The foregoing and further objects of the invention will be apparent from the following description.

The regeneration of the urea in accordance with the invention is carried out by contacting the exhausted or partially exhausted urea with a hot petroleum solvent and preferably in the presence of a relatively small amount of water.

The contacting may be carried out by mixing the urea product with the petroleum solvent, by pouring the petroleum solvent over the urea product, or by percolating the petroleum solvent over the urea. In the latter method the petroleum solvent may be continually recovered and reused until the regeneration process is complete.

The petroleum solvents useful in accordance with the invention may be any of the petroleum solvents conventionally so known and designated, providing that such petroleum solvents are such that wax is soluble therein but urea is not substantially soluble therein. It is preferable that these solvents have a flash-point in excess of 170° F. and ASTM pour point of 0° F. or lower. It is also of advantage if the petroleum solvent has a boiling point low enough so that it may be removed from the dissolved wax by distillation. Lighter fractions of petroleum oil have proved effective, and fractions of the kerosene range, preferably with a boiling point of about 375–500° F. have proved particularly effective. It is necessary that an amount of solvent sufficient to dissolve all the wax in the urea product be used. In most cases amounts of petroleum solvent of at least twice the volume of the urea product to be regenerated, are needed, and preferably volumes of the petroleum solvent equaling at least three times the volume of the urea product to be regenerated, are needed. When the petroleum solvent is used alone to regenerate the urea (that is, without the presence of water) it is necessary to carry the operation out at temperatures of about 200° F. or higher. However, this procedure has several disadvantages, in that decomposition accompanied by discoloration of the urea products result at these high temperatures. It is also found that at these high temperatures the urea products to be treated, as well as the regenerated urea, gradually assume a granular structure, making pumping, filtration and stirring difficult. It has been further found that a regeneration time up to three hours is required when the urea regeneration is accomplished by hot substantially water-free petroleum solvents.

We have found that regeneration of the urea can be carried out at lower temperatures, preferably at temperatures from 180°–200° F. over a relatively short period of time, usually 30–45 minutes, if a relatively small

amount of water is present. The water may be added either by suspending it in the petroleum solvent prior to use or while stirring the urea with the hydrocarbon solvent. The amount of water required is inversely proportional to the temperature employed for regeneration. The higher the temperature, the less water is necessary, and vice versa. The amount of water normally required for best results is one-fourth to five percent and preferably one-fourth to three percent by weight of the urea present.

Thus, while it is possible to carry out the regeneration of the urea without the presence of water, in most cases it is highly desirable, depending upon requirements or conditions dictated by desired freedom from decomposition or facility of operations, to include water.

The following example is furnished by way of illustration, but not of limitation:

EXAMPLE

300 grams of an oil having the following characteristics (flash ° F. 420, viscosity @ 210° F. 45 seconds, ASTM cloud point 50° F., ASTM pour point 40° F.) was contacted with 100 grams of urea in the presence of 5 cc. of methyl alcohol for 45 minutes at a temperature of 70° F. The slurry was then filtered over a Buchner funnel and the filtrate (dewaxed oil) tested for cloud and pour points. The filter cake was suspended in about three times its weight of a kerosene range oil having a flash point of 220° F. and pour point below −20° F. One cubic centimeter of water was added and the resulting mixture agitated at a temperature of 180–190° F. for 45 minutes. This slurry was then filtered over a Buchner funnel and the filter cake washed with an additional volume of cold kerosene solvent. The washed cake was transferred to a beaker and again used for dewaxing a fresh portion of the raw lube stock. This procedure was continued through 20 cycles. The results obtained are illustrated in the table.

TABLE

Regeneration of urea with kerosene range oil at 180–190° F.

