

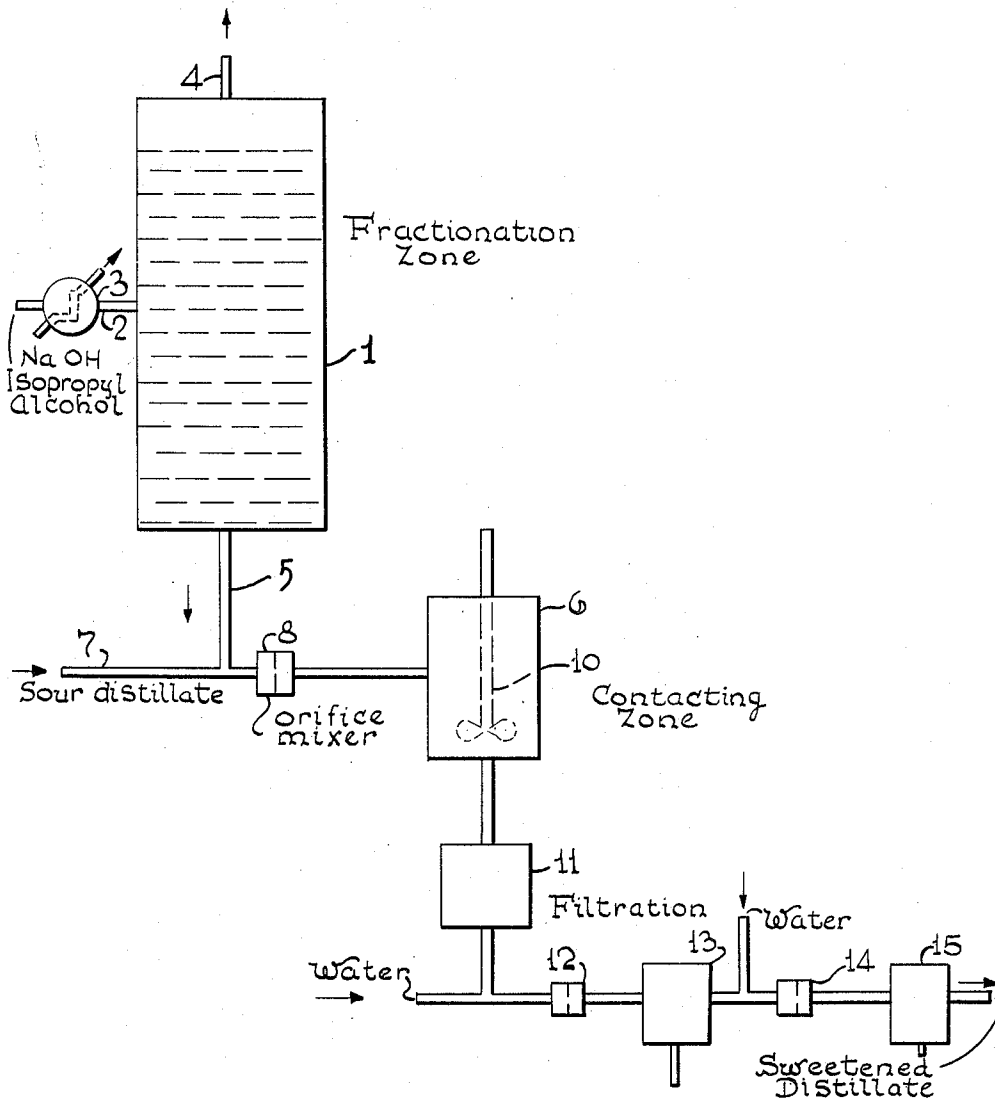
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GASOLINE SWEETENING PROCESS

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GASOLINE SWEETENING PROCESS

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This invention concerns a novel process for the refining of gasoline or naphtha. The process is particularly effective in eliminating objectionable mercaptans from gasoline to provide a "sweetened" product. The process of this invention is characterized by utilization of a novel treating agent consisting of the reaction products of isopropyl alcohol and sodium hydroxide as obtained under conditions to secure the azeotropic distillation of excess alcohol and water resulting from the reaction. The resulting treating agent is then employed to contact the gasoline to be sweetened, and the final gasoline product is secured by filtering and water washing the gasoline after contact with the treating agent.

