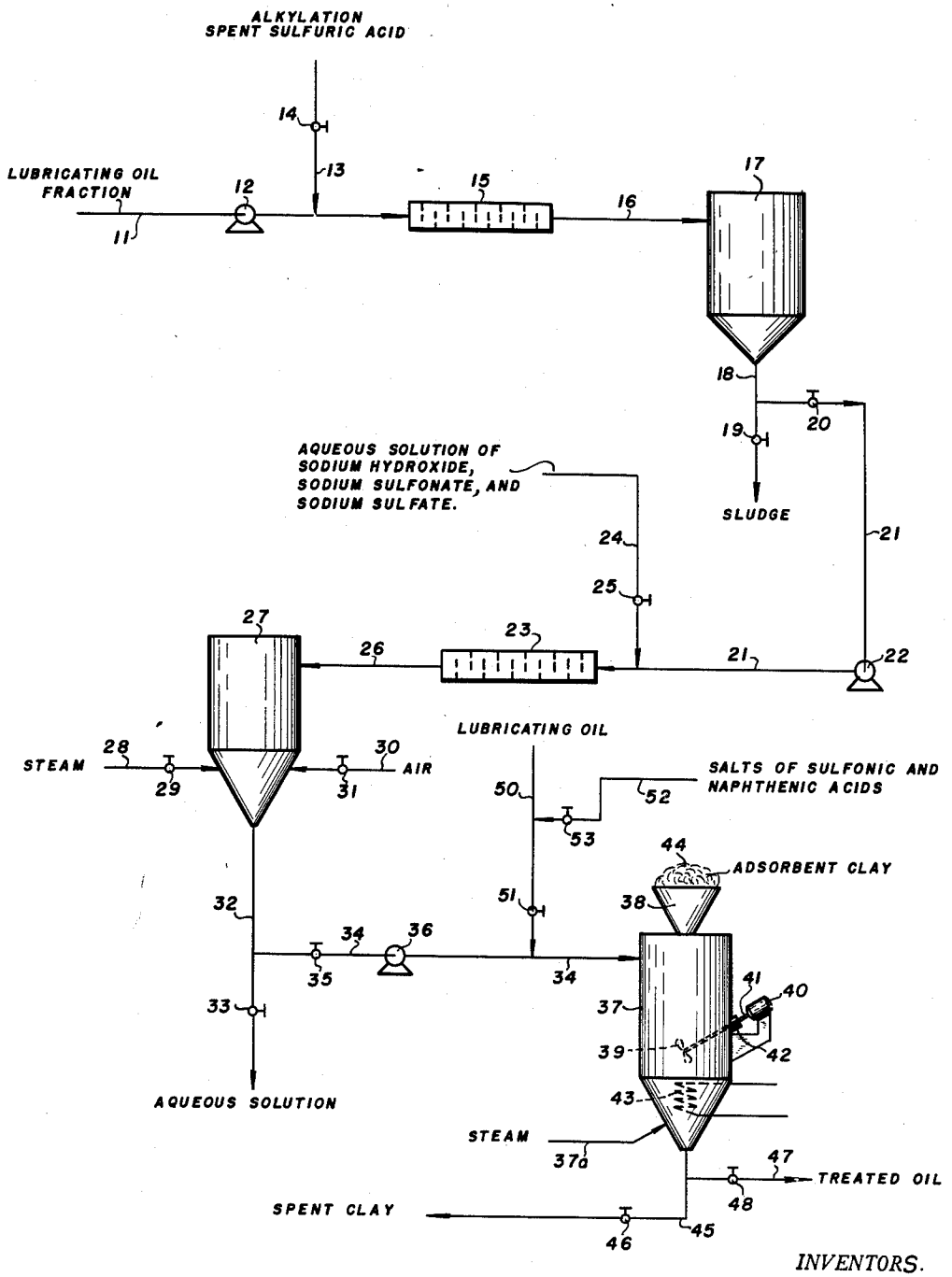
March 13, 1956 C. J. LEWIS ET AL 2,738,314

