United States Patent Office 3,197,400 Patented July 27, 1965



3,197,400

# PROCESS FOR REMOVING SULFUR FROM DIESEL OILS

William L. Fierce and Allen F. Millikan, Crystal Lake, Ill., assignors to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

No Drawing. Filed July 10, 1962, Ser. No. 208,908
10 Claims. (Cl. 208—231)

This invention relates to new and useful improvements in processes for refining mineral oil fractions which contain sulfur compounds and, more particularly, to a process for refining petroleum fractions of the diesel fuel boiling range to produce fractions of improved cetane number and reduced sulfur content. The process of this invention is especially useful for producing diesel fuels of improved cetane number and odor.

In the operation of a diesel engine, a petroleum fuel is injected into the engine combusion chambers containing air which has been previously compressed to a sufficient pressure and temperature to ignite the injected fuel. The ease with which it is ignited after being injected into a combustion chamber, is one of the most important specifications of a diesel fuel. Fuels having poor ignition characteristics exhibit an unduly long ignition lag between the time the fuel is injected and the time it is ignited. This ignition quality of diesel fuels is conventionally expressed in terms of cetane numbers. The cetane number of a given fuel is the percentage of n-cetane, a fast-burning paraffinic constituent, in a mixture of n-cetane and alpha-methylnaphthalene having the same ignition characteristics as the fuel in question. For example, a diesel fuel having a cetane number of 40 would have the same ignition delay characteristics as a mixture of n-cetane and alpha-methylnaphthalene containing 40% by weight of n-cetane. It is important that diesel fuels have good ignition characteristics since the use of fuels having too great an ignition lag, i.e., too low a cetane number, causes excessive engine knocking and rough running, thereby reducing the efficiency and life of the engine.

It is well known to treat diesel fuels with a variety of chemicals to increase their cetane numbers, such as to add certain compounds which will act as ignition accelerators, thereby decreasing the ignition-delay. For example, numerous cetane-number improvers are listed on pages 506 to 510 of "Petroleum Refining with Chemicals," by V. A. Kalichevsky and K. A. Kobe, published by Elsevier Publishing Company in 1956. Improving the cetane number of various petroleum fractions improves the better grades of diesel fuels, and widens the range of available diesel fuels by increasing the ignition quality of lower grade fuels to a point where they can be satisfactorily used.

It is also well known to treat petroleum fractions with a variety of methods to give products with improved odors. Many petroleum fractions, e.g., naphthas, kerosenes, fuel oils, diesel oils, lubricating oils, etc., obtained from many crude oils, have unsatisfactory odor characteristics resulting from the presence of malodorous mercaptans and other sulfur compounds. The removal of these malodorous constituents has often proved difficult by ordinary refining procedures. In the past, the odors of such petroleum fractions have been improved either by removing the mercaptans from the oils or by converting them into substances having lower odor-imparting characteristics. In the past, removal of mercaptans has been accomplished to some extent by clay treating, by treatment with chemicals which form readily extractable derivatives, and by solvent extraction with various acidic materials such as sulfur dioxide, phenol, and concentrated organic acids. In some cases, the removal of mercaptans and other sulfur compounds has been impractical and the sour petroleum fractions have been treated by a sweetening process, such as by the well-known "doctor treatment," in which the sulfur compounds are converted to derivatives of lesser odor. Doctor treatment of petroleum fractions suffers from the disadvantage that the sulfur content of the product petroleum fraction is essentially the same as that of the untreated fraction and extreme care must be exercised not to use excess sulfur, since the presence of a substantial amount of sulfur in the product fractions will be corrosive to metals such as copper and hence the product fractions will be unsuitable for marketing.



It can therefore be seen that many processes are known which can sweeten, reduce the sulfur content, and improve the cetane number of petroleum fractions in the diesel fuel boiling range. However, only a few processes, which can accomplish all of these improvements in one step, are known. In particular, we know of no solvent extraction process for the one-step improvement in these properties. Such a procedure would have the advantage that the materials extracted from the petroleum fractions could be recovered from the solvents and utilized, if so desired.

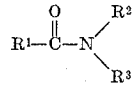
In accordance with this invention, we have discovered that the solvent extraction of sulfur-containing petroleum fractions of the diesel fuel boiling range with a water-soluble dialkyl N-substituted aliphatic acid amide and an aqueous solution of a strong base results in improved diesel fuels. The petroleum fractions treated in accordance with this invention have improved cetane numbers, are substantially free of mercaptans, and have reduced contents of sulfur compounds other than mercaptans. The petroleum fraction can be treated with the substituted acid amide and the aqueous solution of the strong base concurrently, or first with the aqueous solution of the strong base and then with the substituted acid amide.