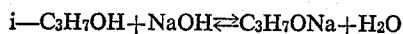
In the petroleum industry it is commonly desirable, in the preparation of a suitable gasoline product, to remove or convert certain malodorous sulfur compounds. Processes by which this may be achieved are generally called sweetening processes, and as indicated by this name are effective to convert or remove malodorous sulfur compounds so as to provide a sweet, or non-odorous product. While many processes are known, or have been proposed for sweetening gasolines, the present process is distinguishable from known processes and provides certain substantial advantages over the presently known sweetening operations. Thus, for example, a conventional sweetening process known to the art entails the contact of a mercaptan containing gasoline with a solid alkali metal alcoholate. Such a process requires preparation of the necessary alcoholate by reaction of sodium with the alcohol. This is commercially undesirable as sodium is a difficult reagent to handle and is relatively expensive. The process of this invention is advantageous over such a process in that pure sodium is not required, and that, furthermore, the sweetening results obtainable are superior to those obtainable by employing pure alkali metal alcoholate.

Similarly, it has been known that some degree of sweetening may be achieved by contacting a sour distillate with a mixture of alcohol and caustic soda or caustic potash. Again, the process of this invention is advantageous in that better sweetening results are obtainable.

The process of this invention is advantageous in requiring a comparatively simple processing sequence, necessitating only the contact of the distillate to be treated with the treating agent followed by simple filtration and water washing steps. The process does not require any facilities for recovery, regeneration or recycling of the treating agent, or constituents of the treating agent.

The nature, objectives and advantages of this process may be fully understood from the following description. Reference will be made to the appended drawing which diagrammatically illustrates a suitable flow plan embodying the process of this invention.

As indicated, a particular point of novelty in the process of this invention concerns the utilization of a particular treating, or sweetening agent. The treating agent is secured by the reaction of isopropyl alcohol and sodium hydroxide under carefully controlled conditions. Isopropyl alcohol and sodium hydroxide are subject to a reaction which may be represented by the following equilibrium:



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It would appear, therefore, that isopropyl alcohol and sodium hydroxide could be reacted together to provide sodium isopropylate. However, the equilibrium of the indicated reaction is actually predominantly to the left so that normally only traces of alcoholate will be formed. It has now been found, however, that a peculiarly effective sweetening agent may be obtained by affecting the equilibrium of the above cited reaction by securing the azeotropic distillation of water, formed on the right side of the equation, with an excess of alcohol. Thus, if sodium hydroxide is reacted with an excess of alcohol under temperature conditions at which an azeotropic mixture of alcohol and water will distill, the reaction may be forced to the right to form a substantial amount of sodium isopropylate. It appears that some free sodium hydroxide may remain unreacted and other compounds, such as sodium oxide and sodium carbonate, are believed to be formed during this step of the process. In any case it has been ascertained that the reaction of isopropyl alcohol and sodium hydroxide under the aforementioned conditions provides a sweetening agent which is distinguishable from either a simple mixture of isopropyl alcohol and sodium hydroxide, or from pure sodium isopropylate. Furthermore it provides a much cheaper sweetening agent than when using pure sodium isopropylate.

The sweetening agent of the nature described is then employed to contact the distillate to be sweetened at temperatures of about 20 to 200° F. and pressures of about 0 to 50 pounds per square inch. It is a particular feature of the process of this invention that the necessary contact of the treating agent with the distillate can be conducted at ambient temperatures and atmospheric pressure. The amount of treating agent to be employed is sufficient to provide about 0.01 to 2.0 percent of active ingredient based on the weight of the distillate treated, and dissolved in sufficient isopropyl alcohol in order to leave 1 to 3% of the alcohol in the gasoline. It is a part of this invention that sufficient treating agent be employed so that the final sweetened distillate, after filtration and water washing steps will contain about 2% of isopropyl alcohol.