TREATMENT OF LUBRICATING OIL WITH ADSORBENT CLAY

Filed May 21, 1952



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United States Patent Office 2,738,314
Patented Mar. 13, 1956

2,738,314

TREATMENT OF LUBRICATING OIL WITH ADSORBENT CLAY

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Application May 21, 1952, Serial No. 289,092
8 Claims. (Cl. 196—147)

The present invention is directed to a method for treatment of lubricating oil. More particularly, the invention is directed to a method for improving the color of a lubricating oil fraction. In its more specific aspects, the invention is concerned with improving the color of lubricating oil fractions by contacting same with an adsorbent clay.

The present invention may be described briefly as involving the treatment of lubricating oil fractions for improving the color thereof by contacting the lubricating oil fraction with an adsorbent clay at an elevated temperature in the presence of small but effective amounts of alkali metal salts of naphthenic and sulfonic acids.

Our invention also contemplates a method for improving the color of lubricating oil fractions by adding to said lubricating oil fractions small but effective amounts of alkali metal salts of naphthenic and sulfonic acids and then contacting the lubricating oil fractions to which the alkali metal salts have been added at an elevated temperature with an adsorbent clay for a sufficient length of time to improve the color of the lubricating oil fraction.

The present invention also embraces a method for treating lubricating oil fractions which have been neutralized with an aqueous solution of alkali metal hydroxide, an alkali metal salt of an inorganic acid and an alkali metal salt of a sulfonic acid following which the neutralized fraction is contacted at an elevated temperature with an adsorbent clay in the presence of small but effective amounts of alkali metal salts of naphthenic and sulfonic acids.

The invention also includes a combination of steps in which the lubricating oil is treated first with alkylation spent acid, second the alkylation spent acid treated oil is neutralized with an aqueous solution of an alkali metal hydroxide, an alkali metal salt of an inorganic acid and an alkali metal salt of a sulfonic acid and following the neutralization treatment the neutralized oil is contacted at an elevated temperature with an adsorbent clay in the presence of small but effective amounts of alkali metal salts of naphthenic and sulfonic acids.

The lubricating oil fraction employed as a feed stock in the present invention may suitably be a distillate lubricating oil fraction, such as a Coastal lubricating oil distillate or a Mid-Continent lubricating oil distillate. Other lubricating oil fractons may also be employed as feed stocks.

The treating reagent employed to neutralize the alkylation spent sulfuric acid treated oil will ordinarily comprise an aqueous solution of an alkali metal salt of preferably water-soluble sulfonic acids, such as a sodium salt of sulfonic acids, an alkali metal hydroxide, such as sodium hydroxide, and an alkali metal salt of an inorganic acid, such as sodium chloride or sodium sulfate.

The water-soluble sulfonic acid from which the alkali metal salts employed in the treating reagent are produced may be either an aromatic sulfonic acid or an alkyl sulfonic acid. For example, the sodium salt may be produced by neutralizing aromatic sulfonic acids resulting from the treatment of benzene, toluene and xylene with strong sulfuric acid. The treating reagent suitably may be prepared by neutralizing the acid treated oil produced in the formation of aromatic solvents. The aromatic sulfonic acids from which the salts are produced for use

in the treating reagent may be obtained from acid solutions resulting from acid treatment of low molecular weight lubricating oils, such as solvent oils having a viscosity of about 75 SSU at 100° F.

It is also possible to employ alkyl sulfonic acids in the preparation of the alkali metal salts of sulfonic acid for use in the treating reagent. For example, heptyl sulfonic acid neutralized with sodium hydroxide may be used. The other alkyl sulfonic acids, such as the other members of the series of paraffinic hydrocarbons, such as hexane, octane, nonane, decane, undecane, dodecane and the like may be employed as starting materials for producing alkyl sulfonic acids. The neutralization agent may conveniently have a composition as follows:

TABLE I

	Percent
Alkali metal hydroxide	0.5–5
Alkali metal salt of sulfonic acid	10–15
Alkali metal salt of inorganic acid	5–7.5
Water	72.5–84.5

The solution of the treating reagent should have a specific gravity no less than 1.10. Solutions of the treating reagent prior to dilution with water may range from 1.2 to 1.3 in specific gravity.

