

UNITED STATES PATENT OFFICE

2,562,767

SWEETENING OF PETROLEUM DISTILLATES

John G. Browder, Houston, and Alvin R. Smith,
Baytown, Tex., assignors, by mesne assign-
ments, to Standard Oil Development Company,
Elizabeth, N. J., a corporation of Delaware

No Drawing. Application March 23, 1950,
Serial No. 151,516

11 Claims. (Cl. 196—29)

1

The present invention involves contacting a sour petroleum distillate having a boiling range of about 200° to 750° F. to which has been added a small amount of methyl alcohol and beta-naphthol in catalytic quantity with a solution of an alkali metal hydroxide to form a mixture thereof and maintaining the mixture undergoing contacting in the presence of a mild oxidizing agent in an amount sufficient to sweeten the distillate, following which the alkali metal hydroxide is separated from the contacted distillate.

The invention is particularly adapted to distillates boiling in the range from about 200° to 750° F. and has a special application to sweetening of kerosenes and the so-called solvent naphthas, the latter boiling in the range of 200° to 450° F.

The methyl alcohol may be employed in an amount in the range from about 0.1 to about 2.5% by volume (based on the sour distillate) with a preferred amount in the range from about 0.5 to about 1% by volume. The beta-naphthol may be employed in amounts based on the sour distillate varying from about 0.05 to about 1.0 gram per liter, the sum total of the methyl alcohol and beta-naphthol not being in excess of about 3.0% by volume of the sour distillate to be sweetened. The beta-naphthol and methyl alcohol are preferably added to the petroleum distillate, but may be added to the mixture of the alkali metal hydroxide and sour petroleum distillate undergoing a sweetening reaction.

The alkali metal hydroxide employed in the present invention preferably should be a solution of an alkali metal hydroxide. Preferably the solution should be an aqueous solution having a Baumé gravity in the range of from about 30° to about 50° Baumé, but solutions of lower strength may be used under some conditions. An aqueous solution of sodium hydroxide of 40° Baumé has been found to give satisfactory results in the practice of the present invention. Other alkali metal hydroxides besides sodium hydroxide may be used. For example, lithium and potassium hydroxide may be used in lieu of sodium hydroxide, but the latter is to be preferred.

The temperature at which the treating operation is conducted will usually be atmospheric and may range from about 60° F. up to 200° F. and sometimes higher temperatures may be employed depending on the boiling range and the type of feed stock being treated. A preferred temperature range may be from about 70° to about 95° F. Satisfactory results have been obtained at

2

atmospheric temperatures encountered in the Texas Gulf Coast area.

The process of our invention may be carried out in suitable equipment which will allow contact of the sour distillate to which methyl alcohol and beta-naphthol have been added with the alkali metal hydroxide and the mild oxidizing agent. For example, pumps, jet mixers, incorporators and contacting towers may be used. Such towers may be equipped with packing, bell cap trays and other similar well known expedients for insuring contact between liquids and between liquids and gaseous material.

The present invention will be illustrated further by the following example:

EXAMPLE I

A solvent naphtha having a copper number of less than 1 and having a boiling point in the range between 290° and 410° F. was divided into 7 portions; one portion was contacted with a solution of 50° Baumé sodium hydroxide and after the contacting operation the sodium hydroxide solution was removed, the naphtha washed with water and submitted to the doctor test and for determination of Saybolt color. A second portion of the solvent naphtha was contacted with the 50° Baumé sodium hydroxide in the same manner as described, but in the presence of 300% of the theoretical amount of oxygen required to sweeten the naphtha. After water washing it was also submitted to the above mentioned tests. The third portion had added to it 0.5% by volume based on the solvent naphtha of methyl alcohol and then contacted with sodium hydroxide solution as mentioned before, in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten. The fourth portion had added to it 0.05% by volume of methyl alcohol and was subjected to contact with sodium hydroxide in the presence of 300% by volume of the theoretical oxygen required to sweeten same. The fifth portion had added to it 0.5 gram per liter of beta-naphthol and was then subjected to contact with portions of the same sodium hydroxide solution in the presence of oxygen in the excess amounts indicated before. The sixth portion had added to it 0.1 gram of beta-naphthol per liter and was subjected to contact with the same (sodium hydroxide) caustic solution in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten. The seventh and last portion had added to it 0.05% by volume of methyl alcohol and 0.1 gram of beta-naphthol per liter