Accordingly, it is the primary object of this invention to provide a method for refining mineral oil fractions. Another object of this invention is to provide a method for refining petroleum fractions of the diesel fuel boiling range containing sulfur compounds. Still another object of this invention is to provide a method for treating petroleum fractions of the diesel oil boiling range to increase cetane number, eliminate mercaptans, and improve the odor characteristics. A further object of this invention is to provide a solvent extraction process for treating petroleum fractions of the diesel oil boiling range containing sulfur compounds to increase cetane number, eliminate mercaptans, and improve the odor characteristics. These and further objects of this invention will become apparent or be described as the specification herein proceeds.

In accordance with this invention, we have found that it is possible to convert diesel-fuel fractions which contain sulfur compounds to products having very good odor ratings, reduced contents of sulfur-containing compounds, and improved cetane numbers. Our process for improving the quality of diesel-fuel fractions consists essentially of a single extraction process. In this extraction process,

a petroleum fraction of the diesel fuel boiling range is first contacted with a solvent comprising a mixture of a water-soluble dialkyl N-substituted aliphatic acid amide and an aqueous solution of a strong base. The composition of the extraction solvent, namely, the concentration of the base and the relative amounts of the substituted acid amide and aqueous solution, is regulated such that extraction of the diesel-fuel fraction therewith effects an increase in the cetane number of the petroleum fraction. The product which is obtained upon treatment of the diesel fuel with our novel solvent combination is then preferably washed with water until it is substantially free of all traces of the solvent. The oil can be dried before use if necessary. As an alternative method of treatment, the diesel-fuel fraction may be contacted sequentially with the individual components of the solvent combination. In this alternative embodiment, the diesel fuel is first contacted with the aqueous solution of a strong base and then with the substituted acid amide. The proces of this invention is generally applicable to mineral oil fractions boiling in the diesel-fuel boiling range, e.g., 170° to 340° C.

The water-soluble dialkyl N-substituted aliphatic acid amides which may be used in accordance with this invention are represented by the formula,



wherein $R^1$, $R^2$, and $R^3$ are the same or different radicals; $R^1$ being selected from the group consisting of hydrogen and lower alkyl radicals, and $R^2$ and $R^3$ are lower alkyl radicals. Preferably, $R^1$ is hydrogen or a $C_1$–$C_4$ alkyl radical, and $R^2$ and $R^3$ are $C_1$–$C_4$ alkyl radicals. Non-limiting examples of compounds which are included within the scope of the foregoing formula and definition are: N,N - dimethylformamide, N-methyl-N-ethylformamide, N,N-diethylformamide, N,N-dipropylformamide, N,N-diisopropylformamide, N-methyl-N-propylformamide, N,N-dibutylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, N - methyl - N - ethylacetamide, N-methyl-N-butylacetamide, N,N-dimethylpropionamide, N,N-diethylpropionamide, N-methyl-N-ethylproprionamide, N,N-dimethyl-N-butyramide, and N,N-dimethyl-n-valeramide.

The strong bases which may be used in accordance with this invention include the alkali metal hydroxides and other bases, inorganic or organic, which have substantially the same basic properties as the alkali metal hydroxides, i.e., are comparable in strength to the alkali metal hydroxides. Examples of strong bases which may be used include alkali metal hydroxides, e.g., sodium hydroxide and potassium hydroxide; alkaline earth metal hydroxides, e.g., calcium hydroxide and barium hydroxide; guanidine and substituted guanidines, e.g., methyl guanidine, ethylguanidine, propylguanidine, and tetramethylguanidine; and quaternary ammonium hydroxides, e.g. tetramethylammonium hydroxide, tetraethylammonium hydroxide, phenyltrimethylammonium hydroxide, and benzyltrimethylammonium hydroxide.

To demonstrate the effectiveness of the process of our invention, several experiments were conducted in which several petroleum fractions were treated under different conditions. A standard procedure was used in all of the experiments. The amounts of the solvent components mixed to form the extraction solvents are shown in terms of volume percent in the tables included with the explanations of the various experiments. In certain cases, the aqueous base was not completely miscible with the organic liquid. In these cases the insoluble portion of the aqueous base was discarded, and the remainder of the mixed solvent was used in the extraction. The solvent



composition data in the tables indicate the amounts of each component initially mixed to form the extraction solvent. Thus these data do not reflect the amounts of aqueous phase discarded. However, the amounts discarded are given in most of the tables in terms of volume percent of the aqueous phase immiscible with the organic liquid.

In each experiment, sufficient amounts of the solvent components were mixed to give a total volume equal to ⅘ the volume of the oil to be extracted. In those cases where a part of the aqueous base is not miscible with the organic liquid and was discarded, the total volume of the solvent was reduced slightly below ⅘ that of the oil volume. The remainder of the solvent was divided into four equal portions. The oil was then extracted in a separatory funnel four times with these equal portions of solvent. In the average run, 500 ml. of oil was extracted with four 100 ml. portions of solvent. The solvent volume was slightly below 100 ml. when part of the aqueous base was not miscible with the organic liquid. In a few cases, the oil volumes were larger or smaller than 500 ml. However, in all cases the volume proportions were the same, and one volume of oil was extracted four times with about ⅕ volume proportion of the solvent. Following the solvent extraction, the oil was washed three or more times with ⅖ volume proportions of water until the final wash was free of the solvent. Finally the oil was dried by filtration through a double thickness of #230 Reeves Angel filter paper (filter paper used for removing entrained water). The volume percent oil recoveries in the tables are based on the volumes of oil obtained after the filtration step.

