

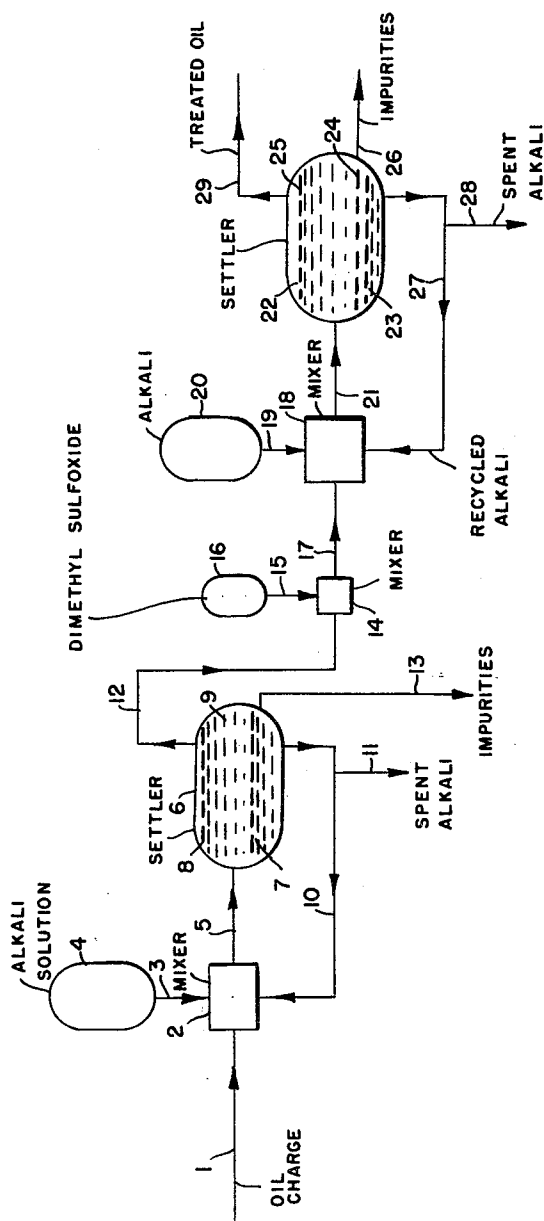
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TREATMENT OF PETROLEUM PRODUCTS

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1

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TREATMENT OF PETROLEUM PRODUCTS

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The present invention relates to the refining of petroleum, and more particularly to the chemical refining of petroleum including both crude petroleum and fractions produced from crude petroleum.

Most crude petroleum contains impurities such as sulfur compounds, phenolic and nitrogenous bodies, acids, and the like, which give the various fractions produced from the crude oil undesirable physical and chemical characteristics. These undesirable characteristics include bad odor, sourness to the conventional "doctor" test, poor color stability in storage, and formation of gummy precipitates in storage. The presence of contaminants of the above type in gasoline fractions frequently reduces the clear octane value of the product as well as the lead susceptibility of the gasoline. The effects produced by harmful contaminants have recently become even more important due to the trend in the automotive industry toward higher engine horsepower and compression ratios. It has also been found that modern methods of processing crude oil at high temperature and pressure conditions intensifies the undesirable effects caused by the impurities.

A number of processes have been developed in an effort to improve the characteristics of gasoline, kerosene, and other petroleum fractions. Although many of these processes have met with some success, each of them has important drawbacks. The well known "hydrofining" treatment of oils, for example, requires expensive equipment and involves high operating costs. In another process, gasolines and kerosenes are treated with copper chloride to convert mercaptans. The presence of copper in the refined material, however, causes the product to be relatively unstable on storage. For this reason, it is necessary to add a metal deactivator to any petroleum fraction which has been treated in this manner.

Among the compounds most widely used for treating petroleum fractions are the alkali metal hydroxides. These chemicals have been added to petroleum products to extract mineral and organic acids for over 50 years. If proper contact is maintained, sodium hydroxide will also reduce the H_2S content of gasoline and, to some extent, remove alkyl and aryl mercaptans.