After contact of the distillate with the treating agent, the distillate is filtered at ambient temperatures and is subjected to a water wash. While about five volume percent water may be employed in a single stage washing of the distillate, it is preferred that two water washes be applied, employing about 5% of water based on the oil in each of the water washes. The distillate resulting from this treatment constitutes an effectively sweetened distillate not necessitating any further processing, although, it is to be understood that the distillate may, if desired, be subjected to other processing steps.

Referring now to the drawing diagrammatically illustrating the process of this invention, the numeral 1 designates a fractionation zone employed for the preparation of the novel treating agent to be employed. Fractionation zone 1 is a fractionation zone containing at least about 20 theoretical plates. It is not suitable to employ a simple distillation stage as zone 1, as a sharp fractionation must be secured. This is based on the fact that an azeotropic mixture of isopropyl alcohol and water containing 9% of water boils at 80.4° C., while pure isopropyl alcohol boils at 82.4° C. It is consequently necessary for economic reasons to secure the azeotropic distillation of the water with a minimum distillation of isopropyl alcohol. Consequently, by introducing a mixture of sodium hydroxide together with an excess of isopropyl alcohol to fractionation zone 1 through line 2, and by heating the mixture to a temperature slightly above 81° C., it is possible to secure the azeotropic distillation of water from the reaction mixture. For this purpose a preheating coil 3, or a reboiler circuit of conventional design may be used in conjunction with fractionation

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zone 1. As a result of this fractionation an overhead stream will be removed from zone 1, through line 4, containing principally the azeotropic mixture of isopropyl alcohol and water together with any excess alcohol which may leave the fractionation zone. The bottom product of fractionation zone 1 removed from line 5, after suitable fractionation, will constitute the desired treating agent. While as indicated, the nature of the treating agent is not fully understood, it is known that the agent comprises substantial proportions of sodium isopropylate, together with minor proportions of sodium hydroxide, unreacted isopropyl alcohol and secondary reaction products. Suitable treating reagents are secured by the admixture of isopropyl alcohol, preferably containing not over 2% of water with 0.5 to 5.0% of sodium hydroxide and distilling at least 50% of the total water resulting from the original alcohol and that from the reaction of the sodium hydroxide with the alcohol. The amount of alcohol removed during the distillation of the isopropyl alcohol-water azeotrope is a function of the efficiency of the fractionation column employed, but will in most cases vary from 5 to 50% of the alcohol admixed with the sodium hydroxide. The aqueous alcohol distillate may be suitably dehydrated as by contact with strong NaOH solution, and recycled to the process. The treating agent thus consists of the reaction product of the sodium hydroxide and isopropyl alcohol containing about 1 to 10% of sodium isopropylate and other extraneous products such as unreacted sodium hydroxide, all dissolved in the isopropyl alcohol. This may be diluted with alcohol to any desired dilution before use. The treating agent of line 5 may then be introduced to a contacting zone 6 for admixture with the sour distillate to be treated which may be introduced to zone 6 by admixture with the treating agent in line 5, as by an orifice mixer, or equivalent means indicated by the numeral 8. Contacting zone 6 may be of any nature adapted to provide a reasonable degree of agitation to the mixture of treating agent and distillate. Thus, if desired, a simple mechanical stirrer 10 may be positioned in the zone so as to at least mildly agitate the mixture of distillate and treating agent. The temperature of contact should be chosen in the range of about 20 to 200° F., although the preferred temperature is about 75° F. The pressure of contact is not critical. The time of contact is a matter of seconds to several hours depending on the degree of contact between the naphtha and the treating agent.