In the tables, the odors of the untreated and treated petroleum fractions are given as numerical ratings, or are indicated by the standard doctor test for mercaptans. In measuring the relative odor of petroleum products, it has not been possible to develop a precise, quantitative measure of odor which is entirely independent of the individual who evaluates the odor. Nevertheless, there are certain procedures for rating odors which have been used in the petroleum industry. Odor evaluation standards and methods have been proposed by a joint committee of the A.S.T.M. and the T.A.P.P.I. A modification of this procedure has been used extensively in the evaluation of the odor of commercial petroleum products. In a typical petroleum company, an odor panel is selected consisting of several, e.g., 10 to 20 or more, individuals who have been tested for their ability to discriminate between and match different odors. One test for a selection of panel members involves correctly matching a series of chemical odors such as very dilute odors of acetic acid, phenol, toluene, and benzene. A second test involves a matching of a variety of different naphthas by odor from a single manufacturing source. A third test involves the matching of mineral spirits obtained from different manufacturers. By use of these screening tests, it is possible to select a panel of 10 to 20 individuals who are especially discriminating in evaluating odors of petroleum products. In the rating of odors of petroleum fractions such as an odorless naphtha, a numerical rating scale has been established to describe odor quality:

TABLE I

| Numerical rating: | Odor quality |
|---|---|
| 1 | Excellent. |
| 2 | Excellent. |
| 3 | Very good. |
| 4 | Very good. |
| 5 | Good. |
| 6 | Fair (just passing). |
| 7 | Borderline. |
| 8 | Borderline. |
| 6 | Poor. |
| 10 | Very poor. |

Where the odors of the various treated and untreated petroleum fractions are given as numerical ratings in the following tables, the above numerical ratings and corresponding odor qualities are utilized. However, when the doctor test is given in lieu of odor test, a negative doctor test indicates that the petroleum fraction is doctor sweet and contains less than 0.001 wt. percent mercaptan sulfur, whereas a positive doctor test indicates that the fraction is not doctor sweet.

When evaluating the odor of petroleum naphthas, the following procedure is used. The members of the odor panel are requested to avoid contact with contaminating odors, e.g., smoking, etc., for at least one half hour prior to the test. The odor evaluation is carried out in an air-conditioned room, at about 75° F. which is as free as possible from extraneous odors. Each member of the test panel rates the odor of a product separately. A non-member of the panel conducts the test and is present to record any pertinent comments made regarding the odor.

To eliminate bias, the product samples are coded, and the panel members are told only the type of product being rated. To avoid odor fatigue, no more than three samples are rated at any one time. Any additional ratings are spaced by at least 3 hours. A total of 7 panel members rate the product and the average of these opinions is reported as the odor rating.

In preparing the naphtha for odor evaluation, a 35-ml. representative portion is poured into a clean, odor-free, 8-ounce, French square bottle. The bottle is sealed with a clean, odor-free screw-on cap. The same bottle is used by all members of the panel. The type bottle used in the evaluation is the same as that used in the screening test for the selection of the panel members. Each panel member evaluates the odor of the naphtha by removing the cap from the bottle, placing his nose at the bottle mouth and sniffing the odor. He checks the intensity of odor and for any foreign or undesirable odor that may be present and then numerically rates the odor using the above-described scale. This method is called the "wet-odor" of the naphtha.

The corrosiveness of the petroleum fractions given in Table II are measured by immersing a copper strip for three hours at 122° F. in the fractions in accordance with the ASTM Copper-Strip Corrosion Test (method D–130) and giving the copper strip a corrosion rating as compared with the copper-strip corrosion test standard. The colors of the various fractions given in some of the tables are determined in accordance with ASTM test method D–155. The calculated cetane numbers are determined in accordance with ASTM test method D–975, Appendix II.

*Example I*

In one experiment, four extractions were carried out to demonstrate the utility of this invention. In this experiment, as in the experiments hereinafter described, N,N-dimethylformamide and sodium hydroxide were utilized as representative of the substituted acid amides and strong bases, respectively. The oil which was used in this experiment was a refinery product known as No. 2 fuel oil. The oil had the following distillation range: I.B.P. 173° C., 10% 222° C., 50% 263° C., 90% 308° C. and E.P. 336° C. It had a total sulfur content of about 0.93% wt., a mercaptan sulfur content of about 0.016% wt., and an initial cetane number of 41.7.