One of the criteria used to judge the quality of kerosene, gasoline, No. 1 and No. 2 fuel oils is its mercaptan content as determined by the so-called "doctor" test. A "doctor" sweet gasoline contains less than 0.0003–0.0006% by weight of mercaptan sulfur. It is important to lower the mercaptan content of a petroleum fraction as low as possible not only from the standpoint of odor but because mercaptans have an adverse effect on octane number and lead susceptibility. Gasolines, kerosenes, etc., that are "doctor" sweet command a premium price in the industry.

It has been found that the treatment of fractions with dilute or concentrated caustic solutions does not provide a "doctor" sweet product where the mercaptan content of the crude oil is appreciable. In other words, it is impossible to produce a "doctor" sweet petroleum fraction consistently by presently known caustic treatment methods. It is particularly difficult to remove alkyl mercaptans from gasoline and other fractions by the use of caustic solutions.

One of the principal objects of the present invention is to provide a method which will produce "doctor" sweet petroleum fractions.

2

Another object of the invention is to provide a method which will upgrade and stabilize the color of petroleum fractions and which will prevent the formation of insoluble matter on storage.

5 Another object is to provide a method which will improve the odor of petroleum fractions.

Still another object of the invention is to provide a method of treating gasoline, kerosenes, No. 2 fuel oils, etc., which can be carried out efficiently and economically.

10 Other objects will become apparent to those skilled in the art from the following detailed description of the invention.

In general, the invention comprises the discovery that unexpected improvements can be made in known refining methods by combining the steps of (1) treating crude petroleum oil or a petroleum oil fraction with dimethyl sulfoxide, and (2) thereafter contacting the oil with particular alkali solutions.

15 It has been found that the treatment of petroleum oil by the process described herein removes objectionable odors, renders the oil stable to a typical stability test (which comprises subjecting a sample of the oil in an open container to a temperature of 212° F. for 24 hours), and that the product is "doctor" sweet. Moreover, the oil is stable and does not lose its color or form precipitates in storage.

The mechanism of the reactions which occur in the treating process of the invention is not fully understood. It is believed, however, that a reaction occurs with mercaptans and other types of sulfur bodies in the oil; and with nitrogenous bodies and phenolic or other hydroxy or carboxylic compounds which may be present. Some of the products of reaction seem to remain in the hydrocarbon, but without any apparent deleterious effect, while others appear in the intermediate layer as sodium salts or soaps and are separated from the hydrocarbon. It will be understood, therefore, that this invention should not be considered as being dependent upon any specific reaction mechanism or theory but is to be based upon the procedure employing certain specific reagents as herein set forth.

In accordance with a preferred embodiment of this invention, the first treatment stage comprises thoroughly admixing with the oil a quantity of dimethyl sulfoxide and thereafter, without intermediate settling or other processing, vigorously admixing with the oil containing dimethyl sulfoxide a quantity of concentrated aqueous alkali metal hydroxide solution.

20 The alkali solution may contain as little as about 3% alkali. Preferably, however, the alkali solution will contain from about 25% to 50% NaOH or KOH. Stronger solutions of caustic alkali may be used but these tend to produce mechanical and handling difficulties particularly where low temperatures are encountered. In general, solutions containing at least 25% NaOH or KOH and preferably at least 35% NaOH or KOH are required for economical results. More dilute solutions require the use of much larger amounts of dimethyl sulfoxide if the process is to be successful. Although sodium hydroxide and potassium hydroxide are my preferred caustic alkali materials, barium hydroxide, calcium hydroxide, ammonium hydroxide, and other highly alkaline salts could serve as suitable substitutes. Additionally, it is possible to use solid alkaline materials in my process such as NaOH and KOH.

25 Where the oil to be treated is unusually sour, it is helpful to thoroughly admix a solution of sodium or potassium hydroxide with the oil before dimethyl sulfoxide is introduced into the system. It has been shown that prewashing the oil with caustic materials reduces the amount of soap formed in the process and also lowers

the dimethyl sulfoxide concentration which is required in the process. The concentration of the caustic solution can vary from about 3% to about 50%.

