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PETROLEUM REFINING

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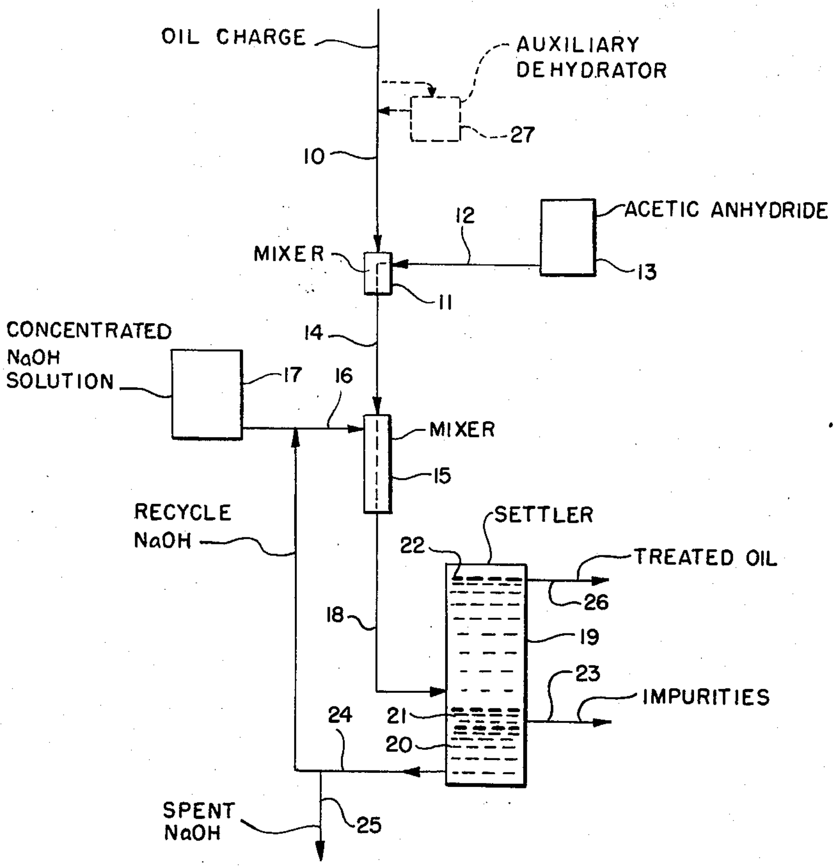

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PETROLEUM REFINING

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This invention relates to the refining of petroleum, and more particularly to the chemical refining of petroleum including both crude petroleum and the fractions produced therefrom in the course of processing the crude petroleum.

The present application is a continuation-in-part of my copending application Serial No. 691,957, now abandoned, filed October 23, 1957.

Most crude petroleums include various constituents, sulfur compounds, phenolic and nitrogenous bodies, acids and the like, which impart to the various fractions produced in the processing of the crude petroleum undesirable physical and chemical characteristics. These undesirable characteristics include bad odor, sourness to the conventional "Doctor" test, poor color stability in storage, formation of gummy precipitates in storages which, in the case of household fuel oils, are particularly deleterious. In the case of gasoline fractions, these undesirable constituents also frequently reduce the clear octane values of the fractions, as well as the lead susceptibility thereof.

Processing of the crude oil under the temperature and pressure conditions normally applied, frequently intensifies the undesirable characteristics noted. In catalytic cracking of petroleum fractions there is produced refractory recycle stock which is withdrawn from the system and which includes a large proportion which falls in the household fuel or burning oil range. This is commonly referred to as "light cycle oil" or "No. 2 fuel oil." This material is found to be unstable in storage, losing color rapidly and developing gummy precipitates and possessing highly undesirable odors, all of which makes the product undesirable and often a source of mechanical difficulty in use.

Various processes are presently employed in an effort to render these burning oil stocks satisfactory for their intended use. Among the more extensively used processes is hydrogenation which necessarily involves expensive equipment and high operating costs. Another process used is the treatment of the oil with concentrated caustic soda solution followed by subjecting the alkali treated oil to the action of electrical precipitators in order to remove, to the greatest extent possible, traces of the alkali reaction products which would otherwise remain suspended in the oil. This process, too, requires expensive equipment and relatively high treating costs.