In each of the extractions in this series of experiments, 1000 ml. of the oil was extracted four times, at ambient temperatures, in a separatory funnel with 200 ml. portions of the solvent. The treated oil was then washed three times with 400 ml. portions of distilled water. The product was then passed through a double thickness of #230 Reeves Angel filter paper to remove entrained water. The compositions of the four solvents used in these extractions and the results of the extractions are shown in Table II.



TABLE II

| Experiment Number | Untreated oil | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Oil/solvent ratio | | 5:1 | 5:1 | 5:1 | 5:1 |
| No. of extractions | | 4 | 4 | 4 | 4 |
| Solvent composition: | | | | | |
| N,N-Dimethylformamide (vol. percent) | | 87.5 | 87.5 | 50.0 | 50.0 |
| Dilute aqueous NaOH (vol. percent) | | 12.5 | 12.5 | 50.0 | 50.0 |
| NaOH (normality) | | 0.0 | 2.0 | 0.0 | 2.0 |
| Vol. percent oil recovery | | 92.0 | 92.4 | 97.8 | 96.4 |
| Properties of product oil: | | | | | |
| Sulfur, total (wt. percent) | 0.93 | 0.77 | 0.76 | 0.90 | 0.92 |
| Sulfur as RSH (wt. percent) | 0.016 | 0.009 | <0.001 | 0.007 | 0.007 |
| Nitrogen (wt. percent) | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| Cetane No. (measured) | 41.7 | 44.0 | 44.0 | 41.2 | 41.2 |
| Cetane No. (measured) increase | | 2.3 | 2.3 | −0.5 | −0.5 |
| Color | 1+ | 1½+ | 1½+ | 1+ | 1+ |
| Odor | 4 | 3 | 4 | 3 | 3 |
| Corrosiveness | 1a | 1a | 1a | 1a | 1a |

In reviewing the results of the experiments shown in Table II, it will be evident that only the solvent of Experiment 2 was effective in increasing the cetane number of the oil, removing substantially all of the mercaptans from the oil and producing a doctor sweet product. The solvent utilized in Experiment 2 contained 7 parts by volume of N,N-dimethylformamide and one part by volume of 2.0 N aqueous sodium hydroxide. In comparing the results of Experiments 1 and 2, it can be seen that extraction of the oil with a solvent containing 7 parts by volume of N,N-dimethylformamide and 1 part by volume of water resulted in the same increase in cetane number as in Experiment 2, viz., from 41.7 to 44.0. However, the solvent of Experiment 1 removed only less than one-half of the mercaptans present in the untreated oil, and the treated oil did not test doctor sweet. Apparently the aqueous cautsic in the solvent of Experiment 2 was one factor responsible for removing substantially all of the mercaptans from the oil. Experiment 4 demonstrates that the proportions of the substituted acid amide and aqueous solution of a strong base are somewhat critical. In this run, extraction of the oil with a solvent comprising 50 vol. percent each of N,N-dimethylformamide and 2.0 N sodium hydroxide produced a product having a lower cetane number than the untreated oil, and the product oil did not test doctor sweet since it contained only slightly less than one-half of the original mercaptan content. The utilization of a solvent consisting of one-half of the N,N-dimethylformamide and one-half of water (Experiment 3) produced results substantially the same as those in Experiment 4.

*Example II*

Since a comparison of Experiments 1 and 2 of Example I demonstrate that the presence of cautsic in the

extraction solvent is necessary to remove mercaptans from oil, another series of experiments was conducted to determine the optimum caustic concentration. In these experiments, samples of a No. 2 fuel oil having a total sulfur content of 0.78 wt. percent (0.007 wt. percent of mercaptan sulfur) and a calculated cetane index of 41.8 were treated under the conditions described in Example I. In these runs, the solvents were composed of 7 parts by volume of N,N-dimethylformamide and 1 part by volume of the aqueous phase, with the concentration of the sodium hydroxide being varied from 0 to 5.0 N. In reviewing the results shown in Table III, it can be seen that the minimum effective concentration of the caustic is 0.7 N. The utilization of at least 0.7 N concentartion of the caustic effected the removal of substantially all of the mercaptans and produced a doctor sweet product. Experiments 8 to 11 demonstrate that as the concentration of the caustic is increased, the total sulfur content of the product oil is reduced, while its cetane number is increased. However, it will also be noted that there is an optimum concentration of the caustic since the amount of the oil recovered is reduced as the concentration of the caustic is increased. It would appear that the optimum concentration of the caustic is about 2.0 N.

