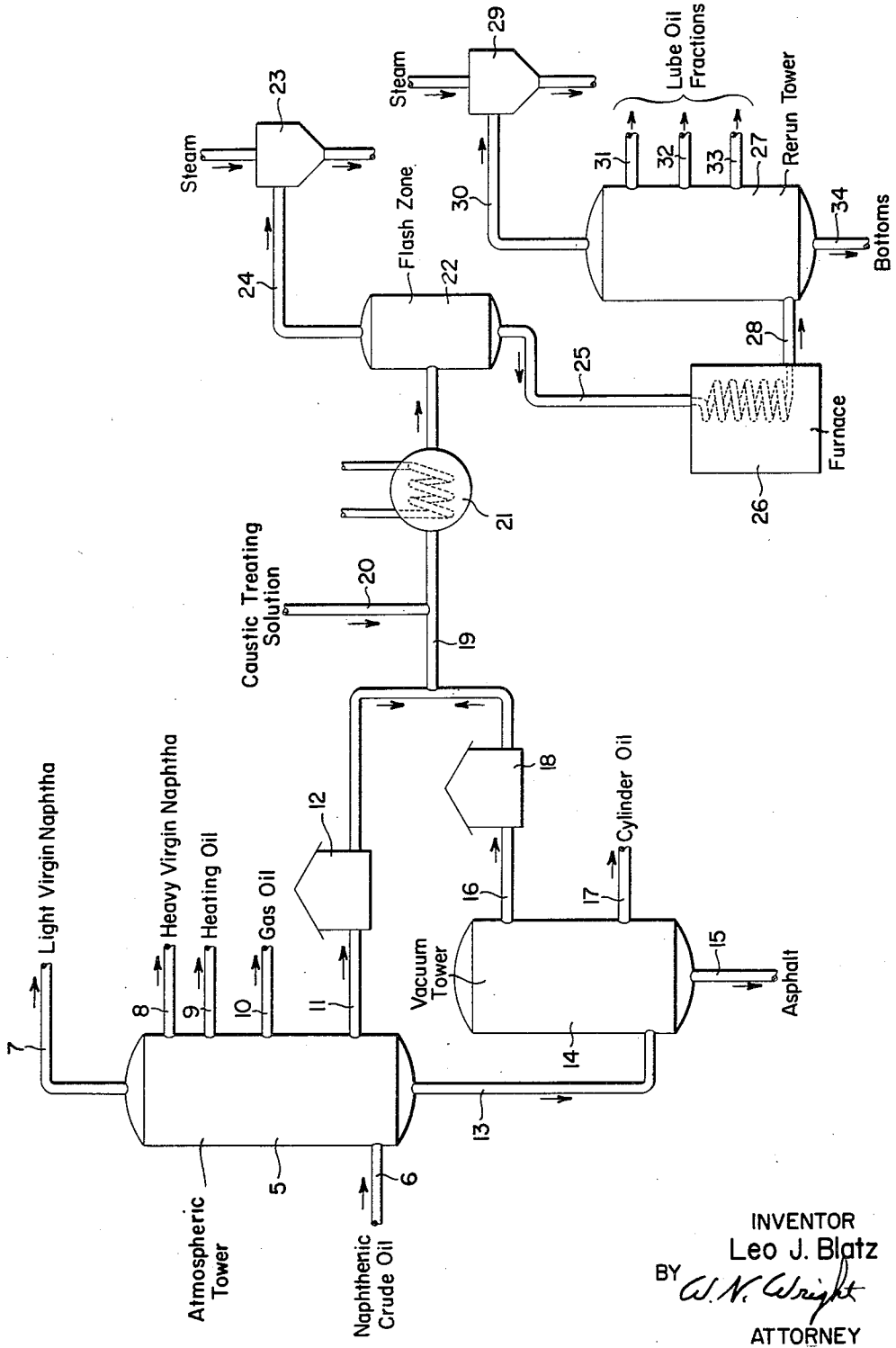
Dec. 11, 1956 L. J. BLATZ 2,773,807

REFINING NAPHTHENIC LUBE-OIL DISTILLATES WITH A EUTECTIC MIXTURE OF SODIUM HYDROXIDE AND POTASSIUM HYDROXIDE

Filed Dec. 24, 1953



INVENTOR
Leo J. Blatz
BY W. N. Wright
ATTORNEY

United States Patent Office 2,773,807
Patented Dec. 11, 1956

2,773,807

REFINING NAPHTHENIC LUBE-OIL DISTILLATES WITH A EUTECTIC MIXTURE OF SODIUM HYDROXIDE AND POTASSIUM HYDROXIDE

Leo J. Blatz, Cranford, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Application December 24, 1953, Serial No. 400,312

3 Claims. (Cl. 196—41)

The present relates to a method of refining mineral lubricating oils. More particularly, it relates to a method of manufacturing lubricating oils from distillate fractions that are in turn derived from naphthenic type crudes. It especially concerns a method for rendering such lubricating oils non-corrosive and for improving their color and color stability by treating them with a eutectic of potassium hydroxide and sodium hydroxide.

It is well known in the petroleum industry to manufacture lubricating oils from naphthenic crude oils. Naphthenic crudes in general contain naphthenic acids and may be characterized broadly by having neutralization numbers in excess of 0.2, and more normally in excess of 0.8 to 1.0. The term neutralization number as used with reference to mineral oils in the present description means that an oil requires treatment with an alkaline reagent in order to render it neutral. Thus, a neutralization number of 1.0 by definition means that the oil in question requires 1.0 milligram of potassium hydroxide per gram of oil in order to neutralize the acidity of the oil.

Naphthenic crude oils are found in various geographic locations. The naphthenic crudes of particular interest to refiners in the United States are the crudes that are obtained from Venezuela, Colombia and the coastal area in Texas. The lube oil distillates obtained from these different crude sources all contain appreciable quantities of naphthenic acids. Such acids must be removed from the lube oil distillates since their presence in a lubricating oil, even in relatively small concentrations, renders the oil corrosive to engine parts at the high temperatures to which such an oil is usually subjected. The removal of these naphthenic acids must be achieved by a refining operation.