Treatment Cycle No.	Cloud Point of Treated Oil	Pour Point of Treated Oil
1	+12	+5
2	+14	+5
3	+12	0
4	+12	0
5	+8	0
6	+8	0
7	+10	0
8	+10	0
9	+10	0
10	+4	−5
11	+8	0
12	+8	0
13	+6	0
14	+6	0
15	+12	0
16	+8	0
17	+8	0
18	+6	0
19	+8	0
20	+6	0

The urea product referred to in the invention may be any urea product formed by contacting urea with a petroleum fraction to remove the wax. The urea may be urea used alone or urea used in any combination. This includes urea used in the urea adsorbent composition described in co-pending application, Serial No. 185,693. This application discloses a method for dewaxing a white petroleum oil. This dewaxing of the white petroleum oil is accomplished by intimately contacting the said white petroleum oil with a composition comprising urea intimately mixed with an adsorbent. This adsorbent may be fuller's earth, silica gel, bauxite, etc.

It may thus be seen from the foregoing that this invention comprises the regeneration of a urea product, said urea product being a product obtained by mixing urea either in combination with another substance, such as a petroleum adsorption product, or urea alone with a wax-bearing petroleum fraction. The product obtained after the regeneration in accordance with the invention is a urea product which has at least substantially the same ability to remove wax from a wax-bearing petroleum oil fraction as new urea. After the urea product has been regenerated several times it has the ability to remove wax from a wax-bearing petroleum oil fraction superior to that of new urea and is ready to be used again for additional dewaxing operations.

The urea product and the petroleum solvent may be contacted at any temperature above 165° F. However, when temperatures above 220° F. are used, difficulties arise. Preferred temperature range in accordance with the invention is 175–210° F. When at least ¼% water by weight of the urea present is used, a temperature range between 180 and 200° F. is preferred. Excellent regeneration results are obtained when, after first contacting the urea with the petroleum solvent and then separating the two, a further treatment of the urea substance with a washing solvent is performed.

We claim:

1. Method for obtaining urea activated for petroleum wax-urea complex formation, which comprises subjecting urea at least twice to the cycle of contacting urea with a wax bearing petroleum oil fraction to thereby obtain a complex between said urea and wax in said fraction, intimately contacting the resulting complex with a petroleum oil fraction of the kerosene range in amount normally sufficient to form a solution of the amount of wax carried by said urea complex, at a temperature not appreciably less than 165° F. and in the presence of about ¼–5% of water by weight of urea, and separating the resulting urea substance.

2. Method for obtaining activated urea from a urea complex resulting from the urea contact treatment of a wax-bearing petroleum oil fraction, comprising the cycle of intimately contacting such a urea complex with a petroleum oil fraction of the kerosene range in amount normally sufficient to form a solution of the amount of wax carried by said urea complex, at a temperature not appreciably less than 165° F. and in the presence of about ¼–5% of water by weight of urea, and separating the resulting urea substance, thereafter contacting the latter with a wax-bearing petroleum oil fraction to thereby obtain a complex between said separated urea and wax in said last mentioned fraction and thereafter subjecting said last mentioned complex to the contacting and separating steps of said cycle.

3. Method in accordance with claim 2 in which said intimate contact is carried out at a temperature ranging from 165–220° F.

4. Method in accordance with claim 2 in which said intimate contact is carried out at a temperature ranging from 175–210° F.

5. Method in accordance with claim 2 in which said intimate contact is carried out at a temperature ranging from 180–200° F.

6. Method in accordance with claim 2 in which said intimate contact is carried out at a temperature ranging from 175–210° F. and said urea complex is a urea complex obtained by intimately contacting urea and an adsorbent with a petroleum fraction.

7. Method in accordance with claim 2 in which said petroleum oil fraction of the kerosene range is present in amount equalling at least two times the volume of said urea product and in which said intimate contacting is carried out at a temperature ranging between about 180–200° F.

8. Method in accordance with claim 2 in which said recovery of the said regenerated urea substance includes the separation of the petroleum oil fraction of the kerosene range and the said urea substance and one further treatment of the urea substance with a washing solvent.

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