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DOCTOR PROCESS

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This invention relates to the treatment of sour hydrocarbon oils by the doctor process. More particularly, it relates to an improvement in conventional doctor sweetening of hydrocarbon oils.

Hydrocarbon oils which have been sweetened by the doctor process have a burning quality and oxidation stability lower than that of the oil prior to the sweetening operation. It is an object of this invention to improve the burning quality of oils sweetened by the doctor process. Another object is to improve the oxidation stability of hydrocarbon oils sweetened by the doctor process. Still another object is to decrease the loss in octane number of naphthas which have been sweetened by the doctor process.

These objects and other objects, which will be apparent in the course of the detailed description, have been attained by introducing into the sour hydrocarbon oil an amount of an essentially water insoluble aliphatic amine prior to sweetening said amine-containing oil by the conventional doctor process.

The aliphatic amines utilized in the process of this invention are the oil soluble amines which are also essentially insoluble in water, or, more particularly, in aqueous caustic solutions. These aliphatic amines include (*a*) primary aliphatic amines containing at least 8 carbon atoms, for example, octylamine, decylamine, laurylamine, cetylamine, sterylamine; (*b*) secondary aliphatic amines containing at least 5 carbon atoms in each aliphatic group, for example, di-n-amylamine, di-isoamylamine, and di-octylamine; (*c*) tertiary aliphatic amines containing at least 3 carbon atoms in each aliphatic group, for example, tri-n-propylamine, tri-isopropylamine, tri-n-butylamine, tri-isobutylamine, tri-n-amylamine, tri-isoamylamine, and tri-octylamine. The tertiary aliphatic amines do not react with free sulfur to form hydrogen sulfide. Since free sulfur is present in the sweet oil in virtually all doctor sweetening operations, the tertiary aliphatic amines are the preferred amines. The tri-n-butylamines are preferred for reasons of cost.

At least an amount of the aliphatic amine must be present in the oil to improve the quality of said oil. In general, at least about 0.001 weight percent, based on oil, of the aliphatic amine should be present. Amounts up to about 10 weight percent may be utilized. These large amounts are particularly suitable when extremely refractory oils are being treated; and when the aliphatic amine is recovered from the sweet oil by treating the oil with an acid that is reactive with the amine to form an oil insoluble salt. This salt may be decomposed by treatment with aqeous caustic solutions to recover the aliphatic amine for reuse in the process. In general, it is preferred to operate with between about 0.01 and 0.1 weight percent of aliphatic amine.

The aliphatic amine may be added to the sour oil prior to the addition of doctor solution, or the aliphatic amine may be added to the mixture of sour oil and doctor solution. In any case, the aliphatic amine must be present in the sour oil prior to contacting the sour oil with free sulfur. It is preferred to add the aliphatic amine to the sour oil prior to commencing the sweetening operation.

The feed to this process may be any hydrocarbon oil which is sour to the doctor test or has a mercaptan (copper) number of at least about 1.

The process is particularly suitable for the treatment of petroleum distillates boiling below about 750° F. Examples of these distillates are industrial naphthas, kerosene, diesel oil, heater oil, gas oil, etc. The process may be used on distillates obtained by the fractional distillation of crude petroleum or on distillates obtained from various conversion processes such as thermal cracking, catalytic cracking, reforming in the presence of hydrogen, etc. Sour petroleum distillates boiling in the heavier-than-gasoline range, i. e., between about 325° and 650° F., e. g., a heater oil boiling between about 330° and 575° F. are a particularly suitable feed.

In the doctor process, the doctor solution is made up of an aqueous solution of an alkali metal hydroxide and the reaction product of litharge and the alkali metal hydroxide. The amount of free-alkali metal hydroxide present in the doctor solution may be between about 5 and 30 weight percent, usually between about 10 and 15%. The plumbite content is commonly given in terms of the percent of PbO theoretically present. This content for a fresh doctor solution is usually between about 1.5 and 2.5 grams of PbO per 100 cc. of solution.

The temperatures at which the sour oil-doctor-sulfur are contacted in conventional doctor treating are between about 60° and 175° F. The treating temperature may be determined by the flash point of the particular sour oil charged to the process. Thus, when operating with naphthas, temperatures on the order of 70° F. may be used; when operating with a kerosene, temperatures between about 90° and 110° F. may be used; and when operating with a high flash point material such as a high boiling furnace oil, temperatures as much as 150° F. or higher may be used. Still another limitation on the contacting temperature may be color formation in the oil, e. g., some kerosenes rapidly develop color bodies when exposed for prolonged times at temperatures above about 120° F.