3

and was subjected to contact with the same caustic solution in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten. The results of these tests are shown in the following table:

Table I

Portion-----	1	2	3	4	5	6	7
<i>Treatment</i>							
50° B _e . Caustic, Per Cent-----		1.0	1.0	1.0	1.0	1.0	1.0
Oxygen, Per Cent Theoretical-----		300	300	300	300	300	300
Methyl Alcohol Per Cent-----			0.5	0.05			0.05
B-Naphthol, gm./l.-----					0.5	0.1	0.1
<i>Tests</i>							
Doctor test-----	DNP	DNP	DNP	DNP	DNP	DNP	Pass
Color-----	30	30	30	30	30	30	30

It will be seen from the foregoing results that the only treatment which caused the solvent naphtha to pass the doctor test was the one where both methyl alcohol and beta-naphthol were present. All of the other treatments reflected that the naphtha was not sweetened by virtue of the fact that it did not pass (DNP) the doctor test. It is of interest to note that the treatments did not affect the color of the solvent naphtha which remained at 30, the original color of the solvent naphtha being 30. Since the alcohol may have a detrimental effect on the flash point of solvent naphthas to which it and beta-naphthol are added prior to contact with caustic solution and oxygen, it may be desirable in the practice of the present invention to remove the alcohol. This may be effectively done by washing the sweetened product with water or by heating the sweetened product to remove methyl alcohol therefrom by simple distillation. Neither one of the treating operations has any effect on the color. A sample of the solvent naphtha treated in accordance with the present invention as shown in column 7 of Table I was divided into three portions. Each of these portions contained a small quantity of alcohol by virtue of the alcohol having been added thereto in admixture with beta-naphthol. One portion was heated to 150° F., the second portion to 200° F. and the third portion to 250° F. The flash points and Saybolt colors of the heated sweetened product were then determined and are shown in Table II:

Table II

Temp., ° F.-----	Room Temp. ¹	150	200	250
Tag Flash, ° F.-----	117	120, 120	121, 121	120, 121
Color, Saybolt-----	30	30	30	30

¹ About 80° F.

It will be noted that heating the solvent naphtha to 150° F. effectively removed the alcohol, as indicated by the specification flash point, and heating the solvent naphtha to as high as 250° F. did not affect the color.

EXAMPLE II

In order to illustrate further the synergistic effect of methyl alcohol and beta-naphthol in the practice of the present invention, a high sulphur refined oil raffinate, from solvent extraction of a hydrocarbon fraction in the kerosene boiling range, having a copper number of 40 was divided

4

into eight portions. One portion was contacted with 50° Baumé sodium hydroxide solution as is in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten and the copper number determines immediately after the treat and after 1, 3, 5 and 24 hours settling. Three of the remaining seven portions had methyl alcohol added to them in varying percentages and were also subjected to treatment with the sodium hydroxide solution in the presence of the aforesaid amount of oxygen. A fifth portion had beta-naphthol added to it and was also subjected to treatment in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten, while the remaining three portions had both methyl alcohol and beta-naphthol added to them and were subjected to contact with the sodium hydroxide solution in the presence of 300% by volume of the theoretical amount of oxygen required to sweeten. The results of these tests showing the copper number immediately after and after 1, 3, 5 and 24 hours of settling and the percentage of reduction in copper number after 24 hours are presented in Table III:

Table III

	High Sulfur Refined Oil Raffinate of 40 Copper Number							
50° Baumé Caustic, Per Cent-----	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Methyl Alcohol, Vol. Per Cent-----	0.05	0.1	0.2			0.05	0.1	0.2
B-Naphthol, gms./l.-----				0.5	0.1	0.1	0.1	0.1
Oxygen, Per Cent of Theor-----	300	300	300	300	300	300	300	300
Copper No. After Treat:								
Immediately after-----	26	34	32	32	36	29	25	26
1 hour after-----	20	24	24	30	35	10	9	10
3 hours after-----	20	19	21	20	35	9	8	8
5 hours after-----	21	16				8	5	7
24 hours after-----	22	10	10	6	15	2-3	2	2-3
Per Cent Reduction in Copper Number After 24 Hours-----	45	75	75	85	60.5	90.2	90.5	90.2