The lube oil distillates from naphthenic crudes usually range in viscosity from about 75 S. S. U. @ 100° F. to about 95 S. S. U. @ 210° F. They may be as high in viscosity as about 110 S. S. U. @ 210° F. The distillates are generally characterized by possessing relatively poor color and color stability. Since these two properties are very desirable and demanded in commercial lubricants, it is also mandatory that the distillates be refined to obtain improvement in these two respects.

Several refining procedures have been conventionally employed for reducing the corrosiveness and for improving the color and color stability of the lube oil distillates that are derived from naphthenic crudes. Perhaps the most popular procedure involves treatment of the distillates with sulfuric acid, followed by rerunning the treated distillates over a slight excess of sodium hydroxide beyond that required to neutralize the acidity of the oil. In the rerunning operation, an excess of caustic to the extent of about 0.02 to 0.04 weight percent (based on the distillate) is generally employed.

While sulfuric acid treatment and a subsequent caustic rerunning operation are generally effective in improving the quality of naphthenic lube oil distillates, this refining method is not entirely satisfactory for at least two important reasons. First, the sulfuric acid employed in the process presents a serious and expensive corrosion

problem in the refinery. Second, waste sulfuric acid and any SO_2 vapors that are evolved during the process constitute very serious pollution problems, especially in built-up areas. Thus, the sulfur dioxide contaminates the atmosphere surrounding the refinery, and the spent acid tends to pollute any body of water into which this waste stream is directed.

Mild hydrogenation has also been proposed as a means for refining the lube oil distillates in question, but this process is very expensive. Only very unique and unusual economic conditions would permit the installation of this method for refining these fractions.