I have found that the various petroleum distillates which possess the aforementioned undesirable characteristics may be rendered entirely free of these characteristics by a simple chemical treatment which is not only highly efficient, but comparatively cheap.

The process of this invention may be applied to the various distillates at appropriate stages following their production in conventional refining operations, or may be applied to the crude petroleum, itself, prior to subjecting it to the usual processing operations. In the case of the catalytically cracked cycle stocks, the process will usually be applied to the cycle stock in order to obviate the undesirable properties imparted to this material by the catalytic treatment.

The process in accordance with this invention comprises the liquid phase chemical treatment of petroleum by two reagents applied to the oil in succession under controlled conditions.

In accordance with a preferred embodiment of this invention, the first treatment stage comprises thoroughly admixing with the oil a small proportion of acetic anhydride and thereafter, without intermediate settling or other processing, vigorously admixing with the oil containing the acetic anhydride a quantity of concentrated aqueous sodium hydroxide solution. The admixture is thereafter allowed to settle, the settling operation resulting in the production of a three-layer system, an upper layer comprising treated oil; an intermediate layer comprising reaction products which I term "soaps"; and a bottom layer comprising the concentrated sodium hydroxide solution, which includes sodium acetate and water produced by the reactions occurring in the treating process.

The treated oil is withdrawn to storage, the intermediate layer to waste or other disposal treatment, and the sodium hydroxide solution is recirculated in the treating system, all as will be more fully described hereinafter.

It is found that treatment of the oil by the process described removes undesirable odors; renders the oil completely stable to the standard stability test (which comprises subjecting a sample of the oil in an open container to a temperature of 212° F. for 24 hours), the resulting stability obviating color loss or formation of precipitates. Moreover, the oil is rendered sweet to the conventional "Doctor" test.

In the case of gasoline distillates, the treatment results in improvement in the clear octane values of stocks, as well as in a considerable increase in the lead susceptibility of these stocks.

The mechanism of the reactions which occur in the treating process of the present invention is not fully understood but it is thought that some type of acylation reaction occurs between the acetic anhydride and the mercaptans and other types of sulfur bodies in the oil, and with the nitrogenous bodies and phenolic or other hydroxy or carboxylic compounds which may be present. Accordingly, I refer to the process as "acylfining." Some of the products of reaction appear to remain in the oil, but without any apparent deleterious effect, while others appear in the intermediate layer as sodium salts or "soaps" and are separated from the oil. It will be understood, therefore, that this invention should not be considered as dependent upon any specific reaction mechanism or theory but is to be based upon the procedure employing certain specified reagents as herein set forth.

As indicated previously, acetic anhydride is my preferred reagent for the first stage treatment and concentrated aqueous sodium hydroxide solution for the second stage treatment. This is primarily because both are readily available in large quantities at relatively low prices. These materials have been successfully used on a commercial scale for the continuous treatment of an average of 5000 barrels per day of light cycle oil from catalytic cracking units and mixtures thereof with straight run gas oil.

Tests on a laboratory scale have shown that other acid anhydrides, both aliphatic and aromatic, may be used, but are generally more expensive and not as efficient in some instances as the preferred acetic anhydride. Other anhydrides include propionic, butyric, and hexanoic anhydrides in the aliphatic category, and phthalic and benzoic anhydrides in the aromatic category these latter, being normally solids, must first be dissolved in a suitable solvent, such as benzol, which will be fully miscible with the oil being treated. Mixtures of the anhydrides can also be used.

It will be obvious that concentrated potassium hydroxide solution may be used in place of sodium hydroxide, but will be more expensive.

The drawing constitutes a flow sheet illustrative of the flow of the oil and the preferred reagents through the system in accordance with the method of this invention.