It will be apparent from the data in Table III that treatment with sodium hydroxide solution in the presence of oxygen results in only 45% reduction in copper number, whereas treatment with varying amounts of alcohol showed reductions between 75 and 85% in the copper number. Treatment of the distillate to which beta-naphthol had been added showed a reduction of about 60% of the copper number, while in the practice of the present invention as illustrated in columns 6 to 8 of Table III, reductions of about 90% were effected. It will be seen that the reduction of the copper number in the practice of the present invention is greater than the average of that effected by the methyl alcohol and the beta-naphthol alone. Thus, it appears that the methyl alcohol and beta-naphthol when used together and added to the sour raffinate has a synergistic effect thereon in catalyzing the sweetening operation.

The Saybolt colors shown in Example I were determined in accordance with the ASTM Test method D156-38 while the flash point was determined in accordance with the ASTM Test method D56-36.

In the foregoing examples, the improvement obtained by the practice of the present invention has been illustrated by the copper number test. This is a well known analytical procedure in the petroleum industry. A description of the method of test may be found in "U. O. P. Laboratory Test Methods for Petroleum and Its Products," Third Edition, page H-61, Universal Oil Products Co., Chicago, 1947. This test is a measure of the mercaptan sulfur content of the oil being tested.

Although not illustrated by the several examples, one of the particular advantages of the

present invention resides in the catalytic effect of the alkali metal hydroxide solution. The alkali metal hydroxide appears to function as a true catalyst since the small amount used may be recycled to treat large quantities of the sour petroleum distillate. A small amount of the alkali metal hydroxide solution may be entrained in the treated naphtha, and, therefore, it may be necessary to replace the entrained amount with fresh solution. In short, it is contemplated in the practice of the present invention that the alkali metal hydroxide solution will be reused over and over again since it is not necessary to regenerate the alkali metal hydroxide solution.

The invention has been described and illustrated by employment of a mild oxidizing agent such as oxygen. It is contemplated that mixtures of oxygen with other gases, such as air may be employed. It is also contemplated that other mild oxidizing agents such as peroxides, permanganates, and the like may be used. For example, a hydrogen peroxide solution may be employed as the mild oxidizing agent.

In practicing the present invention, it is to be understood that the petroleum distillate may be subjected to a preliminary treatment for removal of hydrogen sulfide if the distillate contains hydrogen sulfide. Such preliminary treatment may include washing with a dilute alkali metal hydroxide solution or blowing with a free oxygen-containing gas, such as air. If hydrogen sulfide or other acidic compounds are present and not removed, the alkali metal hydroxide solution employed as the catalyst may very quickly become seriously depleted in activity.

In the practice of the invention, it will be desirable to use an amount of oxygen in excess of the theoretical amount required to sweeten the sour petroleum distillate. Ordinarily, an amount of about 300% of the theoretical amount to sweeten may be employed. However, sweetening in accordance with the present invention may be obtained with considerably lesser quantities of oxygen. In other instances as much as 500% of the theoretical amount required to sweeten may be employed. In fact, sweetening may be obtained in some cases by contact with the oxygen present in the treating vessel. It will be desirable to employ an amount of oxidizing agent at least equivalent to the theoretical amount required to sweeten.

The invention has been described and exemplified by employment of 0.5 to 1% by volume of the catalytic alkali metal hydroxide solution. It is contemplated that as little as 0.1 and as much as 5% by volume, or more, of the alkali metal hydroxide solution, based on the sour naphtha, may be employed. Very good results, however, are obtained with 1% by volume and this amount will be preferred.

It is to be understood that after separation of the alkali metal hydroxide solution the contacted naphtha may be washed with water, if desired, to remove any alkali metal hydroxide which may be entrained therein and to remove methyl alcohol when the fraction treated is a solvent naphtha or kerosene and where the presence of the alcohol may have a detrimental effect on the flash point thereof. In most instances it will be unnecessary to treat the contacted naphtha with water or other aqueous solutions.