Caustic treating of the lube oil distillates with an alkali such as potassium hydroxide or sodium hydroxide has also been attempted. These reagents have proven to be reasonably effective in reducing the acidity of these distillates, but they have not been totally effective in improving their color and/or color stability. As mentioned earlier, these latter two properties are extremely important in commercial lubricants; and a satisfactory means for their attainment must be employed. Caustic treating of naphthenic lube distillates is particularly ineffective insofar as color improvement is concerned when the distillates have viscosities in excess of 500 S. S. U. at 100° F. and especially above 800 S. S. U. at 100° F.

Accordingly, it is an object of the present invention to manufacture lubricating oils from lube oil distillates of naphthenic origin wherein the lube oils are non-corrosive toward engines (e. g. contain substantially no naphthenic acid) and wherein these same oils have improved color and color stability. It is a particular object of the present invention to refine these lube oil distillates by treating them with a eutectic mixture of sodium hydroxide and potassium hydroxide. While treatment of the distillates with either sodium hydroxide or potassium hydroxide alone has been carried out heretofore, it has never before been appreciated nor realized that a eutectic mixture of these two alkalis is unexpectedly superior to either of the alkalis alone in its action on the distillates.

Before going into a complete description of the present invention, it is well to point out that a eutectic mixture of sodium and potassium hydroxides is one which contains about 53.5 weight percent of potassium hydroxide and about 46.5 weight percent of sodium hydroxide. The eutectic may be distinguished from the individual hydroxides primarily by its very low melting point. Thus, the melting point of the eutectic is about 325° F., while the melting points of potassium hydroxide and sodium hydroxide are 650° F. and 550° F., respectively.

Throughout the following description, repeated references will be made to the color and color stability of different lube oil fractions. In all instances the color values will be those that are obtained by use of the TAG-Robinson Colorimeter. This instrument and instructions for using the same are described in complete detail in the TAG Manual for Inspectors of Petroleum, edited by R. M. Wilhelm. This book is published by C. J. Tagliabue Manufacturing Company, Brooklyn, New York. The instrument and the procedure for its use are both well known and widely employed in the petroleum industry for measuring the color of mineral oils.

The color stability or "colorhold" of a lubricating oil as used in this description was determined in each instance by the following procedure. An oil under test was first placed in the TAG-Robinson Colorimeter and its color determined. A 100 ml. sample of the oil was then saturated with air by corking the sample in a partially filled bottle and thereafter shaking the bottle at room temperature. The bottle and its sample were then heated and maintained at a temperature of 212° F. for a period of 16 hours. Following this heating period, the sample was

withdrawn from the bottle, and its color again determined by means of the TAG-Robinson Colorimeter. A comparison of the oil's color values before and after the heating period afforded a direct indication of the color stability or "colorhold" of the oil.

It will be appreciated that the color of any given naphthenic lubricating oil distillate will depend largely upon the viscosity of the oil. The more viscous the oil is, the higher is its boiling range and the lower its color value. In a similar vein, however, the more viscous an oil is, the less critical are its color requirement and its color stability. In any case, however, it is eminently desirable that any given oil possess as great a colorhold value as possible, because with two oils that possess otherwise substantially identical inspections, the oil with the greater colorhold value is always preferred.

In line with these color requirements, it is an object of the present invention to provide a method for producing oils of this quality that are also substantially noncorrosive. This object and other related objects may be realized by the practice of the present invention, as described below.

The present invention consists briefly of the following process steps. First, a naphthenic crude oil is distilled in an atmospheric, a vacuum, or a combination atmospheric and vacuum distillation apparatus to form a plurality of fractions including at least one lubricating oil distillate. The lube distillate or distillates are condensed, blended as necessary and then fed to a rerun tower which may be operated under atmospheric and/or vacuum conditions. In general, the rerun operation is generally carried out under sub-atmospheric conditions.