As illustrated in the flow diagram, the oil to be treated is fed through a line **10** into a mixer **11** wherein the oil is thoroughly admixed with a small quantity of acetic anhydride delivered to mixer **11** through a line **12** from a suitable storage vessel **13**. Mixer **11** may be of any suitable and generally conventional form and as acetic anhydride dissolves very quickly in petroleum oil the mixer may be of very simple construction. Thorough mixing of the acetic anhydride with the oil is thus effected in mixer **11**, whereupon the mixture is passed through a line **14** directly to a second mixer **15** in which the oil containing the acetic anhydride is thoroughly agitated with a quantity of concentrated aqueous sodium hydroxide drawn through line **16** from a storage vessel **17**. Mixer **15** is also of generally conventional form adapted to assure thorough mixing of the oil and alkali solution. The oil and chemical mixture is then introduced through a line **18** into a settling vessel **19** wherein settling and stratification occurs. The alkaline reagent, indicated at **20**, settles to the bottom; the "soap" products of the reaction form a layer, indicated at **21**, at the interface between the oil and the alkaline reagent; and the treated oil, indicated at **22**, collects on top of the other layers. The stratification takes place rapidly and an exceptionally sharp "break" occurs between the layers in this type of treatment. The "soap" reaction products, which may be termed the "impurities," are withdrawn through the line **23** and sent to any suitable place of disposition. The alkaline reagent is withdrawn from the bottom of vessel **19** through a line **24** and recirculated to mixer **15** through line **16**, make-up sodium hydroxide solution being added from tank **17**, as required. A portion of the spent alkaline reagent may be withdrawn continuously or intermittently from the recirculating alkali through a pipe **25** for purification and re-use. The treated oil is withdrawn from the top portion of vessel **19** through a line **26** and sent to storage or to other processing units as may be desired.

The entire procedure is a liquid phase treating process which is conducted at atmospheric temperatures and pressures, although where light gasoline distillates are treated, the operation may be conducted in a closed system under sufficient pressure to prevent vaporization and loss of light fractions.

The acetic anhydride is added to the oil in proportions varying generally with the character and source of the oil to be treated. In general, only a very small amount of acetic anhydride is necessary, this amount being at least 0.001% by weight and preferably varying from about 0.001% by weight to about 1.0% by weight of the oil treated. In terms of volume, about 0.02% to about 0.50% of the anhydride will usually suffice to treat petroleum distillates. In terms of parts per million (p.p.m.) about 200 p.p.m. to 5000 p.p.m. of the acid anhydride will suffice in most cases. Straight run gas oil or lighter distillates from relatively sweet crudes generally require the minimum quantities, while the corresponding boiling range stocks from sour crudes or from catalytic cracking operations, particularly those relatively high in sulfur compounds, phenolic and nitrogenous bodies and organic acids, will require the larger proportions. In the case of light cycle oil from catalytic cracking .05 to .10% by volume of acetic anhydride is found to be most generally applicable. In the case of crude oil, larger quantities, around 0.1% to 1% by weight of the anhydride, are preferably used.

The amount of the acid anhydride and the time of contact with the oil must be such that after subsequent treatment of the mixture of the acid anhydride and oil with the alkaline reagent a sample of the treated oil heated in an oven at 212° F. for 24 hours shows an improved color as compared to an untreated sample of the same oil heated at the same temperature for the same time. In most cases, at least 10 parts of the acid anhydride per million parts of oil is required and in practice 300 to 1000 p.p.m. have given good results in treating kerosene, fuel oils and solvent naphthas. In gasoline where the principal contaminants are mercaptans having the formula RSH where R is an organic radical, a minimum of one mole of acid anhydride per mole of RSH is required for treatment. A practical way of calculating the amount of acid anhydride is to use one mole of anhydride per mole of mercaptan in the gasoline plus 10% by weight of the anhydride. In treating crude oil, where not only RSH compounds but various phenolic derivatives are present, larger amounts of the anhydride are required but usually 1% by weight (10,000 p.p.m.) will suffice.

The sodium hydroxide solution is added to the admixture of the oil with the acetic anhydride immediately following the addition of the latter. The time interval between the additions to the oil of the first and second reagents is variable, it being only important that the acetic anhydride be thoroughly mixed with the oil before the alkali solution is admixed therewith. While ordinarily the alkali will be added immediately after completion of the mixing of the acetic anhydride with the oil, the treatment may be successfully effected even though the alkali is added hours or days after the addition of the acetic anhydride to the oil.

It appears that whatever may be the reactions which occur between the acetic anhydride and the constituents of the oil, these reactions occur substantially instantaneously so that it is only necessary to employ sufficient mixing to assure that the acetic anhydride has been thoroughly distributed through the oil before the alkali solution is applied. It is important to note, therefore, that the reagents should be added separately and successively, the alkali solution following the anhydride addition, but that the time interval between the additions of the reagents is not particularly important.