The drawing constitutes a typical flow sheet illustrative of the flow of oil and the reactants through the system in accordance with the method of this invention. The oil to be treated is fed through line 1 into mixer 2 wherein the oil is thoroughly admixed with a quantity of aqueous sodium or potassium hydroxide solution (about a 5% concentration is preferred) delivered to mixer 2 through line 3 from a suitable storage vessel 4. It should be realized, of course, that the pretreatment of the oil with the caustic solution can be eliminated if desired. Mixer 2 may be of any suitable form which is capable of thoroughly mixing the oil and alkali solution. After leaving mixer 2, the mixture is passed through line 5 to a settling tank 6 wherein the oil is separated from the caustic 7. The treated oil, indicated at 8, collects on top of the caustic layer and above layer 9 which then contains certain impurities such as phenols, soaps, etc. The alkaline reagent is withdrawn from the bottom of vessel 6 through line 10 and is recirculated to mixer 2, make up sodium or potassium hydroxide solution being added from tank 4 as required. When the alkaline reagent is spent, it is withdrawn either continuously or intermittently from the recirculating alkali through line 11 for purification and reuse. The treated oil is withdrawn from the top of vessel 6 through line 12. Impurities from layer 9 are withdrawn through line 13 and sent to a suitable place of disposition.

In the second and essential stage of the treatment, the oil is fed through line 12 to mixer 14 wherein the oil is thoroughly admixed with a small quantity of dimethyl sulfoxide. The additive is delivered to mixer 14 through line 15 from a suitable storage vessel 16. After a thorough mixing of the additive and oil is effected, the mixture is passed through line 17 to a third mixer 18 wherein the oil containing dimethyl sulfoxide is thoroughly agitated with a quantity of an alkali solution drawn through line 19 from storage vessel 20. Mixer 18 is of conventional form adapted to assure a thorough mixing of the oil and the second alkali solution. The oil is then passed through line 21 to a settling vessel 22 wherein settling and stratification occur. The alkaline reagent indicated at 23 settles to the bottom; the soap products of the reaction form a layer indicated at 24, at the interface between the oil and alkaline reagent; and the treated oil indicated at 25 collects above the other layers. Due to the use of the caustic prewash, the amount of soap formed in the subsequent steps of the process is kept to a minimum. The soap reaction products which are considered as the impurities are withdrawn through line 26 and sent to a suitable place of disposition. The alkaline reagent is withdrawn from the bottom of vessel 22 through line 27 and recirculated to mixer 18, make up sodium hydroxide solution being added from tank 20 as required. A portion of the spent alkali may be withdrawn continuously or intermittently from the recirculating alkali through line 28 for purification and reuse. The treated oil is withdrawn from the top of vessel 22 through line 29 and sent to storage or to other processing units as may be desired.

The entire procedure is a liquid phase treating process which can be conducted at atmospheric temperatures and pressures, although where light gasoline distillates are treated the operation may be carried out in a closed system under sufficient pressure to prevent evaporation and loss of light fractions. Dimethyl sulfoxide 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 dimethyl sulfoxide is needed in the process. In terms of parts per million (p.p.m.) about 50 to 1,500 p.p.m. will suffice in most cases. Straight run gas oil or lighter distillates from relatively sweet crudes require the minimum quantities. Where the fraction is from sour crudes or from catalytic cracking operations, particularly those relatively

high in sulfur compounds, phenolic and nitrogenous bodies, and organic acids, however, as much as 10,000 p.p.m. may be required in certain instances. Correspondingly, where very dilute solutions of sodium hydroxide, for example, are used as catalysts in the process as much as 100,000 p.p.m. of dimethyl sulfoxide is then needed. My broad range of additive concentration, therefore, is from 10 to about 100,000 p.p.m. while my preferred range is from about 50 to 1,500 p.p.m. where the second alkali hydroxide solution contains at least about 25% alkali hydroxide. As was indicated above, the amount of dimethyl sulfoxide required in the method is considerably reduced where the oil is prewashed with a caustic solution.

The second addition of sodium hydroxide solution to the oil is made immediately following the addition of the dimethyl sulfoxide to the petroleum. The time interval between the addition to the oil of the dimethyl sulfoxide and the caustic solution is variable, it being only important that the additive be thoroughly mixed with the oil before the alkali solution is added thereto. While the alkali ordinarily will be added immediately after the completion of the mixing of the sulfoxide and the oil, the treatment may be successfully effected even though the alkali is added hours or days after the addition of the sulfoxide to the oil.