TABLE III

| Experiment No. | Untreated oil | 5 | 6 | 7 | 8 | 9 | 10 | 11 |
|---|---|---|---|---|---|---|---|---|
| Oil/solvent ratio | | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| No. of extractions | | 4 | 4 | 4 | 4 | 4 | 4 | 4 |
| Solvent composition: | | | | | | | | |
| N,N-Dimethylformamide (vol. percent) | | 87.5 | 87.5 | 87.5 | 87.5 | 87.5 | 87.5 | 87.5 |
| Dilute aqueous NaOH (vol. percent) | | 12.5 | 12.5 | 12.5 | 12.5 | 12.5 | 12.5 | 12.5 |
| NaOH conc. (normality) | | 0.0 | 0.1 | 0.3 | 0.7 | 1.2 | 2.0 | 5.0 |
| Vol. percent oil recovery | | 91.6 | 91.1 | 92.0 | 91.8 | 91.4 | 90.5 | 88.1 |
| Properties of product oil: | | | | | | | | |
| Sulfur, total (wt. percent) | 0.78 | 0.64 | 0.63 | 0.64 | 0.63 | 0.61 | 0.60 | 0.55 |
| Sulfur as RSH (wt. percent) | 0.007 | 0.004 | 0.002 | 0.003 | <0.001 | <0.001 | <0.001 | <0.001 |
| Doctor test | Pos. | Pos. | Pos. | Pos. | Neg. | Neg. | Neg. | Neg. |
| Cetane No. (measured) | 41.2 | 44.2 | | | 43.9 | | 44.7 | |
| Cetane index (calculated) | 41.8 | 45.7 | 46.0 | 45.5 | 45.5 | 46.0 | 46.2 | 47.4 |
| Cetane index (calculated) increase | | 3.9 | 4.2 | 3.7 | 3.7 | 4.2 | 4.4 | 5.6 |
| Gravity, °API | 32.2 | 34.1 | 34.2 | 34.0 | 34.1 | 34.2 | 34.4 | 35.0 |

*Example III*

Another series of experiments was conducted to demonstrate that so-called weak bases give unsatisfactory results when substituted for sodium hydroxide in the extraction solvent. The bases evaluated were pyridine, triethylamine, ammonium hydroxide, and piperidine. In each of the experiments, the solvents comprise 350 ml. N,N-dimethylformamide and 50 ml. of 2.0 N aqueous base. To test the solvent, a 500 ml. portion of No. 2 fuel oil was extracted four times with 100 ml. portions of the solvent, followed by three washes with 200 ml. portions of water. Table IV shows the results of these extractions. Although all of the solvents were about as effective as the caustic-containing solvent in improving the cetane index and reducing the total sulfur content, none of the solvents containing the weak bases gave a doctor-sweet, mercaptan-free oil product.

TABLE IV

| Experiment No. | Untreated oil | 12 | 13 | 14 | 15 | 16 |
|---|---|---|---|---|---|---|
| Oil/solvent ratio | | 5 | 5 | 5 | 5 | 5 |
| No. of extractions | | 4 | 4 | 4 | 4 | 4 |
| Solvent composition: | | | | | | |
| N, N-Dimethylformamide (vol. percent) | | 87.5 | 87.5 | 87.5 | 87.5 | 87.5 |
| Dilute aqueous base (vol. percent) | | 12.5 | 12.5 | 12.5 | 12.5 | 12.5 |
| Base conc. (normality) | | 2.0 | 2.0 | 2.0 | 2.0 | 2.0 |
| Base used | | Pyridine | Triethyl-amine. | $NH_4OH$ | Piperidine | NaOH |
| Vol. percent oil recovery | | 88.0 | 88.6 | 88.8 | 87.0 | 87.2 |
| Properties of product oil: | | | | | | |
| Sulfur, total (wt. percent) | 0.78 | 0.56 | 0.54 | 0.58 | 0.56 | 0.57 |
| Sulfur as RSH (wt. percent) | 0.007 | 0.005 | 0.007 | 0.004 | 0.004 | <0.001 |
| Doctor test | Pos | Pos. | Pos. | Pos. | Pos. | Neg. |
| Cetane index (calculated) | 41.8 | 46.1 | 47.3 | 45.5 | 46.3 | 46.0 |
| Cetane index (calculated) increase | | 4.3 | 5.5 | 3.7 | 4.5 | 4.2 |
| Gravity, °API | 32.2 | 34.6 | 35.3 | 34.3 | 34.7 | 34.6 |

*Example IV*

Table V contains the results of experiments which were conducted to evaluate a number of organic solvents as substitutes for the substituted acid amides. Organic solvents which were found to be ineffective were p-dioxane, pyridine, acetonitrile, 1-propanol, formula 30 alcohol, ethylene carbonate, ethylene glycol, tetrahydrofuran, diethylene glycol, phenol, nitromethane, dimethylsulfoxide, and acetamide. To evaluate these organic liquids, the procedure hereinbefore described was used to extract samples of No. 2 fuel oil with solvents prepared from 7 parts by volume of the organic compound and 1 part by volume of aqueous sodium hydroxide. The aqueous phase was of 2 strengths: 1.2 N NaOH and 2.0 N NaOH. The 1.2 N NaOH experiments (not tabulated) involved p-dioxane, pyridine, acetonitrile, 1-propanol, formula 30 alcohol, ethylene carbonate, and ethylene glycol. Although in most cases there was an irregular improvement in cetane number, none of these solvents in combination with 1.2 N aqueous NaOH produced a negative doctor test. In the experiments involving 2.0 N NaOH and other solvents (listed in Table V) only a few of the solvents gave doctor-sweet oil products and these few were unable to cause relatively large increases in the cetane index.