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

1. A method for sweetening a sour petroleum distillate containing mercaptans boiling below 750° F. which comprises adding to said distillate an amount of beta-naphthol and methyl alcohol, said methyl alcohol being employed in an amount in the range between 0.5% to 2.5% by volume based on said distillate, and said beta-naphthol being employed in an amount in the range between 0.05 and 1 gram per liter of said distillate and then contacting said distillate containing methyl alcohol and beta-naphthol with a solution of an alkali metal hydroxide while adding a sufficient amount of a mild oxidizing agent to convert the mercaptans to disulfides and to obtain a sweetened distillate.

2. A method for sweetening a sour petroleum distillate containing mercaptans boiling below 750° F. which comprises adding to said distillate an amount of beta-naphthol and methyl alcohol in the range, respectively, from 0.05 to 1 gram per liter of said distillate and from 0.05% to 2.5% by volume based on said distillate, forming a mixture of an aqueous solution of sodium hydroxide and said sour petroleum distillate to which beta-naphthol and methyl alcohol have been added, and then agitating the mixture while adding a sufficient amount of a mild oxidizing agent to convert the mercaptans to disulfides and to obtain a sweetened distillate.

3. A method for sweetening a sour petroleum distillate containing mercaptans boiling below 750° F. which comprises adding to said distillate an amount of beta-naphthol and methyl alcohol in the range, respectively, from 0.05 to 1 gram per liter of said distillate and from 0.05 to 2.5% by volume based on said distillate, forming a mixture of an aqueous solution of sodium hydroxide and said sour petroleum distillate to which beta-naphthol and methyl alcohol have been added, and then agitating the mixture while adding a sufficient amount of air to convert the mercaptans to disulfides and to cause sweetening of said distillate, separating sodium hydroxide solution from said distillate and recovering said distillate.

4. A method for sweetening a sour petroleum distillate containing mercaptans which comprises adding 0.2% by volume of methyl alcohol and 0.1 gram per liter of beta-naphthol to said sour petroleum distillate, forming a mixture of said sour petroleum distillate to which methyl alcohol and beta-naphthol have been added with an aqueous solution of sodium hydroxide having a Baumé gravity of 50°, agitating the mixture while adding a sufficient amount of air to convert the mercaptans to disulfides and to cause sweetening of said distillate, separating said sodium hydroxide solution from said agitated distillate, and recovering said agitated distillate.

5. A method in accordance with claim 4 in which the amount of sodium hydroxide solution is 1% by volume based on the sour distillate.

6. A method for sweetening a sour solvent naphtha containing mercaptans having a boiling point in the range between 200° and 450° F. which comprises adding to said solvent naphtha methyl alcohol in an amount in the range between 0.1% and 2.5% by volume of said solvent naphtha and beta-naphthol in an amount in the range between 0.05 and 1.0 gram per liter of said solvent naphtha, forming a mixture of an aqueous solution of an alkali metal hydroxide and said solvent naphtha to which methyl alcohol and beta-naphthol have been added and then agitating the mixture while adding a sufficient

amount of a mild oxidizing agent to convert the mercaptans to disulfides and to obtain a sweetened distillate.

7. A method in accordance with claim 6 in which the alkali metal hydroxide is sodium hydroxide.

8. A method in accordance with claim 6 in which the aqueous solution is employed in an amount equivalent to approximately 1% by volume of the solvent naphtha.

9. A method for sweetening a sour solvent naphtha containing mercaptans having a boiling point in the range between 290° and 410° F. while maintaining the color of said naphtha which comprises adding to said solvent naphtha 0.05% by volume of methyl alcohol based on the solvent naphtha and 0.1 gram of beta-naphthol per liter of said naphtha forming a mixture of an aqueous solution of sodium hydroxide in said solvent naphtha to which methyl alcohol and beta-naphthol have been added, then agitating the mixture while adding a sufficient amount of

air to convert mercaptans to disulfides and to obtain a sweetened distillate and removing methyl alcohol from said sweetened distillate.

10. A method in accordance with claim 9 in which the methyl alcohol is removed by washing the sweetened naphtha with water.

11. A method in accordance with claim 9 in which the methyl alcohol is removed by heating the sweetened naphtha to a temperature of at least 150° F.

JOHN G. BROWDER,
ALVIN R. SMITH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,457,635	Bond	Dec. 28, 1948
2,494,687	Bond	Jan. 17, 1950