United States Patent Office 2,878,181 Patented Mar. 17, 1959

2,878,181

METHOD OF PREPARING NEUTRAL OILS

George W. Ayers, Chicago, and William A. Krewer, Arlington Heights, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

No Drawing. Application December 30, 1957 Serial No. 705,758

20 Claims. (Cl. 208—263)

This invention relates to a method of reducing the neutralization number of petroleum oils by chemical means and, more particularly, to the transformation of the naphthenic acids present in petroleum oils or fractions thereof into amides by reaction of the naphthenic acids with an amine or amonia in the presence of N,N'-dicyclohexylcarbodiimide.

In the preparation of lubrication oils from crude petroleum, it is the practice to subject both heavy and residual lubricating oil stocks to chemical and physical treatments in order to improve the viscosity characteristics, low temperature fluidity, oxidation stability, and lower the carbon residue, sulfur content, and neutralization values in order that the requirements of modern lubrication can be met by the lubricating oils. One problem that has faced the refiner of lubricating oils is the removal of acidic constituents from the heavy or residual lubricating oil stocks, as, for example, preparing such lubricating oils having low acid numbers as determined by ASTM D975–52T. As the refining operations of dewaxing, deasphalting, and solvent refining exert their influence upon the lubricating oil fractions, the acidic constituents remaining become much more difficult to remove. Refiners have in the past applied various extraction methods employing alkali solutions and/or various organic solvents in their efforts to produce lubricating oils having acceptable neutralization values. Aqueous and anhydrous ammonia have been used, followed by alcohol extractions, to remove the deleterious naphthenic acids. Aqueous ammonia solutions in combination with emulsion breakers, such as methyl alcohol, ethyl alcohol, or acetone, have been applied in various continuous countercurrent extraction processes in an effort to finish lubricating oils for use with various additives that have become necessary to meet the extreme conditions in modern lubrication. In spite of the prior art efforts, in many instances the persistence of acidic constituents or naphthenic acids in finished lubricants has proved detrimental.

This problem is particularly acute in the refining and preparation of heavier lubricating oil distillates and heavy bottoms or residues from petroleum oil fractions which, after dewaxing or deasphalting, contain certain complex acids which are increasingly difficult to remove. These acids may be defined as high molecular weight monocarboxylic acids which are liquids or solids and which are mostly of alicyclic configuration, with greater than about 25 carbon atoms per molecule. These naphthenic acids show little or no unsaturation and consist essentially of cyclic acids and polycyclic acids boiling above about 450° F., and mainly above about 600° F.

It has been found, in accordance with this invention, that these tenacious naphthenic acids, as well as the other organic acids present in crude petroleum, can be transformed into oil-soluble amides by reaction with an amine or ammonia in the presence of N,N'-dicyclohexylcarbodiimide according to the following reaction:

$$R\cdot COOH + H_2N\cdot R' + C_6H_{11}N{=}C{=}NC_6H_{11} \longrightarrow$$

Organic acid; Amine or ammonia; N,N'-dicyclohexylcarbodiimide

$$R{-}\overset{\overset{O}{\|}}{C}{-}NHR' + C_6H_{11}NH\overset{\overset{O}{\|}}{C}{-}NHC_6H_{11}$$

Amide; sym.-dicyclohexylurea

This reaction is carried out by using substantially stoichiometric amounts or equimolar amounts of the amine or ammonia, N,N'-dicyclohexylcarbodiimide and organic acid. It has been found that the amide of the naphthenic acid remains in the oil and the N,N'-dicyclohexylcarbodiimide is transformed to symmetrical dicyclohexylurea which, contrary to expectations, precipitates from the oil and is easily separated.

It is known in the prior art to separate naphthenic acids from oils by treatment with a basic reagent such as an amine, ammonia, or alkalolamine. Such processes are carried out below the temperatures necessary for amide formation, and are followed by separation of the soaps formed and distillation of the soaps to dissociate same and recover the acids and the amine. Liquid ammonia is also used as a solvent for sulfur compounds and other acidic substituents in oils and is generally used in conjunction with a modifying agent which includes amides, sodium amide, amines, and hydrazine. These processes are not related to the present invention because they are either directed to extraction of the naphthenic acids, or separation and purification of the naphthenic acids.

Accordingly, it becomes a primary object of this invention to provide a process for lowering the acid neutralization number of petroleum oil.

Another object of this invention is to provide a process for lowering the acid neutralization number of refined petroleum oils.