It appears that whatever may be the reactions which occur between dimethyl sulfoxide 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 sulfoxide has been thoroughly distributed throughout the oil before the alkali solution is applied. It is important to note, therefore, that the reagents should be added separately and successively, the second treatment with the alkali solution following the sulfoxide addition, but that the time interval between the additions of the reagents is not particularly important.

The caustic alkali solution used in the initial step is preferably one which contains about 5% caustic. It is possible, however, to use solutions containing from as little as 3% caustic up to as much as 50% caustic. The lower concentrations are preferred for removing acidic materials while the more concentrated solutions have a greater capacity for RSH (mercaptan) removal. As was pointed out above, the second alkali treatment solution may contain as little as 3% caustic but preferably at least 25% and even more preferably 40% to 50% caustic should be present.

The treated oil which is drawn off from the upper portion of settler 22 is found to be free of undesirable odors, is completely stable to the standard stability test described above, and is improved in many respects regardless of the nature of the crude oil.

The amount of alkaline reagent added to the mixture of oil and dimethyl sulfoxide should be sufficient to insure intimate contact between the reagents. The volume of the alkali solution used in both the pretreatment and the final treatment can be varied over a wide range. Usually, this range would be between about 0.5% and about 100% based on the volume of the oil. Much greater amounts, however, could be used without difficulty. In practice, the use of 5% by volume of the alkaline solution based on the volume of the oil has been found to be satisfactory. If a longer time of treatment is used, a lower volume percentage of the alkaline reagent can be employed.

The time of treatment of the oil with the dimethyl sulfoxide additive should be sufficient to insure adequate mixing and will vary somewhat depending on the volume of oil treated. Usually one to two seconds is adequate but in some cases from 5 to 30 minutes or more can be used.

In the second treatment of the alkaline reagent, the time of contact is quite short, e.g., one to two seconds to 5 minutes in the mixing step. Larger contact periods, of course, can be used without adversely affecting the process.

In the pretreatment of the oil with the alkaline solution,

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the time of contact can range from about one to two seconds to 30 minutes or more. It has been found that a contact time of about 15 seconds is satisfactory for most purposes.

The temperature at which the oil is held during the process 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 proven to be very satisfactory but higher temperatures, say 150° F. to 200° F., can be used. The caustic-oil contact temperatures are in the same range as those given for dimethyl sulfoxide.

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 when subjected to the usual distillation process, will produce distillate fractions, namely, gasoline, kerosene, and light gas oil, which will be found to be improved in several respects. 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 have good burning qualities, will be free of undesirable odors, and will be completely stable in storage. In many cases the treated crude itself will be reduced in odor, be more stable and when used as a fuel will have improved burning characteristics.

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.

The following examples illustrate the practice of the invention.

Example I

As was pointed out above, the presence of sulfur compounds, and especially mercaptans, in gasolines and other petroleum fractions is undesirable because of their odor, because they contribute to noxious engine exhaust and engine corrosion, and because of the adverse effect that they have on octane numbers and lead susceptibility. In this illustrative example, several petroleum fractions are subjected to the "doctor" test after being treated by the subject process. In each instance the fraction has a noxious odor and is sour to the "doctor" test prior to the treatment. The method consists of adding a given quantity of dimethyl sulfoxide to the hydrocarbon with sufficient agitation to insure that the chemical went into solution. The hydrocarbon is then agitated with a 50% caustic (NaOH) solution and allowed to settle.

Petroleum Fraction	Quantity of Dimethyl Sulfoxide, p.p.m.	Results
Gasolines:		
1.....	800	"Doctor" sweet.
2.....	1,000	Do.
Naphtha: 1.....	1,200	Do.
Kerosenes:		
1.....	300	Do.
2.....	1,000	Do.
3.....	200	Do.
No. 1 Fuel Oil 1.....	1,500	Do.
No. 2 Fuel Oil 1.....	250	Do.