The caustic alkali solution is preferably one which contains not more than 75% water. Preferably the fresh alkali solution will contain about 40% NaOH (44.2°Bé.). Stronger solutions of caustic alkali may be used, but these tend to produce mechanical and handling difficulties, particularly when low temperatures are encountered. In general, however, solutions containing at least 25% NaOH and preferably at least 35% NaOH are required for efficient results. In the course of use, the sodium hydroxide will react with excess acetic anhydride and form sodium acetate, which becomes dissolved in the sodium hydroxide solution, thereby reducing the amount of the NaOH in the latter. However, since the formation of the sodium acetate requires three moles of water of hydration per mole of sodium acetate, the concentration of the sodium hydroxide in water remains high.

Also some water formed in the reactions will be added to the alkali solution, as well as some free moisture which may be present in the oil undergoing treatment.

The reaction of the alkali with the impurities in the oil, as noted previously, produces sodium salts or "soaps" of those impurities which will be salted out and appear as the intermediate layer between the treated oil and the alkaline reagent, as noted previously. Generally the quantity of such "soaps" will run to about 0.1% by volume of the oil treated but may be considerably less in many cases.

The treated oil, which is drawn off from the upper portion of the settler **19**, is found to be free of undesirable odors, sweet to the "Doctor" test, and completely stable to the standard stability test mentioned above, and require no further treatment for utilization for burning oil purposes.

A portion of the spent alkaline reagent will be withdrawn from the process and purified and reconcentrated for re-use in the process. When the concentration of sodium hydroxide in the reagent has fallen to 25%, the material is considered spent and is withdrawn. It may be subjected to distillation, either by vacuum flashing, or otherwise, in order to flash off excess water and thereby reconcentrate the solution. This evaporation of excess water will produce a fractional crystallization of the sodium acetate in the solution and this, too, may be separated in order to restore the sodium hydroxide solution to the desired 40% concentration. As noted, fresh make-up sodium hydroxide solution may be added to the circulating stream of this reagent entering mixer **15** to replace losses thereof in the process.

The amount of alkaline reagent should be sufficient to substantially neutralize the acid formed in the reaction between the acid anhydride and components of the oil and also the acid formed by decomposition of the acid anhydride due to water present in the oil or to the water added with the alkaline reagent. The amount required for neutralization can be calculated from the fact that each mole of acid anhydride produces one-half mole of acid when it reacts with substances in the oil containing —OH and —SH groups and each mole of water produces two moles of acid by reaction with the acid anhydride.

The volume of the solution containing the alkaline reagent will usually be the minimum volume required to obtain optimum contact between the alkaline reagent and the oil being treated. In some cases, this may be as low as 0.5% and in other cases as high as 10% by volume of the oil. In practice, the use of 5% by volume of a solution of the alkaline reagent based upon the volume of the oil has usually been found to be satisfactory. If a longer time of treatment is used, a lower volume percentage of the solution of the alkaline reagent can be employed but the longer treatment may be undesirable because of side reactions such as saponification. While larger volumes of the alkaline reagent solution can be used, say up to 50%, such use has no particular advantage and requires the handling of larger volumes of materials which is generally undesirable.

The time of treatment of the oil with the acid anhydride should be sufficiently long to insure adequate mixing and will vary somewhat depending on the volumes treated. Usually 15 seconds to 5 minutes is adequate but in some cases up to 30 minutes will be used. The reactions between the acid anhydride and substances in the oil containing —SH and —OH groups appear to take place quite rapidly and the maximum mixing time is not critical. In the treatment with the alkaline reagent the time of contact should be sufficient to neutralize the acid in the oil and sufficient to produce a sharp break between the water miscible phase and the oil phase. If the time of contact is too long, the saponification of esters produced by the treatment causes formation of soaps and the net result is a poor break or separation which is readily observed. As a practical matter, the time of treatment can be determined by withdrawing samples of the reaction mixture and testing them to ascertain whether they break properly and whether the oil phase is substantially free from the alkaline reagent. When the alkaline reagent consists of a solution of a caustic alkali and water a sample drawn in a four ounce bottle to which a few drops of an indicator, such as phenolthalein, is added will show tiny red specks if dispersed caustic is present in the oil. If more than a few such specks are present, it is an indication that too much caustic has been added or that the time of contact has not been sufficient to complete the neutralization. In general, the time of contact with the alkaline reagent is quite short, e.g., 15 seconds to 5 minutes.