Another object of this invention is to provide a process for neutralizing the naphthenic acids in petroleum oils.

Still a further object of the invention is to provide a process for neutralizing the naphthenic acid content of refined lubricating oils for the purpose of producing a low neutralization number product.

Another object of the invention is to provide a process for neutralizing the naphthenic acid content of refined lubricating oils to produce a product having a low neutralization number by transformation of the naphthenic acids to oil-soluble amides in the presence of N,N'-dicyclohexylcarbodiimide.

In accordance with this invention, it has been found that the conversion of organic acids, particularly naphthenic acids, into amides proceeds very simply and can be carried out readily in the petroleum oil. In applying the method, an aliphatic amine, an alicyclic amine, an aromatic amine, or ammonia is added to the petroleum oil containing the organic acid, and then N,N'-dicyclohexylcarbodiimide is finally added whereupon the acid and amine (or ammonia) are converted practically quantitatively into an acid amide and the N,N'-dicyclohexylcarbodiimide into symmetrical dicyclohexylurea, which is insoluble in the oil and is percipitated. The amide is soluble in the oil but has no acid neutrailzation number. Hence, if the amine (or ammonia) and N,N'-dicyclohexylcarbodiimide are added to the oil so that one mole of each substance is available per mole of organic acid present, practically all of the organic acid will be converted to the amide, which will remain in the oil, but show no neutralization number, and the N,N'-dicyclohexylcarbodiimide will be hydrated to symmetrical dicyclohexylurea, which will be precipitated.

In carrying out the process of this invention, the acid neutralization number of the petroleum oil containing the organic acids, particularly the high molecular weight

naphthenic acids, is determined analytically and the number of moles of organic acid present in the oil to be treated is calculated by known methods. Following this, equal numbers of moles of an aliphatic amine, alicyclic amine, aromatic amine or ammonia, and of N,N'-dicyclohexylcarbodiimide, are added. The reaction takes place immediately, or upon slight heating, with or without agitation, to produce the amide of the organic acid quatitatively with concomitant precipitation of symmetrical dicyclohexylurea. The precipitate of symmetrical dicyclohexylurea is allowed to settle or may be removed by filtration yielding an oil which has an extremely low acid neutralization number, as compared with the untreated oil or as compared with oils treated by prior art methods.

In order to demonstrate the invention, a number of experiments were conducted wherein several different petroleum oils and fractions were treated with various amines in the presence of N,N'-dicyclohexylcarbodiimide. The results are shown in the following table:

TABLE I

Original Petroleum Oil			Chemicals added to the oil		Acid Neutralization No. of the Processed Oil
Name	Quantity (g.)	Acid Neutralization No.	Name	Weight (g.)	
Lube Extract [1]	40	7.0	n-Dibutylamine N,N'-dicyclohexylcarbodiimide.	0.64 1.03	0.45
Do [1]	40	7.0	Benzylamine N,N'-dicyclohexylcarbodiimide.	0.53 1.03	0.20
Do [1]	40	7.0	Aniline N,N'-dicyclohexylcarbodiimide.	0.46 1.03	0.32
200 Vis. Dewaxed Neutral	200	0.16	n-Dibutylamine N,N'-dicyclohexylcarbodiimide.	0.06 0.1	0.02
Do	200	0.16	Benzylamine N,N'-dicyclohexylcarbodiimide.	0.05 0.1	0.02
Do [1]	200	0.16	Aniline N,N'-dicyclohexylcarbodiimide.	0.05 0.1	0.02

[1] #19 of Table II.

The results shown in Table I demonstrate that the process of this invention is effective in reducing the neutralization number of petroleum oils to values approaching zero, without the necessity of extended processing or complicated techniques. The data show that a dewaxed neutral oil is easier to treat than a "lube extract," by which term is meant the solvent extract obtained in the solvent extraction of mineral lubricating oils. The invention is applicable to any petroleum oil mixture, including diesel fuels, gasolines, kerosenes, gas oils, neutral oils, bright stocks and residual stocks. The efficiency of the method is demonstrated by the low neutralization values obtained in the experiments on lube extracts, which contain especially persistent naphthenic acids and related acidic materials, including petroleum resins.