While enroute to the rerun tower, a eutectic mixture of sodium and potassium hydroxides (preferably in aqueous solution) is injected into the distillate stream. The oil and caustic mixture is then subjected to temperature and pressure conditions which are adapted to flash any water in the mixture from the mixture. The water-free mixture of oil and finely divided caustic is then heated under noncracking conditions in a furnace to vaporize substantially all of the hydrocarbon constituents. The hydrocarbon vapors and caustic are then introduced within a rerun tower. Spent caustic, naphthenate salts, excess caustic and small amounts of tarry materials are removed from the bottom of the rerun tower; and the various lube oil products desired are removed as side stream fractions above the feed inlet to the tower.

The manner in which a rerun tower must be operated in order to provide desired lube oil products is well known in the art, and it is considered that a more detailed description of this phase of the process is not required. The raw lubricating oil distillates cut from the crude that are of particular interest in the present invention are those that possess viscosities in excess of about 80 S. S. U. at 100° F., and particularly those that have viscosities in excess of about 150 S. S. U. at 100° F. As mentioned earlier, the distillates may have viscosities as great as about 110 S. S. U. @ 210° F. The distillates that are especially benefitted by the present invention are those that possess viscosities in excess of 500 S. S. U. @ 100° F., and particularly in excess of about 800 S. S. U. @ 100° F. It will be noted that the lube oil distillates which are derived from naphthenic crudes possess neutralization numbers greater than 0.2 and usually greater than 0.6.

As mentioned earlier in this description, the caustic treating agents of the present invention are preferably aqueous solutions of a eutectic mixture of sodium hydroxide and potassium hydroxide. It is preferred that the caustic solutions have a density in excess of about 10° Bé., and particularly in the range of about 25° to 50° Bé. An especially preferred treating solution is one having a density of about 35° Bé.

The caustic treating solution could be added to an oil in any conventional mixing vessel. It is preferred, however, that the oil and caustic be admixed directly within a conduit which is positioned prior to the rerun tower. It is further preferred that the oil and caustic be admixed at a temperature and pressure such that water is not boiled out of the solution during mixing. These conditions will be obvious to anyone skilled in the art.

The amount of caustic that is added to any given oil will depend primarily upon the acidity of the oil. Thus, an oil which contains a large amount of naphthenic acids will require a larger amount of caustic than will an oil which contains a relatively smaller amount of naphthenic acids. In any event, it is a requirement of the present invention that an excess amount of caustic over and above the amount required to merely neutralize the oil be added to the oil. It is particularly desired that at least 0.06 weight percent excess caustic (based on the oil) be employed. It is preferred that between 0.15 and 0.25 weight percent excess caustic be used. It will be appreciated that amounts of caustic in excess of the stated amounts may be utilized, with the result that correspondingly improved color and colorhold values will be obtained. It has, however, now been established that the amounts specifically called for above satisfactorily fulfilled present quality requirements.

After the caustic solution has been added to a given lube oil distillate, it is desired that the resulting mixture be subjected to conditions of pressure and temperature that are adapted to flash water from the mixture before the mixture is introduced within a rerun tower. Accordingly, the aqueous caustic-oil mixture is preferably passed through a flashing zone wherein such conditions of temperature and pressure are maintained. In general, it will be obvious to those skilled in the art to select conditions of pressure and temperature that will meet this requirement. The conditions in the flashing zone should be such that substantially none of the hydrocarbon components are flashed from the oil and caustic mixture.

After the water in the caustic and oil mixture has been removed therefrom, the water-free mixture is heated to a temperature sufficient to vaporize substantially all of the hydrocarbons present without causing cracking. The resulting vapors, caustic, naphthenates, etc., are then introduced into a rerun tower. The heating may be carried out in any type of furnace or coil such as is conventionally employed in conjunction with petroleum distillation apparatus. The time of heating does not appear to be particularly critical, since it has been found that time periods of as little as 80 to 90 seconds have been sufficient for the successful operation of the invention. Time periods of this order of magnitude generally prevail in conventional distillation coils. It is contemplated that times as short as 20 seconds and even less are satisfactory.