The amount of doctor solution utilized usually is between about 2 and about 50 volume percent based on sour distillate. More usually, the usage is between about 3 and about 15 volume percent.

Free sulfur is added to the contacting zone to effect the sweetening. Frequently more than the theoretical quantity of 0.5 mol, per each mol of mercaptan sulfur present in the sour oil is needed. The use of the theoretical quantity of free sulfur does not always produce an oil that is sweet to the doctor test; this is particularly true with heavier-than-gasoline distillates. The amount of excess free sulfur necessary varies with the sour oil charged and the operating conditions. In general, the higher boiling the sour oil, the more excess sulfur that is needed to produce a sweet product.

Frequently, in addition to the use of free sulfur, free oxygen is introduced into the sweetening zone. The presence of free oxygen has a favorable effect on the usage of free sulfur and also helps to convert some of the PbS formed in the sweetening reaction to the soluble plumbite formed.

The results obtainable with the process are illustrated by the following working examples. It is to be understood that these examples are illustrative only and do not limit the scope of usefulness of the process.

Example A

In this example, the sour oil was a thermally cracked heavy naphtha boiling between about 200° and 390° F. and had a CFR–R octane number of 72.3 clear.

Test 1.—This sour oil was contacted at 100° F. with

4 volume percent of fresh doctor solution containing 1.8 grams of PbO per 100 cc. of solution. The free-sulfur usage was the theoretical requirement. The sour oil, doctor solution and free-sulfur were agitated until the oil was sweet. The sweet oil was decanted from the lower layer of doctor solution and water washed to remove entrained doctor solution. The sweet oil was freed of water by passage through a filter paper coalescer. This oil was sweet to the doctor test.

Test 2.—Another portion of the sour oil was contacted according to the procedure described above except that 0.01 weight percent, based on sour oil, of tri-n-butylamine was added to the sour oil prior to contacting with the doctor solution and free sulfur.

The octane number of the sweet oil derived by the two methods of treating were determined by the CFR–R method and also on samples containing 1.0 cc. and 3.0 cc. respectively of commercial tetraethyllead solution. The results of these tests are set out below:

Sweet Oil	Octane Number CFR–R		
	Clear	1.0 cc.	3.0 cc.
From Test 1	70.9	77.7	83.3
From Test 2	71.8	78.5	84.4

These data show that by having present in the sour oil this small amount of tri-n-butylamine, it is possible to improve the octane number of the sweet oil by virtually one octane unit. In view of the expense of tetraethyllead, this gain in octane number represents a substantial monetary saving in tetraethyllead consumption for a given octane number product.

Example B

The effect of aliphatic amine addition was studied on the production of a turbo-jet fuel. This fuel consists of a blend of a cracked light naphtha, 12 volume percent, and a very high end-point virgin heavy naphtha, 88 volume percent. Only the virgin heavy naphtha fraction is doctor sweetened. The blend of heavy naphtha and light naphtha is more susceptible to oxidation than either component alone. Therefore, the results of these tests are given for the final turbo-jet fuel blend even though only the virgin heavy naphtha portion is doctor sweetened by either the conventional process or the aliphatic amine-doctor process of this invention.

The two components of the jet fuel have the following characteristics:

	Virgin Heavy Naphtha	Cracked Light Naphtha
API gravity	46	78
RVP	0.5	13.7
Mercaptan Number	22	Sweet
ASTM Distillation, ° F.:		
Initial	330	93
10%	343	103
50%	370	126
90%	428	200
Max	460	282

Test 3.—In this test, the virgin heavy naphtha was sweetened in accordance with the process set out in test 1 above, using 34% excess free sulfur.

Test 4.—In this test, the virgin heavy naphtha was sweetened in accordance with the procedure of test 3, except that 0.01 weight percent of tri-n-butylamine was added to the sour naphtha prior to the sweetening operation.

Test 5.—In this test, the sour naphtha was sweetened in accordance with the procedure of test 3 except that 0.01 weight percent of tri-n-butylamine was added to the sweet oil after completion of the sweetening operation.

The sweet virgin heavy naphtha obtained according to the procedures of tests 3–5 was blended with the cracked light naphtha to form a jet fuel which contained 88 volume percent of the heavy naphtha and 12 volume percent of the light naphtha. The blends were then tested for oxidation stability by the ASTM test D–873, except that the test was continued for 16 hours, i. e., 4 times that called for by the ASTM test. The results of these tests are set out below:

Blend Containing Sweet Oil From—	Accelerated Gum (16 hours)
	mg.
Test 3	54.6
Test 4	23.2
Test 5	50.2

These tests show that the presence of tri-butylamine in the sour oil prior to doctor sweetening decreased the gum produced in this test by more than one-half over conventional doctor sweetening. Tri-butylamine is not in itself an antioxidant as is shown by the results of test 5. Apparently, the tri-butylamine is effective only when present in the oil during the doctor sweetening process itself.