The invention is applicable to the treatment of lubricating oil fractions which have been refined, that is, distilled, dewaxed, solvent-extracted, deasphalted and clay-treated in accordance with known procedures. Such lubricating oil fractions include, broadly, bright stocks and neutrals, and the solvent extracts obtained from the refining of bright stocks and neutrals. Bright stocks are the result of the refining of residues and have viscosities in the order of 130 to 250 SUS at 200° F. A neutral is generally defined as the oil obtained from the vacuum distillation of topped crude which, after solvent refining, solvent dewaxing, and clay-finishing, has a viscosity at 100° F. of between about 65 and 350 SUS. Since neutral fractions, bright stocks and their solvent extracts are well known, only a general description of their preparation as an illustration is necessary.

In a typical operation, desalted crude oil is first charged to a distillation unit where straight-run gasoline, two grades of naphtha, kerosene, and virgin distillate are taken off, leaving a reduced crude residue. The reduced crude is continuously charged to a vacuum distillation unit where three lubricating oil distillates are taken off as side streams, a light distillate is taken off as overhead, and a residuum is withdrawn from the bottom of the tower. The three lube oil distillates are subjected to solvent extraction to produce an extract and a raffinate in each instance. The extracts can be treated in accordance with this invention. The raffinates are solvent dewaxed with methylethyl ketone and clay-treated to produce finished neutral oils which can be beneficiated by treatment in accordance with this invention.

The foregoing residuum, the source of bright stock and solvent extracts therefrom, is charged to a propane deasphalting unit wherein propane dissolves the desirable lubricating oil constituents and leaves the asphaltic materials. A typical vacuum residuum charge to the propane deasphalting unit may have an API gravity of 12.9°, viscosity SUS at 210° F. of 1249, flash 585° F., fire 650° F., C. R. of 13.9 weight percent, and is black in color. The deasphalted oil may have an API gravity of 21.5° to 21.8°, viscosity SUS at 210° F. of 165–175, NPA color 6–7, flash 575° F., fire 640° F., and C. R. of 1.7–2.0. The deasphalted oil and various lubricating oil distillates from the reduced crude are separately subjected to solvent extraction for the separation of non-aromatic from aromatic constituents. The refined oils or "raffinates" from such processes are used as blending stocks, and the solvent extracts containing the undesirable aromatic constituents constitute a type of oil that can be treated in accordance with this invention.

For example, a Van Zandt crude oil with an API gravity of 33.1 was topped to remove such light fractions as gasoline, naphtha, kerosene, and a light lubricating distillate. The vacuum residue was a reduced crude having a viscosity of 1251 SUS at 210° F., 2.2 percent sulfur, and an API gravity of 12.6. After propane deasphalting, the oil had a viscosity of 174 SUS at 210° F. and an API gravity of 21.7. This deasphalted oil was treated with phenol to produce a raffinate from which an aviation lubricating oil may be produced. The extract phase from this phenol treatment is ready for treatment in accordance with this invention.

Other solvents than phenol may be used to obtain the extraction product treated in accordance with this invention; for example, liquid sulfur dioxide, nitrobenzene, Chlorex, chlorophenol, trichloroethylene, cresylic acid, pyridine, furfural or the Duo-Sol solution comprising liquid propane, phenol, and cresol may be used. When using phenol, it is possible to vary the characteristics of the extraction product considerably by adjustment of the

amount of water present. A low V. I. cut may be obtained by using water in the phenol during the extraction of a high V. I. cut may be obtained by using anhydrous phenol. Following are the physical characteristics of typical extraction products from lubricating oil stocks derived from various crude oils which may be treated in accordance with this invention.

TABLE II

Sources and physical characteristics of solvent extracts

Extract No.	Crude Source	Solvent	API Gravity	Sp. Gr. at 10° F.	Vis./100° F.	Vis./130° F.	Vis./210° F.	V. I.	Pour	° F. Flash	° F. Fire	Iodine No. (Wijs)	C. R.	Percent Sulfur
1	Van Zandt	Phenol	11.1		23,319	4,750	282	−40	+55				7.2	2.66
2	do	do	15.4		15,000		285	+39						
3	do	do	12.6		36,410	4,310	310.1	−1	+80				4.7	2.27
4	do	do	14.6		19,500	4,305	313	+27	+90				4.7	2.2
5	do	do	15.4		32,500		372	+5	+60				4.13	2.33
6	do	do	13.7		25,000	5,400	355	+27	+80					2.18
7	do	do	8.6		145,000	19,000	616	0	+70					
8	do	do	10.5		12,676	2,514	172.1	−101	+60					2.88
9	Santa Fe Springs.	do	10.2	0.9984			371		+65	520	600	69.4		
10	Texas	Furfural	13.0	0.9791			>1,500		+85	470	515	57.1		
11	Pa	Chlorex	12.2	0.9843			1,365		+85	560	630	71.4		
12	do	Nitro-benzene	10.0	1.000			>1,500		+75	555	640	60		
13	Mid-Cont	Propane-cresol.	14.4	0.9699			>1,500		+100	540	605	63.7		
14	do	Phenol	13.6				41.7	−82	+20					
15	do	Chlorex	13.6				200	−61	+75					
16	do	Phenol	8.9				569		+75					
17	do	Furfural	14.9				50.2	25	+20					
18	Van Zandt	Phenol	13.5	.976	25,000		341	17	+65	530	610		5.76	2.36
19	do	do	10.8		1,327	397	65.4	−71	+35	415	490		0.54	2.85