The mixing of the sour distillate, and the treating agent causes at least partial precipitation of sodium mercaptides which are formed, causing the mixture to have a turbid appearance. Consequently, by passing the mixture from zone 6 through filtration zone 11 the precipitated mercaptides may be removed. The filtrate obtained from zone 11 is then washed with water in at least one, or preferably in two or more stages. Thus, as illustrated, water may be mixed with the filtrate by means of orifice mixer 12 or equivalent, and the water may then be separated from the treated distillate in separation zone 13 by simple phase separation. The upper oil phase collecting in zone 13 is then preferably drawn off for further mixing with water in orifice mixer or equivalent 14, and is separated from the water in the second separation zone 15, to provide the final product consisting of the sweetened distillate. The amount of water employed is to be carefully controlled. About 5 volume percent treat of water may suitably be employed in each of the washing operations, if two stages are employed and the total volume of water used in any case should be no more than about 20% to avoid or minimize extraction of the alcohol. While the temperature of washing may be varied, it is preferably about 60 to 90° F. The water washing is effective to extract certain soluble mercaptides from the distillate so as to further decrease the mercaptan content of the naphtha. Furthermore, as will be brought out,

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the water is effective in hydrolyzing unreacted alcoholate so as to permit the alcohol to remain in the naphtha in an advantageous manner.

Data exemplifying the nature of this invention are given in the following examples:

Example I

Thirteen hundred (1300) grams of 99% isopropyl alcohol were mixed with 20½ grams of flake sodium hydroxide (0.5 mol) and distilled through a Stedman Column having 50 theoretical plates. The uncorrected boiling points of the increments of liquid taken overhead were as follows:

	° C.
15 Initial B. P.-----	80.0
50 cc. overhead-----	80.7
100 cc. overhead-----	81.1
200 cc. overhead-----	81.2
300 cc. overhead-----	81.2
20 400 cc. overhead-----	81.4
500 cc. overhead-----	81.5
600 cc. overhead-----	81.7
650 cc. overhead-----	81.8

These data show that a mixture of the binary azeotrope and pure alcohol distilled during the major part of the distillation, indicating that the reaction of isopropyl alcohol and sodium hydroxide to form alcoholate and water had taken place to a considerable extent.

The undistilled portion from this run weighed 815 grams and consisted of a substantially clear solution at 40° C. On cooling to room temperature it set up to a gel.

Example II

Like proportions of 99% isopropyl alcohol and sodium hydroxide as used in experiment 1 were heated to a temperature of 75° C. and held there for approximately one hour. Only a small amount of the solid caustic has gone into solution and on cooling to room temperature some additional white solid precipitate formed and settled out. The data of this example show that reaction of isopropyl alcohol and sodium hydroxide to form sodium isopropylate is substantially nil in the absence of azeotropic distillation as conducted in Example I.

Example III

Sweetening experiments were conducted using a sour thermally cracked naphtha boiling in the gasoline range. In these runs the amount of sodium hydroxide added as the reaction product of isopropyl alcohol was 100% excess of theory and the amount of isopropyl alcohol was 2% based on the naphtha. Contact was made in all cases by mixing the naphtha and treating agent in a three neck flask for a period of one hour at room temperature (72° F.). Copper numbers were run on the treated stocks, both after filtration and after filtration followed by water washing. Data from these runs are given in Table I.

TABLE I

Treating Agent	Copper Number	
	Filtrated	Filtrated and Washed
Control-----	14	4.0
Sodium Isopropylate ^a -----	5.0	4.0
Reaction Product, Example I-----	4.0	0.5
10% Aqueous NaOH ^b -----	10	9
Alcohol and NaOH ^b -----	2.0	1.5
Alcohol and NaOH ^c -----	3.0	3.0

^a Isopropylate prepared from metallic sodium.

^b Three hundred percent excess of NaOH (instead of 100%).

^c Different from preceding run in that the alcohol and NaOH were preheated at 70° C. for one-half hour.