The temperature of the treatment with the acid anhydride is subject to variation but good results have been obtained by operating at ordinary temperatures and pressures. Temperatures of 90° F. to 110° F., preferably 100° F. to 105° F., have been very satisfactory but higher temperatures, say 150° F. to 200° F. can be used. Lower temperatures in the liquid phase can be used but would require refrigeration which is not economically feasible. Since the reaction between the oil and the acid anhydride proceeds almost instantaneously at ordinary temperatures, there is no practical reasons for using higher temperature. The temperatures used in the treatment with the alkaline reagent are also preferably ordinary temperatures in the same range as those given for the acid anhydride. Higher temperatures in the range of 150° F. to 200° F. can be used but are not required.

Where the oil charged to the process contains more than a trace of free moisture, the oil may be sent through a suitable dehydrating device such as the vessel **27**, shown in broken lines on the flow diagram, before proceeding to mixer **11**. In vessel **27** the excess water may be removed by settling, or by dehydration by contact with concentrated brine, calcium chloride, rock salt or other dehydrating agent. The presence of more than traces of water in the oil results primarily in the wastage of reagents, but does not otherwise affect the result sought by the process.

The process above described may be applied directly to crude petroleum before it is charged to the crude stills, in which instance the oil leaving the settler **19** when subjected to the usual distillation process, will produce distillate fractions, namely, the gasoline, kerosene, and light gas oil, which will be found to be sweet to the "Doctor" test. The gasoline fractions will usually be found to have maximum clear octane values and maximum lead susceptibility as compared with the stocks from the same crude subjected to the same type of distillations, but without previous treatment of the kind described above. Moreover, the kerosene and light gas oil fractions which ordinarily go into burning oils will not only be sweet to the "Doctor" test, but will have good burning qualities, will be free of undesirable odors and will be completely stable in storage.

The same character of improvement will be noted when treating straight run, thermally cracked, or catalytically cracked gas oils which are to be used for burning oils.

Heavy gas oils obtained from the crude distillation and employed as feed stock for catalytic cracking units are additionally found, as a result of the described treatment whether applied to the crude petroleum or to the heavy gas oil directly, to be substantially free of coke-forming constituents, such for example, as organic acids, and thus are greatly improved as feed stocks for catalytic cracking operations.

The following examples illustrate the practice of the invention.

Example I

The following data are taken from a plant scale operation conducted in accordance with this invention.

Charge stock.—Mixture of 70% catalytically cracked light cycle oil—30% straight run light gas oil.

	Before Treating	After Treating
Color (Union Colorimeter)	1.5	1.5.
Odor	Poor	Good.
Stability (212° F./24 hrs.):		
Color	8+	1.5.
Precipitates	Substantial	None.
Doctor	Positive	Negative.
Burning Tests	Poor	Good.

TREATING CONDITIONS

Temperature and Pressure	atmospheric.
Acetic Anhydride added	0.05% by volume of oil.
Sodium Hydroxide Solution (44.2° Bé.)	12% by volume.

In this operation in which 5000 barrels per day of the charge stock were treated in a continuous operation, the sodium hydroxide solution was admixed with the oil within about 15 seconds after the acetic anhydride was added to the oil.

Example II

This example illustrates the importance of using a concentrated solution of the caustic alkali in the second step of the process. To demonstrate this a number of runs were made with the same acid anhydride treatment of the oil followed by a treatment with different concentrations of sodium hydroxide solutions.

The charged stock was a light recycle oil having the following specifications:

API gravity	22.
Initial boiling point, ° F.	438.
End boiling point, ° F.	660.
Flash point, ° F.	222.
Color (Union Colorimeter)	Lighter than 2.
Odor	Unpleasant.

The reagents employed were acetic anhydride (98–99.5% pure) and aqueous solutions of sodium hydroxide having varying concentrations.

The following test procedure was used:

One liter samples of the light recycle oil were employed for each test. The acetic anhydride was first thoroughly mixed with the oil, and the resulting mixture thereafter vigorously agitated with the sodium hydroxide solution, which was then allowed to settle. The treated oil was separated from the reagent and subjected to an accelerated stability test. In this test, 100 ml. of treated oil was placed in a four-ounce (120 ml.) bottle closed with a vented cork and placed in an oven for 24 hours at 212° F. Darkening of oil and precipitate formation was a measure of the long-time storage characteristics of the oil.