Example C

In this example, the effect of the process of this invention on burning quality of a heater oil was determined. The sour oil charged to the sweetening operation was derived by distillation from a high sulfur crude. This heater oil boiled over the range of 330° and 560° F. and had a mercaptan number of 64.

Test 6.—In this test, the sour oil was contacted with 5 volume percent of doctor solution at 120° F. in the presence of 70% of excess free sulfur. Air was used to agitate the oil-doctor mixture. The sweet oil was recovered according to the procedure of test 1.

Test 7.—In this test, the sweetening was carried out in accordance with the procedure of test 6 except that 0.01 weight percent of tri-n-butylamine was added to the sour oil before the doctor sweetening operation.

Test 8.—This test was carried out in accordance with the procedure of test 6 and 0.01 weight percent of tri-n-butylamine was added to the sweet oil.

It has been found that sleeve-type burners in domestic heating installations are most markedly affected by the presence of deposits formed during the burning of the oil. The Jungers burner is an example of an extremely sensitive sleeve-type burner. Because of this sensitivity the Jungers burner has been adopted by many refiners as a standard test burner for determining the burning quality of domestic heating oils. A full scale test using the Jungers burner involves the burning of many gallons of oil and many days of operation. A simple laboratory procedure has been developed which adequately predicts the results obtainable in the full size Jungers burner test. This laboratory method is known as the "steel dish deposit test" or "steel dish gum test."

The steel dish deposit test is carried out as follows: An 18—8 stainless steel dish is maintained at a temperature of 500° F. by means of a hot plate. The dish is saucer-shaped and has the following dimensions: Outside diameter, 2 inches; thickness at the edge, 5/16 inch; thickness at the center of the dish, 3/16 inch. The depression in the dish corresponds to a section of a sphere. The dish is provided with a thermocouple which permits the temperature of the dish to be measured. The dish is placed on a hot plate, the temperature of which is adjusted to maintain the dish at about 500° F. In order to more closely simulate the Jungers burner operation, the oil to be tested is aged in an open vessel at 200° F. for 72 hours. The oil to be tested is dripped at a substantially constant rate onto the dish. The rate of evaporation of the oil from the dish should be substantially equal to the rate of addition of the oil to the dish, i. e., the dish always contains a film of liquid oil. A 400 ml.

sample of oil is used in each test and the oil is added dropwise to the dish at a rate of about 1 ml. per minute. At the completion of the test, the dish is removed from the hot plate and allowed to cool. The difference in the weight of the dish before and after the test is called the steel dish deposit.

The oils derived from tests 6–8 were subjected to the steel dish test with the following results:

Sweet Oil From—	Steel Dish Deposit, mg.
Test 6	49
Test 7	20
Test 8	46

These tests show that the tri-butylamine is not in itself an inhibitor of deposit formation. However, when the tri-butylamine is present in the oil during the doctor sweetening procedure, the deposit forming tendency of the sweet oil is decreased by more than one-half.

Example D

In this example, the raw heater oil of Example C was sweetened according to the procedure described there except that 0.01 weight percent of diphenylamine was added to the sour oil before sweetening. The steel dish deposit of the sweet oil was 48 mg., which shows the diphenylamine was completely ineffective.

Thus, having described the invention, what is claimed is:

1. A doctor sweetening process which comprises (1) adding to a sour petroleum distillate boiling below about 750° F. between about 0.001 and 0.1 weight percent of at least one aliphatic amine selected from the class consisting of (*a*) primary aliphatic amines containing at least 8 carbon atoms, (*b*) secondary aliphatic amines containing at least 5 carbon atoms in each aliphatic group and (*c*) tertiary aliphatic amines containing at least 3 carbon atoms in each aliphatic group, (2) contacting said amine-containing sour oil with doctor solution and with free sulfur in an amount at least sufficient to sweeten said distillate, and (3) separating an essentially sweet amine-containing distillate from doctor solution.

2. The process of claim 1 wherein said sour distillate is a naphtha.

3. The process of claim 1 wherein said sour distillate is a heater oil.

4. The process of claim 1 wherein said amine is tri-n-butylamine.

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