TABLE V

| Expt. No. | Solvent | | Volume percent oil recovery | Properties of product | | | | Calcd. cetane index | Cetane index increase | Aqueous caustic not dissolved (vol. percent) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Aqueous phase | Organic liquid used | | Sulfur, wt. percent | | Doctor test | Gravity ° API | | | |
| | | | | Total | As RSH | | | | | |
| Untreated oil. | | | | 0.78 | 0.007 | Pos. | 32.2 | 41.8 | | |
| 17 | 2.0 N NaOH | Tetrahydrofuran | 80.2 | 0.69 | 0.002 | Neg. | 33.1 | 43.0 | 1.2 | 66 |
| 18 | 2.0 N NaOH | Diethylene glycol | 91.4 | 0.76 | 0.002 | Neg. | 32.4 | 42.1 | 0.3 | 0 |
| 19 | 2.0 N NaOH | Phenol | 80.0 | 0.50 | 0.008 | Pos. | 35.5 | 48.4 | 6.6 | 0 |
| 20 | 2.0 N NaOH | Nitromethane | 88.8 | 0.62 | 0.003 | Pos. | 33.9 | 45.0 | 3.2 | 100 |
| 21 | 2.0 N NaOH | Furfural* | | | | | | | | |
| 22 | 2.0 N NaOH | Dimethylsulfoxide | 92.6 | 0.66 | <0.001 | Neg. | 33.1 | 43.1 | 1.3 | 4 |
| 23 | 2.0 N NaOH | Acetamide | 94.6 | 0.78 | <0.001 | Pos. | 32.3 | 41.0 | −0.8 | 0 |
| 24 | 2.0 N NaOH | N,N-dimethylformamide | 89.2 | 0.59 | <0.001 | Neg. | 34.4 | 45.5 | 3.7 | 10 |

*Reacted with the aqueous caustic and could not be used as an extraction solvent.

*Example V*

Since Example I demonstrated that a solvent comprising 7 parts by volume of N,N-dimethylformamide and one part by volume of 2.0 N aqueous caustic achieved the desired results (Experiment 2), but a solvent comprising 50 volume percent each of N,N-dimethylformamide and 2.0 N aqueous caustic was not an effective solvent (Experiment 4), another series of extractions was carried out in which the proportions of the dimethylformamide and the water were varied, while the total amount of sodium hydroxide present was held constant, to determine the optimum solvent composition. From the results of these experiments shown in Table VI, it can be seen that the best results were obtained by a solvent composed of 7 volumes of N,N-dimethylformamide and 1 volume of the aqueous caustic. When a higher proportion of N,N-dimethylformamide was used, the oil recovery was greatly reduced. However, higher proportions of the aqueous phase caused the cetane number increase to be reduced. In addition, the product oil was not doctor sweet when the aqueous phase comprised above about 25 vol. percent of the solvent. Therefore, it will be evident that the combination solvent must contain at least 75 vol. percent of the amide to obtain satisfactory results.

*Example VI*

Table VII gives data on runs wherein a No. 2 fuel oil was extracted sequentially with N,N-dimethylformamide and 2.0 N sodium hydroxide, rather than with a solvent comprising N,N-dimethylformamide and aqueous caustic. In comparing runs 31 to 34, it can be seen that the order of extraction had no significant effect on the cetane index increase, but that the product oil was sweet only when the aqueous caustic extraction was given first. Apparently, the process involves the formation of sodium mercaptides which are removed by the N,N-dimethylformamide-containing solvent. It will be noted that one drawback of the two-step extraction procedure is that oil recoveries are lowered from about 91–92 volume percent to about 64 volume percent. This is due to the fact that pure N,N-dimethylformamide containing no water can dissolve significant amounts of fuel oil. Experiments 40 and 42 show that this difficulty can be avoided in the two-step procedure by adding water to the N,N-dimethylformamide to reduce the solubility of the oil in the N,N-dimethylformamide.