The only variation in the several tests was in the concentration of sodium hydroxide in the solutions thereof in the several treatments conducted.

For purposes of the comparison, samples of the light recycle oil were treated with aqueous sodium hydroxide solutions having the following concentrations of NaOH by weight: 20%, 25%, 30%, 35% and 40%.

The quantities employed were:

	Percent by volume
Acetic anhydride	0.05
Sodium hydroxide solution	10.0

The following treating conditions were used:

(*a*) Acetic anhydride—oil contact time	30 seconds.
(*b*) Sodium hydroxide—oil contact time	60 seconds.
Setting time (*b*)	60 minutes.
Temperature (atmospheric) Pressure (atmospheric)	75 ° F.

The results obtained were as follows:

Strength of Caustic Solution	Odor	After Accelerated Storage Test	
		Color [1]	Sludge
Untreated	Poor	8+	Yes.
20%	do	Lighter than 4½	Yes.
25%	do	Lighter than 2½	No.
30%	do	2	No.
35%	do	2	No.
40%	Excellent	Lighter than 2	No.

[1] Color Union Colorimeter Scale. A color of 2½ after accelerated storage test is maximum acceptable to meet commercial specifications. A value of 8 is the maximum attainable on the Union scale and corresponds to a cherry red. The color before accelerated storage in each case was lighter than 2.

Example III

This example illustrates the results obtained with varying proportions of acetic anhydride followed by intimate mixing with a 45% solution of caustic soda, the acetic anhydride-oil contact time being approximately 30 seconds and the sodium hydroxide solution-oil contact time being approximately 5 minutes.

The oil treated was a straight run sour naphtha and the results were evaluated by a Doctor test and by analysis for percent R—SH sulfur in the product. The untreated naphtha was shown to be sour by the Doctor test and the percent R—SH sulfur was 0.027% by weight.

In this case, after the treatment with the acetic anhydride and the caustic soda solution, the oil samples were still sour by the Doctor test. However, the percent R—SH sulfur had been materially reduced as shown by the following table:

Percent by Vol. Acetic Anhydride	Percent by Weight R-SH Sulfur
0.03	0.009
0.05	0.004
0.07	0.003
0.10	0.002

Tests were also made in which the sour naphtha was premixed with a 45% NaOH solution in water for 5 minutes. In the resultant oil the R—SH sulfur was reduced from 0.027% to 0.016%. This oil which had previously been mixed with the sodium hydroxide solution was then treated with varying proportions of acetic anhydride from 0.01% to 0.10% by volume and thereafter treated with 45% NaOH solution for 5 minutes, the results being generally comparable to those obtained without first treating the oil with the sodium hydroxide solutions. From these results it appears that while a pretreatment of the oil with the alkaline reagent may be employed it affords no particular advantages.

Example IV

This example illustrates the effect of using different anhydrides on a straight run sour naphtha. The sour naphtha after washing with 3% of sodium hydroxide to remove hydrogen sulfide had a copper number of 18 and contained 0.06% sulfur. After treating this naphtha with a 45% aqueous solution of NaOH for 5 minutes it still had a copper number of 18 and contained 0.06% sulfur.

When samples of the untreated naphtha were mixed with various anhydrides using 2 moles of anhydride per mole of R—SH sulfur for 30 seconds followed by mixing the resultant product with a 45% sodium hydroxide solution for 5 minutes, the following results were obtained:

Anhydride:	Copper No.
Untreated naphtha	18.
Acetic anhydride	Less than 1.
Benzoic anhydride	Do.
Butyric anhydride	Do.
Hexanoic anhydride	1.
Propionic anhydride	Less than 1.
Maleic anhydride	9.
Succinic anhydride	11.

Example V

This example illustrates the use of an alkaline reagent consisting of potassium hydroxide dissolved in water and mixtures of potassium hydroxide and potassium acetate. In this case a No. 2 catalytically cracked fuel was used and the results were evaluated by the color of the oil after an accelerated storage stability test in which the oil was heated for 24 hours at 212° F. The color evaluation was made according to the method used by the National Petroleum Association employing a Union Colorimeter.