Examples of refined lubricating oils that may be beneficiated by this invention are shown in Table III, which also shows the characteristics of the 200 vis. dewaxed neutral oil shown in Table I.

TABLE III

Base oils

Mineral Oil	API Gravity	COC Flash, °F.	COC Fire, °F.	SUS at 100° F.	SUS at 210° F.	Vis. Index	NPA Color	Percent Carbon Residue	Percent Sulfur	Stable Pour, °F.
100 Vis. Neutral	33.6	405	450	103.2	39.7	101	+2	0.00	0.12	+5
70 Vis. Neutral	36.6	370	405	71.3	36.9	111	+1	0.00	0.18	0
150 Bright Stock	26.8	570	630	2,511	156.0	99	6+	0.73	0.53	−5
200 Vis. Neutral	29.2	445	480	205.1	46.5	94	+2	0.00	0.43	+5

Various alkyl, cycloalkyl, aryl, aralkyl and alkylaryl derivatives of ammonia or amines may be used in carrying out this invention. These may be primary or secondary amines. Examples include methylamine, vinylamine, allylamine, dimethylamine, ethylamine, diethylamine, n-propylamine, di-n-propylamine, n-butylamine, n-amylamine, n-hexylamine, laurylamine, ethylenediamine, trimethylenediamine, tetramethylenedimine, pentamethylenediamine, hexamethylenediamine, cyclohexylamine, dicyclohexylamine, aniline, benzylamine, methylaniline, o-toluidine, m-toluidine, p-toluidine, o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, o-anisidine, p-anisidine, p-phenetidine, benzidine, and o-dianisidine.

From the foregoing description of the amines, it is seen that ammonia or any primary or secondary organic amine which shows even slight solubility in petroleum oil, is suitable for the purpose of the invention. The amine reactant (or ammonia) and the N,N'-dicyclohexylcarbodiimide may be added to the petroleum oil or extract in a number of ways. The two reactants may be added separately or simultaneously. The two reactants may be added as such or in solution in a petroleum oil. Addition may be made directly to the storage tank containing the oil to be treated with subsequent circulation therein, or the reactants may be added by a proportionating pump while same are in solution in an oil.

The process is preferably at ambient temperature. In cold weather it may be necessary to warm the oil with the added reactants. The reaction has been found to be almost instantaneous and quantitative if the reactants and oil are heated to a temperature of about 100° to 120° F. Occasionally it may be desirable to heat the mixture of oil and reactant to 150° F. Temperatures which cause decomposition of the oil and/or the reactants are to be avoided. Low temperatures which require long processing times are, of course, uneconomical.

The process of this invention may be carried out by adding the reactants to an unfinished lubricating oil after the dewaxing step and during or after the clay-treating step. The precipitate of symmetrical dicyclohexylurea can be removed during filtration of clay from the oil.

The object of this procedure, that is adding the reactants during or after the clay-treating, is to produce an oil of lower neutralization number than would be obtained through the use of clay alone. In case of usage with clay, a quantity of reactants less than that equivalent to the organic acids present may be used. When used in the clay-treating step, it is preferable to add the clay to the dewaxed oil in the usual manner and to add the reactants of this invention, preferably in oil solution, to the oil-clay mixture while on its way to the filter, after which the mixture is further handled in the usual manner. The known procedures of clay-treating are applied and natural clays, Filtrol, and the like may be used as is well known in the prior art. Clay-treating temperatures are often 400° F. or higher, and at this temperature the reaction of this invention is very rapid and the products should remain in contact with the clay as short a time as possible.