TABLE VI

| Experiment No. | Untreated oil | 25 | 26 | 27 | 28 | 29 | 30 |
|---|---|---|---|---|---|---|---|
| Oil/solvent ratio | | 5 | 5 | 5 | 5 | 5 | 5 |
| No. of extractions | | 4 | 4 | 4 | 4 | 4 | 4 |
| Solvent composition: | | | | | | | |
| N,N-dimethylformamide (vol. percent) | | 93.75 | 87.5 | 81.25 | 75.0 | 62.5 | 50.0 |
| Dilute aqueous NaOH (vol. percent) | | 6.25 | 12.5 | 18.75 | 25.0 | 37.5 | 50.0 |
| Aq. NaOH not dissolved (vol. percent) | | 20.0 | 10.0 | 2.7 | 2.0 | 0.0 | 0.0 |
| NaOH conc. (normality) | | 4.0 | 2.0 | 1.33 | 1.0 | 0.67 | 0.50 |
| Total NaOH used (moles) | | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Vol. percent oil recovery | | 78.8 | 88.8 | 92.8 | 93.8 | 95.0 | 94.6 |
| Properties of Product Oil: | | | | | | | |
| Sulfur, total (wt. percent) | 0.78 | 0.40 | 0.58 | 0.69 | 0.73 | 0.76 | 0.77 |
| Sulfur as RSH (wt. percent) | 0.007 | <0.001 | <0.001 | <0.002 | <0.001 | 0.001 | 0.001 |
| Doctor test | Pos. | Neg. | Neg. | Neg. | Pos. | Pos. | Pos. |
| Cetane index (calculated) | 41.8 | 50.6 | 46.5 | 43.5 | 42.7 | 41.5 | 41.6 |
| Cetane index (calculated) increase | | 8.8 | 4.7 | 1.7 | 0.9 | −0.3 | −0.2 |
| Gravity, ° API | 32.2 | 36.7 | 34.5 | 33.2 | 32.7 | 32.3 | 32.2 |

TABLE VII

| Experiment No. | | 31 | 32 | 33 | 34 |
|---|---|---|---|---|---|
| First extraction series: | | | | | |
| Solvent used [1] | | NaOH | NaOH | DMF | DMF:$H_2O$ |
| Oil/solvent ratio | | 10 | 10 | 5.6 | 5.6 |
| No. of extractions [2] | | 3 | 3 | 4 | 4 |
| Second extraction series: | | | | | |
| Solvent used [1] | | DMF | DMF:$H_2O$ | NaOH | NaOH |
| Oil/solvent ratio | | 5.6 | 5.6 | 10 | 10 |
| No. of extractions [2] | | 4 | 4 | 3 | 3 |
| Vol. percent oil recovery | | 64.0 | 90.4 | 64.4 | 90.4 |
| Properties of product oil: | | | | | |
| Sulfur, total (wt. percent) | 0.81 | 0.26 | 0.62 | 0.25 | 0.65 |
| Sulfur as RSH (wt. percent) | 0.007 | <0.001 | <0.001 | <0.001 | <0.001 |
| Doctor test | Pos. | Neg. | Neg. | Pos. | Pos. |
| Cetane index (calculated) | 41.5 | 55.5 | 44.8 | 56.1 | 44.3 |
| Cetane index (calculated) increase | | 14.0 | 3.3 | 14.6 | 2.8 |
| Gravity, ° API | 32.2 | 39.1 | 33.8 | 39.3 | 33.6 |

[1] The solvents used were as follows:
NaOH—2.0 N NaOH,
DMF—N,N-dimethylformamide,
DMF:$H_2O$—7 parts of N,N-dimethylformamide and 1 part of water.
[2] Each oil product was finally washed three times with 1/5 volume portions of water and dried by filtering.

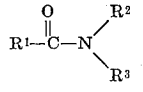
*Example VII*

The experiments described in the previous examples show that extraction of a No. 2 fuel oil in accordance with this invention increases the cetane number, substantially removes all of the mercaptans, and reduces the content of other sulfur compounds. However, the effect of this solvent extraction process on odor could not be measured, because the fuel oil had an odor rating of 3 (very good). In order to demonstrate the effect the process of our invention has an the odor of the petroleum fraction, a light cycle oil was extracted with a solvent comprising 87.5 vol. percent N,N-dimethylformamide and 12.5 vol. percent of 2.0 N aqueous caustic. The untreated oil had a total sulfur content of 1.21 wt. percent, which included a mercaptan sulfur content of 0.01 wt. percent, an odor rating of 8, and a calculated cetane index of 36.1. Extraction of the cycle oil in the manner hereinbefore described produced a product having a total sulfur content of 0.89%, and which was substantially free of all mercaptan sulfur. The calculated cetane index was increased 4.6 units to 40.7 and the final odor rating was three.

It can therefore be seen that we have discovered an extraction process which is effective for increasing the cetane number, improving the odor, and reducing the sulfur content of diesel-fuel fractions. Although our invention was demonstrated in the foregoing examples using dimethylformamide and sodium hydroxide as representatives of the solvent components, the same contacting conditions will generally be applicable when other components are used. It can be concluded that a solvent composed of 7 volumes of a substituted acid amide and 1 volume of 2.0 N aqueous strong base gives about the optimum results in terms of the yield and properties of the product oil. The treated oil is preferably water-washed to remove traces of the substituted acid amide remaining in the product oil. Satisfactory results can be achieved by batch-type or continuous extraction procedures. The oil can be contacted concurrently or sequentially with the substituted acid amide and aqueous base, provided it is contacted first with the aqueous base in a 2-step procedure.

