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METHOD OF SWEETENING HYDROCARBON OILS WITH ALKALI POLYSULPHIDES

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This invention relates to a method of treating hydrocarbon fluids and the like, with particular reference to sweetening petroleum hydrocarbon oils, vapors and gases.

It has for its purpose the conversion of certain malodorous sulphur compounds occurring in petroleum hydrocarbons into less obnoxious substances. This method of treatment is generally termed "sweetening" and the malodorous substances sweetened are mercaptans.

One of the prerequisites of a good motor fuel is that it shall not possess a disagreeable odor. This is practically synonymous with saying that it shall not contain mercaptans. These malodorous substances at some stage of the refining process are accordingly usually either completely removed from the petroleum oil being processed or are converted by some means to less obnoxious substances. The latter method is employed in many cases and the conversion is accomplished by some means of oxidation wherein the mercaptans are changed principally to disulphides. The usual and accepted method for detecting the presence of mercaptans is the so-called "doctor" test, the details of which are given in most handbooks and testing manuals pertaining to petroleum products. A positive "doctor" test indicates the presence of mercaptans.

We have discovered that certain alkali polysulphides quickly and completely sweeten such mercaptan-bearing hydrocarbon oils, vapors and gases. This sweetening or oxidizing effect is exhibited in a general way by the higher polysulphides of the alkali and alkaline earth metals and most particularly by the higher polysulphides of sodium, potassium and ammonium. We have found that this sweetening effect on mercaptans is very pronounced in the polysulphide range from about the tetrasulphide to the pentasulphide or, taking the sodium polysulphides by way of illustration, from about $Na_2S_{3.5}$ or Na_2S_4 to Na_2S_5. Sweetening becomes much less pronounced as the polysulphide composition approaches Na_2S_3.

It has been found to be desirable to include a strong base or caustic alkali, such as sodium hydroxide, in the sweetening solution; and such desirability is demonstrated by the results of the following tests, conducted at 26° C. (79° F.) in a non-oxidizing atmosphere:

1. Five volumes of aqueous $Na_2S_{4.5}$ solution, containing 278 g. of $Na_2S_{4.5}$ per liter, was agitated with 60 volumes of a synthetic solution of n-butyl mercaptan (0.04 per cent mercaptan sulphur) in a petroleum fraction:

After 1 minute: Very positive or sour to "doctor" test.

2. One volume of 30° Bé. NaOH (300 g. of NaOH per liter) was added to mixture in (1):

After 1 minute agitation: Negative, or sweet, to "doctor" test.

3. Five volumes of $(NH_4)_2S_{4.6}$ solution, containing 377 g. of $(NH_4)_2S_{4.6}$ per liter, and 5 volumes of c. p. NH_4OH were agitated with 60 volumes of n-butyl mercaptan in a petroleum fraction (0.04 per cent mercaptan sulphur):

After 10 minutes: Sour, although less positive, or sour, than original.

4. Five volumes of 30° Bé. NaOH substituted for NH_4OH in (3):

After 1 minute agitation: Sweet.

The concentration of excess caustic in the polysulphide treating solution may vary within very wide limits, the minimum requirement for sweetening being that sufficient caustic be always present to react with all of the hydrogen sulphide formed in the polysulphide-mercaptan reaction in order to keep the sweetening reaction proceeding to completion. The caustic concentration may be as high as 300 to 450 g. per liter of NaOH. A concentration of the order of 200–225 g. (or above) per liter is advantageous from the standpoint of producing a product which is non-corrosive to the well-known copper strip test at 122° F. and also of more quickly sweetening higher mercaptans and refractory gasolines.

As evidence of the effect of NaOH concentration in producing non-corrosive sweetened products with alkaline polysulphide solutions, the following data are submitted when an iso-butyl mercaptan stock (0.04 percent mercaptan sulphur) has been treated with sodium polysulphide solutions containing various concentrations of NaOH. Six volumes of mercaptan stock were in each case sweetened with one volume of polysulphide-sodium hydroxide solution.

Concentration of NaOH, grams per liter of treating solution	Concentration of $Na_2S_{4.64}$, grams per liter of treating solution	Reaction of sweetened stock to copper strip corrosion test at 122° F.
438.7	115.7	Negative after 3 hours.
263.2	173.5	Negative after 3 hours.
197.4	173.5	Negative after 3 hours. (Slight indication of corrosion)
150.0	173.5	Positive in less than 2 minutes.
65.8	173.5	Positive in less than 1 minute
272.7	31.5	Negative after 3 hours

It is desirable to have the polysulphide concen-

tration fairly high for highly efficient sweetening, but again this may vary over a wide range depending on the characteristics of the stock treated, degree of contact between treating solution and stock treated, throughput of plant, etc. A preferred, very effective and relatively inexpensive treating solution comprises $Na_2S_{4.5}$ and NaOH in the following concentrations:

$Na_2S_{4.5}$, 180 g. per liter
NaOH, 225 g. per liter

While we prefer the concentration of $Na_2S_{4.5}$, for instance, in our treating solutions to be around 180 g. per liter, or of $Na_2S_{3.5}$ to be about 150 g. per liter, good results are obtained with concentrations varying from 25–75 g. per liter of $Na_2S_{4.5}$ to 400 or 450 g. per liter; and from 20–60 g. per liter of $Na_2S_{3.5}$ to 350 or 400 g. per liter.