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It will be noted that the reaction product prepared from the azeotropic distillation of the alcohol and sodium hydroxide is more effective as a sweetening agent than the pure alcoholate prepared from metallic sodium. The aqueous alkali is quite ineffective and the suspensions of solid NaOH are only reasonably so. It will be noted from the data of Table I that as indicated by the copper number, the contacting of the naphtha with the treating agent of this invention, followed by filtration was effective to substantially reduce the mercaptan content of the naphtha. Thus, the copper number, as a result of this treatment was lowered from 14 to 4. However, on washing the distillate after filtration by employing two water washes (each 10 volume percent based on the oil), further mercaptans were removed to provide a final copper number of 0.5. In addition, excess isopropylate was hydrolyzed by the water wash so that the final distillate contained about 2 percent of isopropyl alcohol.

Example IV

It has been shown that engine stalls due to carburetor icing at atmospheric temperatures from 30 to 55° F. with high relative humidities are encountered with all makes of cars. Under comparable conditions, a commercial premium grade gasoline containing solvent oil resulted in the following number of stalls when operating a 1947 automobile engine at 40° F. and 100% humidity. Corresponding data are given for the number of stalls resulting when 99% isopropyl alcohol was added to the gasoline, as for example, by means of the process of this invention.

Isopropyl Alcohol Concentration in Gasoline, Percent by Vol.	Number of Engine Stalls Due to Carburetor Icing
0	14
1	3
2	2
2.5	0

It is to be seen therefor that the process of this invention, as conducted to provide a sweetened gasoline containing about 1 to 3% of isopropyl alcohol, furnishes a desirable gasoline product.

As described, therefore, this invention concerns the sweetening of sour distillates with a treating agent obtained by reacting isopropyl alcohol with sodium hydroxide while azeotropically distilling water from the reaction mixture. The distillate to be treated with this sweetening agent is particularly contemplated to be a gasoline distillate consisting of hydrocarbons boiling in the gasoline boiling range, or from about 50 to 440° F. While the process is primarily intended for treatment of such distillates, more broadly the process may be applied effectively to any desired hydrocarbon fraction, or mixture boiling below about 700° F. Contact of the distillate with the treating agent is effective to convert mercaptan compounds to insoluble mercaptides largely removable by filtration and to soluble mercaptides removable by water washing. It is a particular feature of

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this invention that the final water washing is not only effective in removing soluble mercaptides, but is also effective in causing hydrolysis reactions to proceed so as to leave free isopropyl alcohol in the final distillate.

By this means the characteristics of the final gasoline distillates obtained from the process are enhanced as regards stalling characteristics in automotive engines under conditions of low atmospheric temperature and high humidity.

What is claimed is:

1. A process for sweetening a mercaptan-containing hydrocarbon distillate which comprises the steps of: mixing sodium hydroxide with an amount of isopropyl alcohol largely in excess of the amount of the said alcohol theoretically required to form sodium isopropylate therefrom, distilling from the last named mixture an azeotropic mixture of water and isopropyl alcohol through a distillation temperature range of from about 80° C. to less than 82° C., whereby there is left a distillation residue comprising undistilled isopropyl alcohol and the reaction product of sodium hydroxide and isopropyl alcohol, contacting the said hydrocarbon distillate with the said distillation residue, and thereafter filtering and water washing the said hydrocarbon distillate.

2. Process as defined by claim 1 wherein said azeotropic distillation is conducted to remove from the mixture of isopropyl alcohol and sodium hydroxide at least 50 percent of the total water in the mixture resulting from the original alcohol and from the reaction of the sodium hydroxide with the alcohol.

3. Process as defined by claim 1 wherein the original mixture subjected to azeotropic distillation comprises isopropyl alcohol and from 0.5 to about 5.0% of sodium hydroxide.

4. Process as defined by claim 1 wherein said petroleum distillate is contacted with sufficient of said distillation residue to effect contact with from about 0.01 to 2.0 percent by weight of said reaction product, based on the weight of the petroleum distillate.

5. Process as defined by claim 1 wherein said azeotropic distillation is conducted to remove from 5 to 50 percent of the isopropyl alcohol present in the original mixture of sodium hydroxide and isopropyl alcohol.

6. The process defined by claim 1 in which the said contact of the distillate with the said distillation residue is carried out at a temperature of about 20 to 200° F., and at a pressure of about 0 to 50 p. s. i. g.

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