The present invention may be better understood by reference to the attached figure which illustrates a preferred embodiment of the same. In the figure a naphthenic crude oil is introduced into an atmospheric distillation tower **5** via line **6**. In tower **5** the crude oil is fractionated into a plurality of conventional petroleum fractions. Thus, the crude oil in the figure is fractionated into a light virgin naphtha in line **7**, a heavy virgin naphtha in line **8**, a heating oil in line **9** and a gas oil in line **10**. The aforementioned distillate fractions may be conducted to storage or to any desired subsequent refining operation. For example, the gas oil fraction in line **10** may be fed directly to a catalytic cracking unit. A bottom side stream fraction comprising a lube oil distillate fraction of the type of concern to the present invention is withdrawn from tower **5** through line **11** and is transferred to a storage tank **12**. A fraction of this character may generally have a viscosity of about 75 to 200 S. S. U. at 100° F.

Reduced crude is withdrawn from the bottom of tower **5** through line **13** and is introduced within vacuum tower **14** where it is fractionated to form a plurality of fractions including an asphaltic bottoms in line **15** and a lube oil

distillate fraction in line 16. Other fractions such as a cylinder oil fraction may be withdrawn as by means of line 17. The fraction of interest to the present invention, however, is the aforementioned lube oil distillate fraction in line 16. This fraction is transferred to storage tank 18 and is then combined with the fraction in tank 12 in line 19. At this point it will be noted that the lube oil distillates in tanks 12 and 18 are liquids and will conventionally possess temperatures of the order of about 100° F., at the point of blending.

The combined lube oil distillates in line 19 are mixed with an aqueous solution of a eutectic mixture of sodium and potassium hydroxides, which is introduced within line 19 via line 20. The caustic solution is preferably about 35° Bé. in strength.

The lube oil distillate and caustic mixture in line 19 is heated by a suitable means 21 to a temperature of about 200° to 350° F., and is then introduced within flash zone 22. Flash zone 22 is preferably operated at a sub-atmospheric pressure as by means of a steam ejector 23 which is connected to the top of zone 22 by line 24. In any event, zone 22 is maintained at temperature and pressure conditions that are adapted to flash and remove water contained in the zone without also removing substantial amounts of hydrocarbons. Thus, a particularly attractive set of operating conditions for zone 22 comprise a temperature of about 300° F., and a pressure of about 250 mm. Hg. It is contemplated that temperature ranges of about 200° F. to 350° F. and pressures of 100 to 760 mm. Hg. may be employed at this point.

Water which is present in zone 22 is flashed overhead through line 24 and the resulting mixture of lube oil distillate and colloidal caustic particles is transferred by means of line 25 to furnace 26. Here the stream is heated to a temperature sufficient to vaporize substantially the entire body of distillate without cracking, and the vapors are then introduced into rerun tower 27 through line 28. Peak temperature of about 600° to 750° F. may be employed for the stream passing through furnace 26. A residence time in furnace 26 of about 80 to 90 seconds at these temperatures will be generally sufficient in most instances.

Rerun tower 27 is preferably operated at a sub-atmospheric pressure, namely about 50 to 250 mm. Hg. absolute and preferably about 150 mm. Hg. absolute. The sub-atmospheric pressure may be realized by means of steam ejector 29 which is connected with the top of tower 27 by means of line 30.

The number and type of lube oil fractions that are withdrawn from tower 27 will necessarily vary with product demand and the physical characteristics of the original feed stock in line 6. In general, however, it will be preferred to withdraw a plurality of lube fractions as by means of side stream lines 31, 32 and 33. It is particularly contemplated that tower 27 be operated to provide side streams of about 85 to 95 S. S. U. vis/100° F. in line 31, about 500 S. S. U. vis/100° F. in line 32 and about 1200 S. S. U. vis/100° F. in line 33. A mixture of tarry materials, alkali naphthenates, excess alkalis and so forth is removed as a bottoms product from tower 27 via line 34.