Similarly to the practicability of maintaining ammonium polysulphide solutions substantially alkaline (with strong bases, as sodium hydroxide) when they are utilized as sweetening agents, we have found that it is also necessary from a practical viewpoint to maintain a substantially high alkalinity in treating solutions comprising the readily hydrolyzable alkaline earth polysulphides. We have found, for example, that calcium polysulphides approximating CaS_4 very quickly sweeten mercaptans when an excess of solid $Ca(OH)_2$ is present.

The sweetening effect of alkali and alkaline earth polysulphides on mercaptan-bearing hydrocarbon oils is further exemplified and substantiated by the data submitted in the table below. All polysulphide solutions contain a substantial amount of the corresponding hydroxide or of sodium hydroxide and are reacted in the approximate volume ratio of 1:6, treating solution to stock treated. The latter is a synthetic solution of n-butyl mercaptan (0.04 per cent mercaptan sulphur) in a light petroleum fraction.

Polysulphide	Reaction to "doctor" test after agitation
Na_2S_3(NaOH)	After 10 minutes: Incompletely sweetened, but greatly improved.
Na_2S_4(NaOH)	Less than 1 minute: Sweet.
$Na_2S_{4.6}$(NaOH)	Less than 1 minute: Sweet.
$K_2S_{4.3}$(KOH)	Less than 1 minute: Sweet.
$(NH_4)_2S_{4.6}$(NaOH)	Less than 1 minute: Sweet.
CaS_4(Solid $Ca(OH)_2$)	Less than 1.5 minutes: Sweet.

In preparing polysulphide solutions as above, elementary sulphur (precipitated or the usual flowers) was added to aqueous solutions of the simple or mono-sulphides which had been prepared with concentrations of approximately 145 g. of Na_2S, 205 g. of K_2S and 160 g. of $(NH_4)_2S$ per liter. With the desired amount of elementary sulphur added, solution of the sulphur was permitted to take place at atmospheric temperature, which readily occurred with occasional agitation of the mixture. Elevating the temperature of the mixture to hasten solution of the sulphur is inadvisable in certain cases, especially if air is present, and was not practiced since it causes decomposition of the polysulphides. A minimum access of air during the storage of the solutions and during the treating operation is advantageous in avoiding similar deleterious effects.

Calcium polysulphides may be conveniently prepared by heating, for 20 or 30 minutes, a mixture of calcium hydroxide and flowers of sulphur in water at about the boiling point of the solution. We have found that approximately 1.5 parts of sulphur to 1 part of $Ca(OH)_2$, by weight, reacted in this manner produces an effective sweetening agent when employed under alkaline conditions.

In addition to n-butyl and the lower mercaptans, higher polysulphides in similar concentrations to those solutions in the aforementioned illustrations quickly and completely sweeten hydrocarbon solutions of secondary and tertiary butyl and iso- and n-amyl mercaptans. In the case of n-heptyl mercaptan, as an example of the higher mercaptans, and some types of refractory petroleum naphthas, the time required for complete sweetening is quite long. We have found that a small quantity of alcohol (as little as 1 or 15 per cent by volume) added to the polysulphide treating solution causes the most difficult gasolines and the higher mercaptans to be completely sweetened in one to three minutes of agitation. For example, a very sour cracked naphtha which was still slightly sour after 10 minutes agitation with an alkaline $Na_2S_{4.6}$ solution, was sweet in less than 1 minute when a fresh portion of the naphtha was agitated with the same polysulphide solution to which had been added 3 per cent by volume of ethyl alcohol. Potassium polysulphides more effectively sweeten refractory mercaptans than do the corresponding sodium polysulphides. For example, a very refractory naphtha required the addition of alcohol to an $Na_2S_{4.5}$ treating solution for rapid sweetening, whereas a solution comprising $K_2S_{4.3}$ and a caustic alkali sweetened the naphtha in slightly over 2 minutes. The particular alcohol added to the treating solutions is relatively unimportant, cost of such being the principal factor involved. The utility of the alcohol appears to reside in its property of aiding in bringing the mercaptans in the hydrocarbon solvent into more intimate contact with the active sweetening substances in the aqueous treating solution. We prefer to incorporate methyl or ethyl alcohol in our treating solutions when necessary, although propyl and butyl alcohols, while much less effective, may also be employed. No more than 1 to 5 per cent by volume of the treating solution need usually consist of alcohol, although more may be used if desired. Depending upon the solubility of the alcohol in the hydrocarbon liquid treated, some alcohol will be lost in the hydrocarbon phase, and it is accordingly preferred to maintain the alcohol in the treating solution at a minimum consistent with the requirements.