Example II

This example illustrates the effectiveness of caustic solutions of varying concentrations in the subject process. In each test, a sour No. 1 fuel oil having a noxious odor is treated with dimethyl sulfoxide with sufficient agitation to place the chemical in solution and is then contacted with the caustic solution. The samples can be tested within seconds after the caustic was added.

6

Petroleum Fraction	Quantity of Dimethyl Sulfoxide, p.p.m.	Percent NaOH	Results
No. 1 fuel oil.....	250	50	"Doctor" sweet.
Do.....	1,500	25	Do.
Do.....	100,000	5	Do.
Do.....	1,000	40	Do.
Do.....	500	45	Do.
Do.....	200	50	Do.
Do.....	1,200	35	Do.

Example III

This example illustrates the use of the three-step procedure of the subject process. Certain samples of No. 1 fuel oil from unusually sour crudes are washed with 15-30% solutions of NaOH and are then allowed to settle. The resultant oil layers are treated with dimethyl sulfoxide and are then agitated with a 50% caustic solution in the manner described in Example I. As is evident from the table, the use of the caustic prewash reduces the quantity of the additive needed to produce a "doctor" sweet product.

Caustic Prewash	Sulfoxide Concentration	Results
None.....	900	Sour.
None.....	1,200	"Doctor" sweet.
5% NaOH.....	800	Do.
45% KOH.....	500	Do.

The above results also show that as the caustic concentration in the pretreatment step increases, the quantity of dimethyl sulfoxide needed to produce a "doctor" sweet stock decreases.

The present invention provides an effective, low cost process for the treatment of hydrocarbon fractions. The use of a caustic prewash is helpful in treating unusually sour crudes in that it reduces the quantity of soaps produced and the amount of dimethyl sulfoxide needed in the process.

The "doctor" sweet test referred to herein is a standard test method described in the publication, "UOP Laboratory Test Methods for Petroleum and its Products," 3rd Edition, Universal Oil Products Company, 1948, pages H21-22.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

The invention is hereby claimed as follows:

1. A method of refining petroleum oil which comprises: admixing with a petroleum oil stock selected from the group consisting of gasoline, kerosene, No. 1 fuel oil, and No. 2 fuel oil in the liquid phase dimethyl sulfoxide in the amount of from about 10 to about 100,000 p.p.m. by weight of the oil; agitating the admixture with an alkali; and thereafter separating the treated oil from the resultant mixture.

2. A method of refining petroleum oil which comprises: admixing with a petroleum oil stock selected from the group consisting of gasoline, kerosene, No. 1 fuel oil, and No. 2 fuel oil in the liquid phase dimethyl sulfoxide in the amount of from about 50 to about 1,500 p.p.m. by weight of the oil; agitating the admixture with a concentrated alkali hydroxide solution containing at least 25% by weight of alkali hydroxide; and thereafter separating the treated oil from the resultant mixture.

3. A method of refining petroleum oil which comprises: admixing with a petroleum oil stock selected from the group consisting of gasoline, kerosene, No. 1 fuel oil, and No. 2 fuel oil in the liquid phase dimethyl sulfoxide in the amount of from about 50 to about 1,500 p.p.m. by

7

weight of the oil; agitating the admixture with a concentrated alkali hydroxide solution containing from about 40% to about 50% by weight of alkali hydroxide; and thereafter separating the treated oil from the resultant mixture.

4. A method of refining petroleum oil which comprises: admixing with a petroleum oil stock selected from the group consisting of gasoline, kerosene, No. 1 fuel oil, and No. 2 fuel oil in the liquid phase from about 10 to about 100,000 p.p.m. of dimethyl sulfoxide; agitating the admixture with an alkali hydroxide solution containing from about 3 to about 50% by weight of alkali hydroxide, the volume of said alkali hydroxide solution being sufficient to obtain intimate mixing; and thereafter separating the treated oil from the resultant mixture.

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5. A method of refining petroleum oil as in claim 1 wherein the petroleum oil stock is gasoline.

6. A method of refining petroleum oil as in claim 1 wherein the petroleum oil stock is kerosene.

7. A method of refining petroleum oil as in claim 1 wherein the petroleum oil stock is selected from the group consisting of No. 1 fuel oil and No. 2 fuel oil.

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