This procedure is illustrated by the following specific example:

A 170 viscosity neutral oil having 0.16 neutralization number was treated with equivalent quantities of normal butyl amine and N,N'-dicyclohexylcarbodiimide and heated to 400° F. with 8 lb. clay per barrel of oil. After maintaining the mixture at approximately 400° F. for ½ hour, the mixture was filtered and the oil comprising the filtrate was essentially clear and free of separated solid matter. This filtered oil had an acid number below 0.1.

From the foregoing, it is apparent that the reactants of this invention may be added either during or after the clay-treating procedure. It is preferred that the reactants of this invention be added to the hot oil-clay mixture just before it passes to the rotary filter. This procedure is particularly applicable to those lubricating oils which have the neutralization number (1948 method) of under about 0.4, in which case the precipitate of symmetrical dicyclohexylurea is removed with the clay. For oil having a neutralization number of above about 0.4, a portion of the precipitate of symmetrical dicyclhexylurea may dissolve in the oil at the clay-treating temperature. For such oils the preferred procedure would be to add the reactants of this invention after the clay-treating step has been completed. An alternate procedure would be to treat the hot oil to which has been added the reactants of this invention with hot alcohol such as methanol, ethanol, or butyl alcohol to dissolve and remove as a separate phase the symmetrical dicyclohexylurea. The alcohol solution along with the urea compound may be removed from the finished oil during that step in which the "stink oil" is removed after clay-treating.

What is claimed is:

1. The process of preparing petroleum oils of low neutralization number which comprises treating said petroleum oil with a basic nitrogen compound capable of amide formation in the presence of N,N'-dicyclohexylcarbodiimide and separating the oil phase from the reaction products.

2. The process in accordance with claim 1 in which said oil is a lubricating oil fraction.

3. The process in accordance with claim 1 in which said oil is a solvent extract obtained by the solvent extraction of lubricating oil fractions.

4. The process in accordance with claim 1 in which the basic nitrogen compound is an amine.

5. The process in accordance with claim 4 in which the amine is an aliphatic amine.

6. The process in accordance with claim 5 in which said aliphatic amine is n-butylamine.

7. The process in accordance with claim 4 in which the amine is an aromatic amine.

8. The process in accordance with claim 7 in which the aromatic amine is benzylamine.

9. The process in accordance with claim 7 in which the aromatic amine is aniline.

10. The process in accordance with claim 7 in which the aromatic amine is a toluidine.

11. The process in accordance with claim 4 in which the amine is cyclohexylamine.

12. The process in accordance with claim 4 in which the amine is dicyclohexylamine.

13. The process of transforming the acidic constituents in lubricating oil fraction into soluble amides, whereby the neutralization number of the oil fraction is reduced, which comprises treating said lubricating oil fraction with an equivalent amount of an organic amine capable of amide formation and in an amount sufficient to react with said acidic constituents in the presence of N,N'-dicyclohexylcarbodiimide, and separating the oil phase from the reaction products.

14. The process in accordance with claim 13 in which said lubricating oil fraction is selected from the group consisting of refined neutral oils, refined bright stock oils, solvent extracts from the manufacture of neutral oils, and solvent extracts from the manufacture of bright stock oils.

15. The process in accordance with claim 14 in which said lubricating oil fraction is a refined neutral oil.

16. The process in accordance with claim 14 in which said lubricating oil fraction is a solvent-extract from the manufacture of bright stock oils.

17. The process of preparing petroleum oils of low neutralization number which comprises treating said petroleum oil with an equivalent amount of an organic amine and an equivalent amount of a N,N'-dicyclohexyldicarbodiimide, whereby the acidic constituents are transformed to amide and said N,N'-dicyclohexyldicarbodiimide separates from the oil phase as symmetrical dicyclohexylurea, and recovering the oil phase having a reduced neutralization number.

18. The process in accordance with claim 17 in which said reaction is carried out at a temperature between about 80° to 150° F.

19. The process in accordance with claim 17 in which said petroleum oil is an unfinished lubricating oil which has been dewaxed and treated with clay at elevated temperatures and said petroleum oil is cooled to about 150–200° F., treated with said organic amine and N,N'-dicyclohexyldicarbodiimide and filtered to remove the clay and precipitate of symmetrical dicyclohexylurea.

20. A process in accordance with claim 19 in which said petroleum oil is a 200 vis. dewaxed neutral oil.

References Cited in the file of this patent

UNITED STATES PATENTS

2,152,720	Yabroff	Apr. 4, 1939
2,634,231	Johnstone	Apr. 7, 1953
2,797,240	Amiard	June 25, 1957
2,817,684	Bartnick	Dec. 24, 1957