The embodiments of this invention in which an exclusive property or privilege is claimed are defined as follows:

1. A petroleum fraction sweetening solvent comprising a solution of at least 75.00–93.75 vol. percent of a water-soluble dialkyl N-substituted aliphatic acid amide of the formula,



wherein $R^1$ is selected from the group consisting of hydrogen and $C_1$–$C_4$ alkayl radicals and $R^2$ and $R^3$ are $C_1$–$C_4$ alkyl radicals, the remainder of said solution being a 0.7–5.0 N aqueous solution of a strong base selected from the group of alkali metal hydroxides, alkaline earth metal hydroxides, guanidine, hydrocarbyl-substituted guanidines and quaternary ammonium hydroxides.

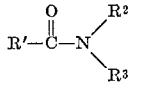
2. A method of treating a petroleum fraction which consists in:

(a) Contacting a sulfur-containing petroleum fraction of the diesel fuel boiling range with a water-soluble dialkyl N-substituted aliphatic acid amide and an aqueous solution of a strong base of 0.7–5.0 N selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, guanidine, hydrocarbyl-substituted guanidines, and quaternary ammonium hydroxides, the volume of amide to aqueous base solution being within the range of about 3:1 to 15:1 inclusive, said petroleum fraction being contacted with said aqueous solution no later than it is contacted with said amide, said amide, aqueous solution, and strong base being used in amounts to effect an increase in the cetane number of said petroleum fraction, and

(b) Recovering a raffinate phase predominating in a petroleum fraction of improved cetane number.

3. The method in accordance with claim 2 wherein said petroleum fraction is contacted with said aqueous base solution before it is contacted with said amide.

4. The method in accordance with claim 2 wherein amide is of the formula,



wherein R′ is selected from the group consisting of hydrogen and $C_1$–$C_4$ alkyl radicals and $R^2$ and $R^3$ are $C_1$–$C_4$ alkyl radicals.

5. The method in accordance with claim 4 wherein said petroleum fraction has a boiling range from about 170°–340° C. and a mercaptan sulfur content of about 0.007–0.016 wt. percent and is contacted with the solvent of claim 1 and in which said strong base is an alkali metal hydroxide and the petroleum fraction/solvent ratio is 5:1.

6. A method of treating a petroleum fraction of the diesel fuel boiling range in the absence of an oxidizing agent which comprises:

(a) Contacting the sulfur-containing petroleum fraction with an amide selected from the group consisting of N,N-dimethylformamide, N-methyl-N-ethylformamide, N,N-diethylforamide, N,N-dipropylformamide, N,N-diisopropylformamide, N-methyl-N-propylformamide, N,N-dibutylformamide, N,N-dimethylacetamide, N,N-diethylacetamide, N-methyl-N-ethylacetamide, N-methyl-N-butylacetamide, N,N-

dimethylpropionamide, N,N - diethylpropionamide, N-methyl-N-ethylpropionamide, N,N - dimethyl-N-butyramide, and N,N-dimethyl-n-valeramide and an aqueous solution of a strong base of 0.7–5.0 N selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides, guanidine, hydrocarbyl-substituted guanidines, and quaternary ammonium hydroxides, the volume of amide to aqueous base solution being within the range of about 3:1 to 15:1 inclusive, said petroleum fraction being contacted with said aqueous solution no later than it is contacted with said amide, said amide, aqueous solution, and strong base being used in amounts to effect an increase in the cetane number of said petroleum fraction, and

(b) Recovering a raffinate phase predominating in a petroleum fraction of improved cetane number.

**7.** The method in accordance with claim **6** in which said petroleum fraction has a boiling range from about 170°–340° C. and a mercaptan sulfur content of about 0.007–0.016 wt. percent and is contacted with said aqueous base solution before it is contacted with said amide.

**8.** A method of sweetening a sour petroleum fraction containing mercaptans which consists in:

(a) Contacting said petroleum fraction with dimethylformamide and a 2.0 N aqueous solution of sodium hydroxide, the volume of amide to aqueous base solution being about 7:1, said petroleum fraction



being contacted with said aqueous solution no later than it is contacted with said amide, said amide, aqueous solution and strong base being used in amounts to effect an increase in the cetane number of said petroleum fraction,

(b) Recovering a raffinate phase predominating in a petroleum fraction of improved cetane number, and

(c) Washing said raffinate with water until same is substantially free of said amide.

**9.** The method in accordance with claim **8** wherein said petroleum fraction is contacted with said aqueous solution of sodium hydroxide before it is contacted with said dimethylformamide.

**10.** The method in accordance with claim **9** wherein said dimethylformamide includes a minor amount of water.

**References Cited by the Examiner**

UNITED STATES PATENTS

2,556,837 6/51 Browder et al. _____ 208—206

OTHER REFERENCES

Gruse et al.: Chemical Technology of Petroleum, third edition, 1960, McGraw-Hill Book Co. Inc., New York, N.Y.; TP. 69, O.G. 76, 1960, Chapt. VII, see Chapt. VII–3, pages 297–304.

ALPHONSO D. SULLIVAN, *Primary Examiner.*