The oil was treated with 0.05% by volume of acetic anhydride for 30 seconds and the resultant mixture was then shaken for 60 seconds with the alkaline reagent.

The following results were obtained:

Alkaline Reagent		Accelerated Storage Stability Test, 24 Hrs. at 212° F., N.P.A.
Percent KOH	Percent $KOOCCH_3$	
--------	------------	8+.
50	------------	less than 2.
40	------------	Do.
30	------------	2½.
20	------------	8+.
10	------------	black.
40	11.5	less than 2.
20	33.5	less than 2½.
10	45.0	less than 4.
2	53.5	less than 4½.

The original color of this oil was less than 2 but it will be observed that after the accelerated storage stability test the color was very dark, being greater than 8. On the other hand, treatment with solutions of the alkaline reagent containing 30% to 50% by weight of KOH gave an oil which, even after the accelerated storage stability test had a color varying from less than 2 to 2.5. When the concentration of KOH in the solution of the alkaline reagent was reduced to 20% the oil after an accelerated storage stability test again had a color greater than 8 and when the concentration was 10% KOH, the oil after the accelerated storage stability test was black. Where the solution of the alkaline reagent also contained potassium acetate it was possible to decrease the amount of KOH and still obtain improved stability. However, the relative concentration of KOH was still high because the amount of water was less. Thus, when the KOH was 20% by weight, the potassium acetate was 33.5% by weight, and the water was 46.5% by weight so that the relative concentration of KOH in water was about 30%. In all of these tests the amount of water was always less than 75% for effective results.

From the foregoing it will be seen that this invention provides an exceptionally effective, simple, low cost process for the treatment of petroleum oils by which exceptional improvement in the physical and chemical properties thereof is effected. Distillate products, such as the gasoline fractions and burning oil fractions, when treated by the method in accordance with this invention become finished stocks requiring no further processing before use.

Since, as noted previously, some earlier and existing refining methods employ agitation of petroleum stocks with highly concentrated alkali hydroxide solutions, the present invention may also be considered to constitute an improvement in such earlier methods, the improvement comprising the step of admixing with the oil, in advance of the agitation thereof with the alkali solution, a relatively small proportion of an organic acid anhydride, more specifically, with acetic anhydride.

The copper number refers to the number of milliliters of standard cupric ammonium sulfate solution required to react with 100 ml. of sample (gasoline, kerosene, oil, etc.). The solution is standardized so that one ml. of solution is equivalent to one mg. of copper.

The Cu^{++} ion reacts with mercaptans to form copper mercaptides.

$$Cu^{++} + RSH \rightarrow Cu(SR)_n + 2H^+$$

Cu atomic wt.	63.54
S atomic wt.	32.06
Two S	64.12

Since 1 atom of Cu reacts with 2 atoms of S, it can be said that 1 ml. of the copper solution is equivalent to 1 mg. of mercaptan S. Therefore,

$$\text{Percent marcaptan sulfur} = \frac{\text{Cu No.} \times .001}{\text{Sp. gr. of sample}}$$

The invention is applicable to the treatment of various types of gasoline, tractor fuel, diesel fuels, jet fuels, heating oils, illuminating products, solvents and other types of oils as defined in Encyclopedia of Chemical Technology under the heading "Petroleum Products", pages 164–175.

Other variations and modifications of the details of this invention will be apparent to those skilled in the art within the scope of the appended claims without departing from the spirit of this invention.

The invention is hereby claimed as follows:

1. The method of refining petroleum oil, comprising admixing with a petroleum oil stock in the liquid phase an organic acid anhydride in a minimum amount of at least 0.001% by weight of the oil, thereafter agitating the admixture with a concentrated aqueous alkali hydroxide solution containing at least 25% by weight of alkali hydroxide, the amount of said alkali hydroxide being sufficient to neutralize the acid of said anhydride produced by reactions between said anhydride and other substances present in said oil, the volume of said concentrated alkali hydroxide solution being sufficient to obtain intimate mixing, and separating the treated oil from the resultant mixture.