The treating reagent employed in the process of the present invention should contain the several components recited before. It is necessary to have the inorganic salt present to confer gravity differential between the oil being treated and the treating reagent to facilitate settling and preven emulsions. The alkali metal salt of sulfonic acid is believed to act as a solutizer for the alkali metal salts of organic and inorganic acids which result from neutralization of such acidity with the free alkali metal hydroxide in the treating reagent. On omission of the alkali metal salts of sulfonic acid, the salts resulting from neutralization may remain in the oil and contribute to unsatisfactory results in that they may serve as nuclei for water and contribute to emulsion formation.

The alkali metal hydroxide in small amounts allows neutralization of organic and inorganic acidity and in the presence of the alkali metal salts of sulfonic acid and an inorganic acid is effective in neutralizing substantially larger quantities of organic and inorganic acidity than is possible conventionally.

The adsorbent clay employed in the practice of the present invention may be either a selected natural clay or an acid treated clay. There are many adsorbent clays commercially available which may be used in the practice of the present invention. It should suffice to say that the adsorbent clay should be of the type conventionally employed in lubricating oil contacting operations. Reference is made to Kalichevsky and Stagner, Chemical Refining of Petroleum, Reinhold Publishing Corporation, New York, 1942 for the type of contact clays which may be employed in the practice of the present invention.

The contacting operation in the practice of the present invention ordinarily will employ an amount of contact clay or adsorbent clay in the range from about 0.1 to about 1 pound of contact clay per gallon of oil. Amounts in the range from about 0.10 to 0.5 pound of contact clay per gallon of oil will give good results.

The contacting operation may be conducted at a temperature in the range from about 300° to about 500° F. Good results have been obtained at 400° F.

The oil should remain in contact with the clay for a time in the range from about 10 minutes to about 120 minutes with the preferred time of about 30 minutes.

The alkali metal salts of the sulfonic acids and naphthenic acids employed in the practice of the present invention either in the contacting operation or added to the oil prior to the contacting operation should be the

sulfonic and naphthenic acids normally encountered in petroleum refining operations. For example, the sulfonic acids may be either the mahogany or the green acids. The mahogany acids will be preferred and are predominantly oil soluble acids. However, the green acids are soluble to some extent in oil and may be employed in the practice of the present invention.

The naphthenic acids are those acids normally encountered in petroleum fractions boiling in the range of lubricating oil. It has been found that a mixture of sulfonic and naphthenic acid salts having a molecular weight of about 600 give satisfactory results when added to oil and the oil then contacted with clay to improve the color thereof.

In neutralizing acid oils such as those containing natural organic acidity or those containing acidity resulting from treatment such as with alkylation spent acids, it will be desirable to use an amount of treating reagent in the range from about 5% by volume based on the oil being treated to about 20% by volume. Satisfactory results may be obtained by employing amounts of treating reagent supra in the range from about 5% to 10% by volume.

It is contemplated that the present invention is applicable to treatment of oils containing organic or inorganic acidity or to neutralized oils which contained organic or inorganic acidity. Thus, in accordance with our invention, it is possible to contact oils with adsorbent clay in the presence of salts of sulfonic and naphthenic acids and obtain beneficial results in that the color of the oil is substantially improved over that obtainable in the absence of the salts of sulfonic acids and naphthenic acids.

The present invention will be further illustrated by reference to the drawing in which the single figure is a flow diagram of a preferred mode.

Referring now to the drawing, numeral **11** designates a charge line containing a pump **12** by way of which a lubricating oil fraction, such as a Coastal lubricating oil distillate, is introduced into the system from a source, not shown. The lubricating oil flows through line **11** and has introduced to it by way of line **13** controlled by valve **14** an amount of alkylation spent sulfuric acid in the range from about 3 pounds to about 50 pounds of spent sulfuric acid per barrel of oil. In this particular instance it may be assumed that the amount of spent sulfuric acid is about 15 pounds per barrel of oil. The oil-containing sulfuric acid then flows into incorporator **15** which is of the baffle plate type but may be any mixing device, such as a contacting tower, a jet mixer, a centrifugal pump or an agitating device similar to those available on the market. The oil and acid are intimately admixed in incorporator **15** and are then discharged by line **16** into a settler **17** wherein a separation is made between the sludge resulting from the treating operation and the acid treated oil. The sludge is withdrawn from the settling tank **17** by line **18** controlled by valve **19** and may be discharged from the system or further used or, if desired, recovered for concentration.

After the sludge has been drawn off through line **18**, valve **20** in line **21** is opened and the acid treated oil is pumped from tank **17** through line **21** by means of pump **22** into an incorporating device **23** which is similar to incorporating device **15** in admixture with an aqueous solution of a treating reagent introduced into line **21** by line **24** controlled by valve **25**. The aqueous solution of the treating reagent has been described hereinbefore.

In incorporator **23** the aqueous solution of the treating reagent and the acid treated oil are intimately admixed and the organic and inorganic acidity of the oil are substantially neutralized by the treating reagent. The mixture then flows by way of line **26** into settling zone **27** which is provided with line **28** controlled by valve **29** and line **30** controlled by valve **31** which allows the contents of tank **27** to be steamed and blown with air as desired. The temperature in tank **27** may be maintained in the range from 40° to 210° F. with the higher temperature preferred to allow substantial neutralization of acidity.

After the oil in tank **27** has been neutralized, the aqueous solution of treating reagent may be withdrawn therefrom by way of line **32** controlled by valve **33** for recovery of the aqueous solution for re-use as desired or the recovery of the chemicals contained in the aqueous solution. After the aqueous solution has been drawn off through line **32** the neutralized oil is withdrawn from tank **27** by line **34** containing valve **35** by pump **36** into a clay contacting drum **37** which is provided with a clay hopper **38** and a mixing device powered by a prime mover **40** through a shaft **41** extending into the vessel **37** through a stuffing box **42**. The tank **37** is also provided with a heating means illustrated by a steam coil **43** to maintain an elevated temperature in the range given for the contacting operation. Clay, such as natural clay **44**, shown in the hopper **38**, is dumped into the tank **37** which contains the neutralized oil.

The prime mover **40** is started which causes the agitator **39** to rotate and the contents of the tank **37** are heated to a temperature in the range given for a time in the range given to cause substantial removal of color bodies from the oil. In addition, superheated steam may be injected into the bottom of tank **37**, through line **37***a* to provide additional agitation as well as further heating.

After the contacting operation has been concluded, the spent clay is removed from drum **37** by line **45** controlled by valve **46** and thereafter, after removal of the clay, the treated oil of improved color is withdrawn by line **47** controlled by valve **48**. This oil is suitable for use in lubricating operations.

Instead of batch clay contacting as descripted, the contacting step may be carried out in a continuous manner by mixing the hot oil and clay in a tank to form a slurry of clay in oil, passing the slurry through a vessel wherein superheated steam is blown through the slurry, and continuously withdrawing a stream of slurry to a rotary filter to separate clay and oil.

In the practice of our invention it is possible to proceed directly with contacting the oil in contact drum **37**, by-passing the system up to line **34** by causing valve **35** to remain closed and pump **36** to be inoperative. In operating in accordance with this procedure, a lubricating oil fraction which may contain organic acidity may be introduced either in a treated or untreated condition into the system by a branch line **50** by opening valve **51**. Simultaneously, there is introduced by way of line **52** on opening valve **53** a mixture of salts of sulfonic and naphthenic acids. This conveniently may be a mixture in approximately equal quantities of the sulfonic acid salts and the naphthenic acid salts and for each of introduction may be in a carrier oil, such as a lubricating oil fraction.

For example, the stream introduced by line **53** may be 50% oil and 50% of equal parts of sodium sulfonates and naphthenates, the latter having a molecular weight averaging about 600.

The amount of alkali metal salts added to the lubricating oil either directly or indirectly may be in the range from about 0.05% by weight to about 0.3% by weight. Good results have been obtained with 0.1% by weight of combined sodium sulfonates and naphthenates.

In order to illustrate the invention further the following examples are given:

Example I

A low cold test lubricating oil distillate obtained by distilling a Coastal crude oil was treated with 21 pounds of 98% black sulfuric acid per barrel of lubricating oil. This acid treated oil was separated from the sludge that resulted and was then treated with the treating reagent given supra, water washed and finished by blowing with air. The treated oil had the following inspection characteristics:

TABLE II

Color, Tag-Robinson	10
Colorhold	6
Ash	0.005
Water soluble ash	0
Neutralization No.	0.006
Steam emulsion No., ASTM D157–15T	425

The oil treated with the treating reagent as outlined had a high steam emulsion number which is a measure of the emulsion characteristics of the oil, the larger the number the greater tendency of the oil to form emulsions. The colorhold test is the Tag-Robinson color of a specimen of the oil after holding it for 16 hours at 212° F. in an open bottle. This colorhold test is a measure of the color stability of lubricating oil under high temperature conditions and long storage time. The operations described in this example are operations prior to the present invention, in that, when using the treating reagent specified, the composition of which was given before, it was necessary to use the commercial 98% black sulfuric acid. When attempts were made to use alkylation spent acids which are available in the modern petroleum refineries, it was found that oils so treated with the treating reagent had an objectionable odor imparted to them which might affect deleteriously their marketability. Consequently, in the present invention, where the oil is contacted with adsorbent clay in the presence of the naphthenic and sulfonic acid salts, the oil may be treated with alkylation spent sulfuric acid and objectionable odors not imparted to the oil.

To demonstrate such feature of the present invention the same low cold test distillate distilled from Coastal crude was treated with 16 pounds of alkylation spent sulfuric acid per barrel of oil, the acid sludge settled and removed and the acid treated oil was treated with 6 volume per cent of the treating reagent supra. The acid-treated and neutralized oil was then divided into two portions. One portion was given two washes with water in the amount of 10–15 volume per cent while the other portion received no washing treatment. The two portions were then contacted for 30 minutes at 400° F. with an acid treated natural clay and a selected natural clay. The results of these contacting operations with the two clays are given in Table III.

TABLE III

	A		B	
Treatment Before Contacting	2 Water Washes	2 Water Washes	None	None.
Contacted 30 Min. at 400° F.:				
Type Clay	Acid Treated Natural.	Selected Natural.	Acid Treated Natural.	Selected Natural.
Dosage, Lbs./Gal.	0.2	0.2	0.2	0.2.
Inspections:				
Color, Tag-Robinson	10	8½	10¼	9½.
Colorhold	4¾	3¼	9	6.
Ash	0.001	0.004	0.002	0.001.
Water Soluble Ash	0	0.002	0	0.
Neutralization No.	0.02	0.04	0.06	0.05.

The runs designated "A" are the runs conducted prior to the present invention whereas the runs designated "B" are the runs in accordance with the present invention. It will be seen from the data in Table III that the present invention results in a product of improved color and the ash content including water soluble ash is not affected deleteriously; in fact the data indicate an improvement. The neutralization numbers of the product treated in accordance with the present invention, while slightly higher than those obtained heretofore, are quite satisfactory. It may be concluded from these data that the present invention results in an improvement in that spent alkylation acid may be used to treat such lubricating oil fractions without imparting objectionable odor characteristics and allowing an improved color to be obtained.

Comparing the data in Table III with the data in Table II, it may be seen that our invention allows the obtaining of an improved color, reduction of ash content and substantially unchanged neutralization number.

In order to illustrate the invention further a lubricating oil distillate from a Coastal crude was treated in a commercial operation with 18 pounds of alkylation spent sulfuric acid and then neutralized with a solution of the treating reagent described supra. The neutralized solution was then washed with water four times and blown bright with air. The so-treated lubricating oil distillate was divided into five portions. One portion was tested as is, the second portion was contacted at a temperature of 400° F. with 0.3 pound per gallon of selected natural clay and the third, fourth and fifth portions had added to them varying amounts of a solution of naphthenic and sulfonic acid salts in oil. The third, fourth and fifth portions were contacted like the first and second portions with selected natural clay in an amount of 0.3 pound per gallon of oil at 400° F.

The results of these operations are presented in Table IV.

TABLE IV

	Color	Colorhold	Wt. Percent Salts [1] Added	Ash	Water Soluble Ash	Steam Emulsion No., ASTM D157–159
1. Base Stock	4¾	3¼	0	0.003	0.001	400
2. 1 after contacting [2]	7¼	3¼	0	0.004	0.002	153
3. 1 after contacting [2] plus salts	9¾	7¾	0.14	0.002	0.001	215
4. Same as 3	9¼	5	0.21	0.003	0.001	127
5. Same as 3	7¼	4	0.28	0.002	0.001	227

[1] Added as 50% salts of sulfonic and naphthenic acids in oil concentrate. Average molecular weight of salts is estimated at 600. Composition of salt is estimated at 50% sulfonate and 50% sodium naphthenate.

[2] All contacts were made with 0.3 pound per gallon selected natural clay.

It may be seen from the inspection data given in Table IV that addition of salts in varying amounts resulted in a markedly improved original color and colorhold and decreased substantially the steam emulsion number of the oil. The steam emulsion number of the oils treated, as shown in this example, and represented in Table IV may be compared with the steam emulsion number of the oil and inspection characteristics represented by the data

given in Table II. It will be seen that the fourth and fifth portions have steam emulsion numbers lower than any of the operations other than in the present invention.

To illustrate the effectiveness of the present invention on oils which have not been treated with sulfuric acid and which contain organic acidity, a diesel lubricating oil was extracted with phenol to form a raffinate which was treated in accordance with the present invention with an aqueous solution of an alkali metal hydroxide, an alkali metal salt of sulfonic acid, an alkali metal salt of inorganic acid as described supra. The treatment with the treating reagent, a description of which has been given before, resulted in the oil having added to it or formed therein salts of naphthenic and sulfonic acids. This so-neutralized oil was divided into two portions, one of which was washed with water to remove the salts and the other was contacted with clay without any water washing operations. Inspection characteristics of the oil before extraction with phenol, the phenol raffinate, the phenol raffinate after contacting with clay without any pretreatment and the phenol raffinate after treatment with the treating reagent and water washing prior to and followed by clay contacting and the phenol raffinate after treatment with the treating reagent followed by clay contacting without any intermediate water washing. The results of these several treating operations are given in Table V.

TABLE V

	Chg.	Phenol Raffinate	Phenol Raffinate Clay Contacted [1]		
			As is	After treatment with an Aqueous Solution of Sodium Hydroxide, Sodium Sulfonate and Sodium Sulfate	After treatment with an Aqueous Solution of Sodium Hydroxide, Sodium Sulfonate and Sodium Sulfate+ Water Wash
Gr.	21.0				
V/100	2,037	1,135	1,092	1,131	1,098
V/210	98.0	81.5	80.3	81.7	80.7
Viscosity Index	36.0	64.1			
Neut. No.	1.5	0.32	0.116	0.011	0.003
Color, Tag-Robinson	1¾		10¾	18	9¾

[1] All contacts with 0.4 lb./gal. acid-treated clay for 30 min. at 400° F.

The data in Table V and in column 5 thereof shows the prior art practice where the oil was treated with treating reagent and washed with water and then clay contacted. The fourth column of data show the practice of the present invention while the third column of data is the oil contacted with clay without any neutralization. It will be noted that the treatment in accordance with the present invention resulted in a substantial lowering of the neutraliation number and a substantial appreciation of the Tag-Tobinson color. The foregoing data illustrate that our invention is not to be restricted to oils which have been treated with acid prior to the neutralization operation.

From the foregoing specific examples and the description taken with the drawing, it is clear that we have described an improved process for contacting lubricating oil with adsorbent clay.

The nature and objects of the present invention having been completely described and illustrated, what we wish to claim as new and useful and to secure by Letters Patent is:

1. A method for improving the color of a lubricating oil fraction which comprises contacting the lubricating oil fraction with an adsorbent clay at a temperature within the range of 300 to 500° F. in the presence of a mixture of approximately equal amounts within the range of .14% to .28% of alkali metal salts of naphthenic and sulfonic acids.

2. A method for improving the color of a lubricating oil fraction which comprises adding to said lubricating oil fraction a mixture of approximately equal amounts within the range of .14% to .28% by weight of alkali metal sulfonates and alkali metal naphthenates and then contacting said lubricating oil fraction containing said added sulfonates and naphthenates at a temperature in the range from 300° to 500° F. with an adsorbent clay for a sufficient length of time to improve the color of said lubricating oil fraction.

3. A method for improving the color of a lubricating oil fraction which has been neutralized with a treating reagent comprising an aqueous solution of an alkali metal hydroxide, an alkali metal salt of an inorganic acid and an alkali metal salt of a sulfonic acid which comprises contacting said neutralized lubricating oil fraction with an adsorbent clay at a temperature within the range 300 to 500° F. in the presence of a mixture of substantially equal amounts within the range of .14% to .28% by weight of alkali metal salts of naphthenic and sulfonic acids.

4. A method in accordance with claim 3 in which from 5% to 20% by volume of treating reagent is used.

5. A method for improving the color of a lubricating oil fraction which comprises treating a lubricating oil fraction with a reagent comprising an aqueous solution of an alkali metal hydroxide, an alkali metal salt of an inorganic acid and an alkali metal salt of sulfonic acid at a temperature in the range from 40° to 210° F. in a liquid phase, separating said aqueous solution from said treated lubricating oil fraction, contacting said treated lubricating oil fraction with an adsorbent clay at a temperature in the range between 300° and 500° F. in the presence of a mixture of substantially equal amounts within the range of .14% to .28% by weight of alkali metal salts of naphthenic and sulfonic acids, separating said adsorbent clay from said contacted lubricating oil fraction and recovering said contacted lubricating oil fraction.

6. A method in accordance with claim 5 in which from 5% to 20% by volume of treating reagent is used.

7. A method for improving the color of a lubricating oil fraction which comprises treating said lubricating oil fraction with alkylation spent sulfuric acid, separating said alkylation spent acid from said treated lubricating oil fraction, treating said alkylation spent sulfuric acid treated lubricating oil fraction with an aqueous solution of an alkali metal hydroxide, an alkali metal salt of an inorganic acid and an alkali metal salt of a sulfonic acid at a temperature in the range from 40° to 210° F. in the liquid phase to neutralize said acid treated oil, contacting said neutralized acid treated oil at a temperature in the range between 300° and 500° F. with an adsorbent clay in the presence of a mixture of substantially equal amounts within the range of .14% to .28% by weight of alkjai metal salts of naphthenic and sulfonic acids, and recovering an oil from said contacting operation of improved color.

8. A method in accordance with claim 7 in which from 5% to 20% by volume of treating reagent is used.

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