The lube oil fractions in lines 32, 32 and 33 may be further compounded in accordance with conventional refining practice. Thus, products of intermediate viscosity may be blended from adjacent product fractions and the usual anti-oxidants, detergents, anti-wear and anti-rusting additives that are well known in the art may be added to improve other lubricating oil properties.

Example 1.—The following example will serve to better illustrate the principles and scope of the present invention. In this example, which utilized apparatus substantially identical to that illustrated in the attached figure, a Colombian crude oil was first fractionated in an atmospheric pipe still to form a plurality of distillate fractions including a light naphtha, a heavy naphtha, a heating oil, a gas oil and a light lubricating oil. The light lube oil distillate fraction had an API gravity of 24.1, a viscosity of 151 S. S. U./100° F., a neutralization number of 2.9, a TAG-Rob. color of 9¾ and a colorhold value of 2¼. The volume of this fraction constituted about 14 volume percent of the crude oil and boiled in the range from about 500° F. to 850° F. (obtained by ASTM 10 mm. distillation and converted to 760 mm.).

The bottoms from the atmospheric pipe still was sent to a vacuum pipe still and there fractionated into a plurality of distillate fractions including a top side stream, a heavy lube oil distillate fraction, and a cylinder oil fraction. The heavy lube oil distillate fraction in this case had an API gravity of 20.0, a viscosity of 1243 S. S. U. /100° F., a neutralization number of 2.1 and a color value of ¾ TAG-Rob. This particular distillate fraction constituted about 16 volume percent of the original crude oil. The bottoms fraction from the vacuum pipe still was an asphaltic material, and boiled in the range from about 750° F. to 1000° F. (data obtained by converting results of ASTM 10 mm. distillation to 760 mm.).

The light lube oil distillate from the atmospheric still and the heavy lube oil distillate from the vacuum still were combined to form a blend which had a gravity of 22.6° API., a viscosity at 100° F. of 281 S. S. U., a neutralization number of 3.3, a TAG-Rob. color of 1 and a colorhold value of 1. The blend was made up of about 65% by volume of the light distillate and 35% by volume of the heavy distillate.

Samples of the blend described above were treated separately with potassium hydroxide alone, sodium hydroxide alone and with a eutectic mixture of the two hydroxides. In every instance the hydroxides were added to the samples of oil in the form of concentrated solutions having Baumé gravities of about 30°. In every instance, an amount of caustic in excess of that required to neutralize the acidity of the oil was added to the oil. The percentage excess (based on the weight of the oil) was controlled at three different concentration levels.

Each oil and caustic mixture was then heated in a batch still to about 350° F. at atmospheric pressure in order to flash off water from the mixture. Each water-free sample was then distilled at increasing temperature (400°–600° F.) and decreasing pressure (8 to 2 mm. mercury absolute) into a plurality of distillate fractions and the individual fractions evaluated for their color and colorhold values. From these data, color and color stability values for three different lube oil stocks were determined. The color values for these stocks are presented in Table I below and the colorhold data in Table II below:

TABLE I

Color inspections of rerun oils

	NaOH			KOH	Eutectic		
Percent Excess Caustic	0.06	0.15	0.25	0.06	0.06	0.15	0.25
Color, TAG-Rob.:							
100 SSU/100° F.	17¼	17¼	17½	17¼	17½	17½	17½
500 SSU/100° F.	9¾	10¼	10¼	9¾	9¾	10¼	10½
2,000 SSU/100° F.	5½	7¼	7	6	6½	8¾	8½

TABLE II

Color stability of rerun oils

Caustic	NaOH			KOH	Eutectic		
Percent Excess Caustic	0.06	0.15	0.25	0.06	0.06	0.15	0.25
Colorhold, TAB-Rob.:							
100 SSU/100° F.	16	17	17½	16½	17	17	17¼
500 SSU/100° F.	9¼	9¾	10	9	9¼	9¾	9¾
2,000 SSU/100° F.	2½	4¼	4	3	2¾	4½	6

It is apparent from Table I above that the eutectic mixture of sodium hydroxide and potassium hydroxide is equal or superior to either hydroxide alone in improving the color of naphthenic lube oil distillate fractions. More important, however, it is apparent from Table II that the eutectic mixture is more effective than either hydroxide alone in imparting color stability to such distillate fractions. This improvement in color stability is particularly marked for distillate fractions that have a viscosity in excess of about 500 S. S. U. at 100° F. and at the higher levels of excess caustic employed.

It will be noted in Table I above that there are less data presented for potassium hydroxide than for sodium hydroxide or for the eutectic mixture. The superiority of the eutectic over potassium hydroxide, however, is considered to be completely self-evident in view of the recognized equivalency of potassium hydroxide and sodium hydroxide and in further view of the data that are presented in Example 2 below.

Example 2.—The unique ability of a eutectic mixture of sodium and potassium hydroxide for improving the color stability of naphthenic lube oil distillates as contrasted to either hydroxide alone was further demonstrated by distilling a heavy Colombian crude lube oil fraction in the manner described in Example 1, in the presence of 0.04% excess caustic. Separate tests were made with sodium hydroxide, potassium hydroxide and the eutectic mixture. Each distillation was carried out to provide a 32% cut overhead. Analyses were made on each such overhead fraction, the results of which analyses are as follows:

TABLE III

Colombian distillate rerun over caustic materials

		Inspections for 0–32% Overhead Product		
Caustic Material [1]		NaOH	KOH	Eutectic [2]
Product Inspections	Feed to Rerun			
Color, TR	½	8¾	8½	8¾
Colorhold, TR		3¾	4	5¾
Gravity, °API	18.8	18.8	18.9	18.9
Vis., SSU/100° F	2,411		1,100/1,200	
Vis., SSU/210° F	108.6	66.6	69.3	66.1

[1] 0.04 wt. percent excess based on oil feed to distillation (excess above that required to neutralize 1.9 Neut. No. of raw distillate).
[2] Eutectic mixture of 56.5% C. P. KOH and 43.5% C. P. NaOH.

The results presented in Table III above clearly illustrate the outstanding ability of the eutectic mixture of sodium hydroxide and potassium hydroxide for improving the color stability of naphthenic lube oil distillates. It will be particularly noted that the distillate fractions of concern in this instance possess a viscosity at 100° F. of between 1100 and 1200 seconds. Thus, the eutectic is particularly more effective than either sodium- or potassium-hydroxide alone in improving the colorhold of distillate lubes that possess viscosities in this range. It is considered that distillates which possess even greater viscosities (e. g. up to 95 S. S. U./210° F. and even 110 S. S. U./210° F.) will also be particularly benefited by treatment with the eutectic rather than either hydroxide alone.

What is claimed is:

1. A method of refining a lubricating oil distillate derived from the fractionation of a naphtenic crude oil, said distillate having a viscosity of at least 1100 SUS at 100° F., wihch comprises the steps of treating the distillate with a eutectic mixture of sodium hydroxide and potassium hydroxide in an amount at least about 0.06 percent by weight in excess of the amount of hydroxide required to neutralize the acidity of the distillate, and then redistilling the distillate in the presence of the added hydroxides.

2. A method is defined by claim 1 wherein the distillate has a viscosity of at least 2000 SUS at 100° F.

3. A method as defined by claim 1 wherein the distillate has a viscosity of at least 2000 SUS at 100° F. and wherein the amount of eutectic employed is about 0.25 weight percent in excess of the amount required to neutralize the acidity of the distillate.

References Cited in the file of this patent

UNITED STATES PATENTS

1,903,407	Pew	Apr. 4, 1933
2,451,025	Ellender	Oct. 12, 1948

FOREIGN PATENTS

224,901	Germany	Oct. 22, 1925