2. The method of refining petroleum oil, comprising admixing with a petroleum oil stock in the liquid phase acetic anhydride in a minimum amount of at least 0.001% by weight of the oil, thereafter agitating the admixture with a concentrated aqueous alkali hydroxide solution containing at least 25% by weight of alkali hydroxide, the amount of said alkali hydroxide being sufficient to neutralize the acid of said anhydride produced by reactions between said anhydride and other substances present in said oil, the volume of said concentrated alkali hydroxide solution being sufficient to obtain intimate mixing, and separating the treated oil from the resultant mixture.

3. The method of refining petroleum oil according to claim 2 wherein said petroleum oil stock is crude petroleum.

4. The method of refining petroleum oil according to claim 2 wherein said petroleum oil stock is a distillate fraction.

5. The method of refining petroleum oil according to claim 2 wherein said petroleum oil stock is the light cycle stock, commonly designated as "No. 2 Fuel Oil," obtained from the catalytic cracking of petroleum.

6. The method of refining petroleum oil comprising admixing with a petroleum oil stock in the liquid phase a small volume in the range from about 0.02% to 0.50%

by volume of acetic anhydride based on the volume of the oil, thereafter agitating the admixture with 0.5 to 50 volume percent of aqueous sodium hydroxide solution containing at least 35% by weight of sodium hydroxide, the amount of sodium hydroxide being sufficient to substantially neutralize the acetic acid in the admixture, and separating the treated oil from the resultant mixture.

7. The method of refining crude petroleum oil comprising admixing with a crude petroleum oil stock in the liquid phase a small amount within the range of about 0.10% to about 1% by weight of acetic anhydride, thereafter agitating the admixture with aqueous sodium hydroxide solution containing at least 35% by weight of sodium hydroxide, the amount of sodium hydroxide being sufficient to substantially neutralize the acetic acid in the resultant mixture, and separating the treated oil from the resultant mixture.

8. The method of refining petroleum according to claim 6 wherein said petroleum stock is a distillate fraction.

9. The method of refining petroleum oil according to claim 6 wherein said petroleum oil stock is the light cycle stock commonly designated as "No. 2 Fuel Oil" obtained from the catalytic cracking of petroleum.

10. The method of refining petroleum oil comprising admixing with a petroleum oil stock in the liquid phase acetic anhydride in an amount ranging from about 0.02% to about 0.50% by volume, thereafter agitating the admixture with aqueous sodium hydroxide solution containing at least about 35% by weight of sodium hydroxide, the amount of sodium hydroxide being sufficient to substantially neutralize the acetic acid in the resultant mixture, separating the treated oil from said solution and reaction products, and returning said sodium hydroxide solution to contact with further quantities of said admixture.

11. The method of refining petroleum oil comprising admixing with crude petroleum oil before distillation thereof acetic anhydride in an amount ranging from about 0.1% to about 1.0% by weight, thereafter agitating the admixture with 0.5 to 50 volume percent of aqueous sodium hydroxide solution containing at least about 35% by weight of sodium hydroxide, separating the treated crude oil from the sodium hydroxide solution and reaction products, and thereafter subjecting the treated crude oil to distillation.

12. The method of refining petroleum oil comprising admixing with a petroleum oil stock in the liquid phase 0.001 to 1.0% by weight of at least one organic acid anhydride from the group consisting of acetic, propionic, butyric, hexanoic, benzoic and phthalic anhydrides, thereafter directly subjecting the admixture containing the anhydride to intimate agitation with 0.5 to 50 volume percent of a concentrated solution containing at least 25% by weight of an alkali hydroxide from the group consisting of sodium hydroxide and potassium hydroxide, the amount of said hydroxide being sufficient to substantially neutralize the acid formed from said anhydride, and separating the treated oil from the resultant mixture.

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2,462,391	Hartough et al.	Feb. 22, 1949

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,889,195 June 2, 1959

Charles O. Hoover

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 30, for "storages" read -- storage --; column 6, line 30, for "temperature" read -- temperatures --; column 7, line 73, for "Setting" read -- Settling --; lines 74 and 75, same column, should read as shown below instead of as in the patent -

Temperature (atmospheric) - - - 75° C.
Pressure (atmospheric)

column 8, first table, under the heading "Odor", the first five items in the column should read as shown below instead of as in the patent -

Poor
do
Good
do
do

same column 8, line 60, for "solutions" read -- solution --; column 10, line 24, for "marcaptan" read -- mercaptan --.

Signed and sealed this 16th day of February 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents