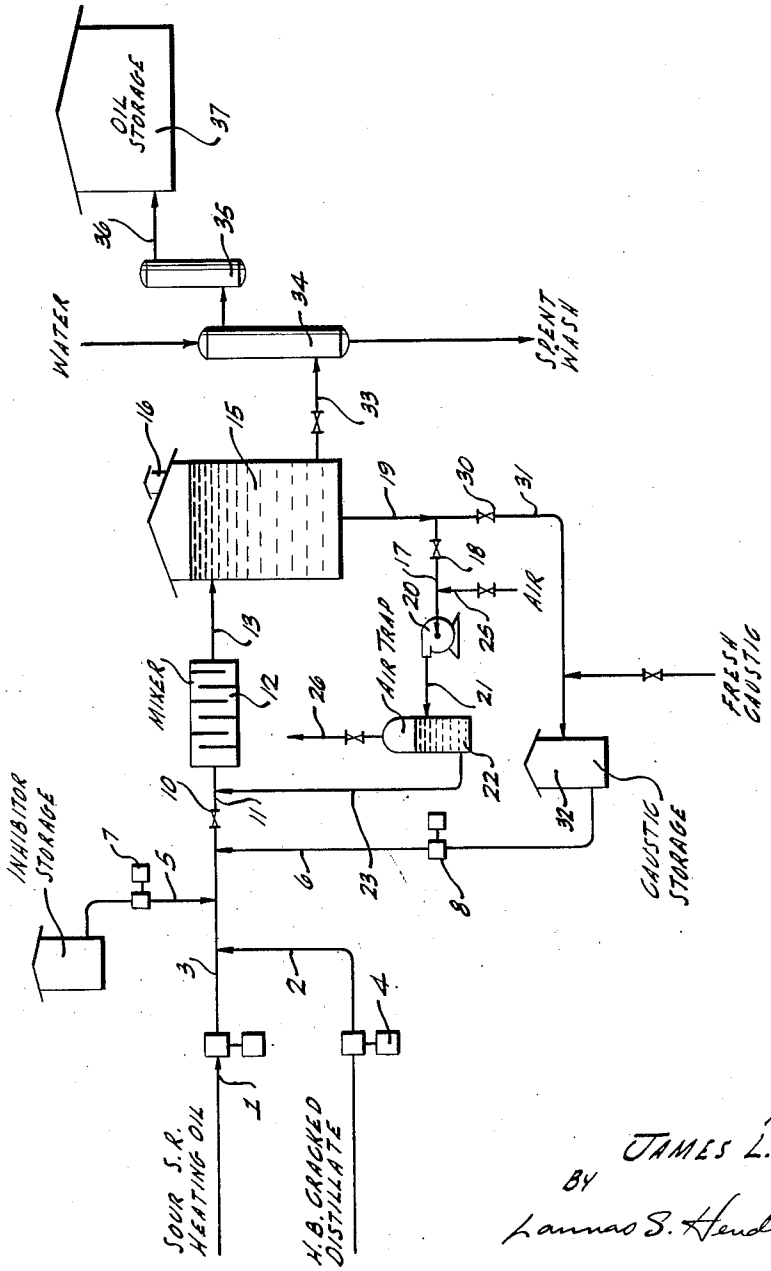
May 21, 1957 J. L. KELLER 2,793,171

INHIBITOR SWEETENING OF STRAIGHT-RUN HEATING OILS CONTAINING ADDED OLEFINS WITH A PHENYLENE-DIAMINE, ALKALI AND OXYGEN

Filed April 22, 1954



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United States Patent Office 2,793,171 Patented May 21, 1957

2,793,171

INHIBITOR SWEETENING OF STRAIGHT-RUN HEATING OILS CONTAINING ADDED OLEFINS WITH A PHENYLENE-DIAMINE, ALKALI AND OXYGEN

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Application April 22, 1954, Serial No. 424,921

4 Claims. (Cl. 196—29)

This invention relates to the sweetening of straight-run heating oils, and other high-boiling, saturated fractions, such as may be derived by distillation of petroleum oils or shale oils. These distillates are distinguished from gasoline fractions by their higher boiling range. The usual type of heating oils, i. e. stove oils, furnace oils, etc. ordinarily are composed of wide-cut distillates boiling within the range of about 350° to 750° F. Narrow-boiling cuts within this broad range include for example diesel fuels, light and heavy gas oils, kerosene, and the like. The term "straight-run distillates" denotes herein those distillates obtained by simple distillation of crude oils, or reduced crudes, wherein essentially no cracking has taken place. The sweetening of cracked distillates forms no part of the present invention.

The term "sweetening" is well understood in the art as designating processes whereby mercaptans are either removed from hydrocarbon distillates, converted to hydrogen sulfide and hydrocarbon fragments, or converted by oxidation to more innocuous sulfur compounds which remain in the distillate. The present procedure is concerned with the latter category of sweetening procedures. It is believed that such processes operate by oxidizing the mercaptans to disulfides and other sulfur compounds which are relatively odorless. Many such oxidation procedures have been proposed in the past, mostly for the sweetening of gasolines.

The primary object of this invention is to provide sweetening procedures which are sufficiently economical to be applied to low-cost products such as heating oils. More specifically, an object is to provide sweetening methods which require a minimum of process equipment, and a minimum of handling. A further objective is to provide sweetening methods which do not require excessive lengths of time, thereby avoiding unduly lengthy holdup periods in the treating vessels. Another object is to provide sweetening procedures which do not appreciably impair the burning qualities of the fuel oil. Other objects will be apparent to those skilled in the art from the following description.

Essentially, the procedural steps involved in this invention comprise first admixing with the straight-run heating oil a small proportion, of a cracked distillate boiling within the heating oil range, a small proportion of a phenylene diamine type inhibitor, and then agitating the mixture in the presence of an aqueous caustic solution and air. The temperature of treatment should be maintained between about 85° and 140° F., under which conditions sour stove oils containing for example up to about 0.04% of mercaptan sulfur by weight may be rendered substantially sweet to the doctor test, and olfactorily, within a period of about 5 to 48 hours. At the end of the treating period the mixture of oil and caustic is transferred to a settling tank where the aqueous caustic is allowed to settle and separate. The supernatant hydrocarbons are then drawn off and washed with water if necessary to remove traces of caustic, and then sent to

storage. The phenylene diamine inhibitor remains in the final product and imparts thereto the additional long-range benefit of retarding gum formation, which may result in the clogging of burner tips, valves and transfer lines.

It has long been known that certain petroleum fractions containing dissolved mercaptans could be sweetened by storing the same in the presence of air and the phenylene diamine type of gum inhibitors. This basic procedure is described in U. S. Patent No. 2,508,817. Ordinarily the preferred type of inhibitor is an N,N'-dialkyl substituted para-phenylene diamine, such as the N,N'-di-secondary butyl compound. The exact mechanism by which sweetening is brought about under these conditions is not clearly understood, nor is there any generally accepted theoretical explanation. It has recently been proposed (Rosenwald Petroleum Processing, September 1951, pages 969–973) that olefins may play an important role in this type of "inhibitor" or "tank" sweetening. However it is not possible to generalize, or to say with any certainty that this proposed reaction mechanism would extend to the sweetening of all types of hydrocarbons, regardless of their boiling range, and to all types of mercaptans regardless of their configuration and boiling range, and regardless of the configuration and boiling range of the olefins concerned. It has been found in fact that certain types of olefins appear to be much more active in their sweetening capacity than are other olefins. Moreover, the secondary and tertiary mercaptans apparently are more difficultly converted to disulfides than are the primary mercaptans.

Many other alternative oxidation procedures have been proposed for converting mercaptans to disulfides. However, all of the known methods possess one or more disadvantages which render them unsuitable for the economical treatment of low cost heating oils. For example, a seemingly simple procedure has been proposed (U. S. Patent No. 2,608,522) involving the treatment of heating oils with strong caustic solutions, ranging between 50° and 55° Baumé, while agitating the mixture in the presence of air. The use of strong caustic solutions is highly disadvantageous because they tend to discolor the oil, and also show a marked tendency to become emulsified in the oil, requiring several stages of washing for complete removal. Moreover, there is considerable question as to whether this procedure will actually effect sweetening, in the sense of actually extracting and/or oxidizing sufficient mercaptan to give a sweet product. The strong caustic and air treatment is likely to produce peroxides or hydroperoxides, which interfere with the detection of mercaptans by the standard doctor test, or by the copper number test. Distillates treated by this process may appear sweet to the doctor test, but mercaptan analyses frequently show an actual mercaptan level above the minimum which is regarded as sweet by the doctor test. To be doctor-sweet and odor-sweet, the distillates should contain less than about 0.0005% by weight of mercaptan sulfur, although this figure varies slightly for different distillates. However, it is not always necessary that the oil be rendered doctor-sweet; the prime objective is to produce an odor-sweet oil, and heating oils are frequently observed to be odor-sweet at mercaptan sulfur levels as high as about 0.0025% by weight.

It has now been discovered that doctor-sweet and odor-sweet straight-run heating oils may be obtained by simply adding to the oil about 5–25 pounds of the phenylene diamine inhibitor per 1000 barrels of oil, about 0.5% to 50% by volume of cracked distillates boiling within the same range, and then agitating the resulting solution for about 5–48 hours in the presence of air or oxygen and about 0.1% to 10% by volume of aqueous caustic solution, e. g. sodium hydroxide. The treatment may be

carried out in a vented storage tank to provide air by simple diffusion, or air may be continuously bled in through a circulating pump which is used for agitation. In sweetening such high-boiling stocks it has been found that low temperatures are relatively ineffective. Temperatures below about 75° F. require several days or weeks of storage for adequate sweetening. The cost of maintaining continuous agitation for such extended periods, and the large investment in storage equipment, are objectionable factors in producing cheap stove oils. It is therefore necessary to employ temperatures between about 85° and 140° F., and preferably between about 100° and 130° F. Higher temperatures tend to cause discoloration, and to promote the formation of emulsions. The use of the cracked stock to provide olefins has been found to be essential; an identical treatment of the straight-run stock alone results in substantially no sweetening.

The cracked stocks employed herein must be within the boiling range of the heating oil, and may be either sweet or sour. If sour oils are employed, they are sweetened along with the straight-run oil. If low boiling stocks are employed, the flash point of the heating oil may be reduced to below the specified minimum. It is not essential that the cracked stock have the same boiling range as the heater oil, it must merely boil well within, i. e. above, the minimum boiling point of the heating oil. For this purpose cracked stocks boiling anywhere between about 350° and 800° F. may be employed. Such stocks include for example cycle oils from thermal cracking units, or catalytic cracking units, and the bottoms from such cracking operations. Such products ordinarily will contain between about 10% and 30% by volume of olefins, and will have a flash point of between about 140° and 220° F. The minimum stove oil specifications require a flash point of 115° F. In addition to thermal and catalytic cracking stocks, other olefin-containing, high-boiling hydrocarbons may be employed, such for example as coker-distillate fractions and the like. Preferably about 1% to 5% by volume of such cracked stocks are employed. Higher proportions may sometimes be employed, but since these cracked oils usually promote gum and sludge formation, are undesirably dark in color, and may impair the burning quality of the stove oil, the lesser proportions, i. e. 5% or less, are preferred for producing No. 1 stove oils.

The caustic solutions employed herein may comprise aqueous solutions of sodium hydroxide, potassium hydroxide, lithium hydroxide, etc. In order to avoid emulsion problems, color deterioration, and undue peroxidation, it is highly desirable to use caustic solutions containing less than about 25% by weight of solid caustic. Referring to sodium hydroxide solutions, those containing between about 5% and 25% may be employed, corresponding to 7.4° to 31° Bé., respectively.

Reference is now made to the accompanying drawing which illustrates one particular method for carrying out the invention. The sour stove oil to be sweetened is brought in through line **1** from the fractionation system, with or without any desired intervening pre-treatment. It is economically advantageous to bring the oil directly from the distillation system so as to avoid reheating the oil to the desired sweetening temperature. However heating oils from other refinery sources may be employed.

The high-boiling cracked distillate is brought in through line **2**, and admixed with the sour stove oil in line **3**. The proportion of cracked distillate may be controlled by means of proportioning pump **4**. The mixture of straight-run and cracked stock then flows further through line **3**, and is admixed therein with the inhibitor from line **5**, and then with aqueous caustic from line **6**. The inhibitor may conveniently be admitted in the form of a concentrated or dilute solution thereof in hydrocarbons, alcohols, or other suitable solvent. The quantity of inhibitor and caustic may be controlled by means of proportioning pumps **7** and **8** respectively. The order of mixing the above ingredients is not critical, and hence any other sequence may be employed.

After admixing the desired proportions of heating oil, cracked distillate, inhibitor and caustic, the mixture is allowed to flow through open valve **10**, line **11**, baffle-plate mixer **12**, and line **13** into treating tank **15**. Tank **15** may be of any suitable design, preferably heat-insulated, which will provide sufficient capacity for the desired operation. In most cases it will be found that sufficient air may be provided by means of a vent **16**, allowing for air diffusion and diurnal breathing in and out of the tank. Other types of treating tanks may provide inadequate aeration, in which case air may be introduced in a manner to be subsequently described.

After treating tank **15** has been filled with an initial charge, valve **10** is closed and valve **18** is opened to initiate the sweetening cycle. It will be understood that the aqueous caustic tends to settle out in treating tank **15**, and means must hence be provided for continuously redispersing the aqueous caustic, as well as providing contact with air. These objectives may be accomplished in a variety of methods, only one of which is illustrated herein. In the illustrated procedure a small stream is continuously withdrawn from the bottom of tank **15** through line **19**, passed through valve **18**, line **17**, circulating pump **20**, line **21**, air trap **22**, line **23**, and thence, through baffle plate mixer **12**, back to tank **15**. In the event that the tank **15** is not constructed to provide adequate aeration, air may be continuously admitted to line **17** through valved line **25**. Passage of the mixture of air and oil through pump **20** and line **21** provides sufficient agitation to saturate the liquids with air. The slurry of oil and air is then preferably admitted to an air trap **22** to separate undissolved air, which is continuously or intermittently exhausted through line **26**. It is usually preferable to admit air in this manner, and to avoid the introduction of air directly into the large treating tank **15**. The purpose of this procedure is to avoid frictional contact of air with oil in a large treating tank, which presents an extended liquid surface area. Such surfaces frequently accumulate large static electric charges, resulting in explosions. The small air trap **22** provides insufficient air-liquid interface area to accumulate any appreciable static charges. In another modification, air-trap **22** may be inserted in line **13**, whereby more extensive air-liquid mixing is obtained in mixer **12**.

After the sweetening cycle has been continued in this manner for a sufficient length of time, the circulating pump **20** is shut off, valve **18** is closed, and the contents of tank **15** are allowed to coalesce and settle for a period of e. g. 15 minutes to several hours. Valve **30** is then opened, permitting the lower layer of caustic to be withdrawn through line **31** and sent to storage vessel **32** for reuse with the next charge of stove oil. The sweetened stove oil is then withdrawn through line **33** and passed through a countercurrent water-washing tower **34** to remove traces of caustic. It has been found that the water washing step is not always necessary, especially where dilute caustic solutions are employed. Frequently it is only necessary to pass the sweetened oil, after a suitable settling period, through a salt filter, which is packed with coarse granules of sodium chloride. Such a salt filter is illustrated herein at **35** for use in conjunction with the water-washed oil from tower **34**. The salt filter **35** removes the last traces of emulsified caustic and water haze from the treated oil, which is then passed through line **36** to ultimate storage **37**.

The above described mode of operation is only one feasible procedure and it will be obvious that many other modifications could be employed. The following examples may serve to illustrate more specifically certain critical features of the invention, without however limiting the same to the non-critical features.

EXAMPLE I

Sweetening experiments were carried out at 110° F. using a sour, straight-run stove oil obtained by distillation of a Montana crude oil. This stove oil was blended with various proportions of a cracked cycle oil from a thermal cracking unit. The cycle oil was also derived from a Montana crude. The principal characteristics of the stove oil and the cycle oil were as follows:

	Stove oil	Cycle oil
Gravity, ° API at 60° F	43.5	32.4
Boiling range, ° F	340–528	408–463
Acid solubility, percent by Vol	20	58
Aromatics, percent by Vol	20	45
Olefines, percent by Vol	Trace	13
Color, Saybolt	+21	−16
Flash point, ° F	128	171
S, mercaptan, percent by Wt	0.0220	0.0044
S, total, percent by Wt	0.16	0.43

The resulting mixtures were then blended with various proportions of Tenamene No. 2 inhibitor (N,N'-di-sec-butyl-para-phenylene diamine) and agitated in the presence of air and 2% by volume of an aqeous 10% caustic soda solution. The results for various treating periods were as follows:

Table 1

Experiment No.	1	2	3	4
Stove oil, percent by vol	100	100	98	95
Cycle oil, percent by vol	0	0	2	5
Inhibitor, lb./M bbl	0	10	10	10
Analyses, initial:				
Gravity, °API 60° F	43.5	43.5	43.3	42.8
Color, Saybolt	+21	+21	+22	+19
Mercaptan S, percent by wt	0.0220	0.0220	0.0191	0.0207
Analyses after treatment:				
Mercaptan S, percent by wt.—				
after 8 hours	0.0201	0.0174	0.0075	0.0043
after 24 hours	0.0193	0.0177	0.0025	0.0016
after 32 hours	0.0197	0.0171	0.0017	0.0012
after 2 days	0.0209	0.0160	0.0011	0.0010
after 5 days	0.0210	0.0092	0.0004	0.0006
Color, Saybolt after 5 days	+21	+12	+7	+9

Experiment No. 1 shows that substantially no sweetening takes place by treatment with caustic and air alone. Experiment 2 shows that adding inhibitor, but no cracked stock, gives only slightly improved results. In experiments 3 and 4, employing small proportions of cracked stock and inhibitor, the product is odor-sweet after 24 hours of treatment, and doctor-sweet after 4–5 days of treatment. By increasing the proportion of inhibitor to e. g. 20 lbs./M bbl. of oil, and/or by raising the temperature, and/or by increasing the proportion of cracked stock, the sweetening is further accelerated so that doctor-sweet products are obtained after 24 hours of treatment. In all cases, the slight color degradation noted is not of critical significance, as is the case when strong caustic and/or high temperatures are employed.

EXAMPLE II

Experiments similar to those of Example I were carried out at 80° F., using a stove oil and cycle oil derived from the same crudes, but exhibiting very slightly different properties. The results were as follows:

Table 2

Experiment No.	5	6
Stove oil, percent by vol	95	90
Cycle oil, percent by vol	5	10
Inhibitor, lb./M bbl	20	30
Analyses, initial:		
Gravity, °API 60° F	42.0	41.0
Color, Saybolt	+21	+20
Mercaptan S, percent by wt	0.0224	0.0218
Analyses after treatment:		
Mercaptan S, percent by wt.—		
after 2 days	0.0190	0.0139
after 7 days	0.0080	0.0042
after 11 days	0.0077	0.0037
after 17 days	0.0046	0.0014
Color, Saybolt after 17 days	−15	−10

The resulting products were odor- and doctor-sour even after 17 days of treatment, proving that low temperature treatment is ineffective, even at high concentrations of inhibitor and cracked stock. The color degradation was also marked as a result of the extended treatment.

From the above it will be seen that the methods described herein provide highly economical means for producing odor-sweet and/or doctor-sweet heating oils. However, the foregoing disclosure should not be considered as limiting, since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A method for sweetening a sour, straight-run fuel oil distillate boiling substantially entirely above 350° F. without substantial color degradation thereof, which comprises admixing with said straight-run distillate a small proportion, between about 1% and 5% by volume, of a cracked mineral oil fraction boiling within the boiling range of said straight-run distillate and containing a substantial proportion of high-boiling olefins, admixing therewith a minor proportion of an N,N'-dialkyl p-phenylene diamine inhibitor, agitating the resulting mixture in the presence of oxygen and in intimate contact with between about 1% and 10% by volume of a caustic solution containing between about 2% and 25% by weight of solid caustic dissolved in water, continuing said agitation at a temperature between about 100° and 130° F. for a period of time between about 5 and 48 hours, and then separating said aqueous caustic solution, thereby obtaining a sweetened, gum-stable product.

2. A process as defined in claim 1 wherein said caustic is sodium hydroxide.

3. A process for sweetening a sour, straight-run fuel oil boiling between about 350° and 750° F. without substantial color degradation thereof, which comprises admixing with said stove oil a small proportion, between about 1% and 5% by volume, of a cracked mineral oil fraction boiling within the range of said stove oil and containing a substantial proportion of high-boiling olefins, admixing therewith a small proportion of an N,N'-dialkyl-p-phenylene diamine inhibitor, agitating the resulting mixture in the presence of air and in intimate contact with between about 1% and 10% by volume of an aqueous caustic solution containing between about 2% and 25% by weight of solid caustic dissolved in water, continuing said agitation at a temperature between about 100° and 130° F. for a period of time between about 5 and 48 hours, and then separating said caustic solution, thereby obtaining a sweetened, gum-stable stove oil.

4. A process as defined in claim 3 wherein said caustic is sodium hydroxide.

7

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8

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