We have also found that alkaline solutions of polysulphides lower than Na_2S_3 or $Na_2S_{3.5}$, for example, readily sweeten mercaptan-bearing petroleum hydrocarbon oils if elementary sulphur is dissolved in the oil, either naturally existent therein or purposely added, in quantity sufficient to increase the sulphur ratio in the polysulphide up to the composition for rapid sweetening.

A preferred method for utilizing our process for sweetening hydrocarbon oils comprises intimately contacting the sour hydrocarbon fluids with sodium polysulphide solutions containing about 180 g. per liter (1.5 lb. per gallon) of polysulphides of the approximate composition represented by the formula $Na2S_{4.5}$ and approximately 225 g. per liter (1.88 lb. per gallon) of NaOH. Preferably, the contacting is carried out in a continuous system, but batch agitation may be employed if desired. In either case, any well known means of contacting and agitation may be used, so long as air or other oxidizing atmosphere in the system is maintained at a minimum. A non-oxidizing gas may be employed to produce agita-

tion of the treating mixture or to maintain a non-oxidizing atmosphere in the system during the treating operation, or during preparation of the polysulphide solutions and their storage. We prefer to treat the hydrocarbon fluids at ordinary atmospheric temperatures, or from about 40° to 90° F., although the process may be operated at temperatures from 32° F. to 130–140° F. If the material to be treated arrives at the polysulphide treating stage at a temperature in excess of 100° F. we prefer to let the material cool to, or artificially decrease the temperature to 80° or 90° F. before subjecting it to the polysulphide treatment.

After intimately contacting the hydrocarbon fluid with the alkaline polysulphide solution, the former is separated from the treating solution by settling and decantation, or by other separating means.

A good commercial grade of elementary sulphur may be used to prepare the sodium polysulphide stock, weighing the required amount of sulphur for an $Na_2S_{4.5}$ solution, for example, into a stock solution of sodium monosulphide prepared by dissolving Na_2S in a minimum amount of water and adjusting the resulting solution (by analysis or calculation) so that it contains approximately 145 g. of Na_2S per liter (1.2 lb. per gallon). While this concentration of Na_2S in the base or stock sodium mono-sulphide solution is preferable, the concentration may vary over quite a wide range without materially affecting the resulting polysulphide treating solutions. It may be increased up to 200 g. per liter or a stock solution may be employed with Na_2S concentrations of approximately 75 to 100 g. per liter.

By way of definition, ammonium compounds are classed with those of the alkali metals, sodium, potassium, etc. See page 657, Mellor, "Modern Inorganic Chemistry", Longmans, Green and Co., 1925. Alkali hydroxides, caustic alkali, strong bases and sodium hydroxide, for instance, are used as synonymous terms. While the first definition above classes ammonium hydroxide as an alkali hydroxide, it is not so considered in the present method or treating agent for it is a "weak" base, is usually termed such, and is insufficiently "strong" for best utility in the process just described.

From the foregoing it is believed that the various steps of the process may be readily understood by those skilled in the art, and it is apparent that changes may be made in the details disclosed, without departing from the spirit of the invention, as expressed in the claims.

What is claimed and desired to be secured by Letters Patent is:

1. A process of sweetening sour hydrocarbon oils without the aid of lead compounds, which comprises as the initial step agitating the oil while at atmospheric temperature with an aqueous solution consisting of a strong base and a polysulphide higher than the trisulphide of an element of the group consisting of the alkali and alkaline earth metals, and separating the oil from the treating solution.

2. A process of sweetening sour hydrocarbon oils without the aid of lead compounds, which comprises as the initial step subjecting the oil while at atmospheric temperature to the action of an aqueous treating solution consisting of a strong base and a sodium polysulphide higher than the sodium trisulphide, and separating the oil from the treating solution.

3. In a process of oxidizing mercaptans to the disulphide form without the aid of lead compounds, the step which consists in initially subjecting a sour hydrocarbon oil containing the said mercaptans while at atmospheric temperature, to the action of an aqueous treating solution consisting of a strong base and a sodium polysulphide higher than the trisulphide, and separating the oil from the treating solution.

4. A process of sweetening sour gasolines without the aid of lead compounds, which comprises as the initial step agitating the gasoline while at atmospheric temperature with an aqueous solution consisting of sodium hydroxide and sodium polysulphide higher than sodium trisulphide, and separating the oil from the treating solution.

5. A process of sweetening mercaptan-bearing petroleum oils without the aid of lead compounds, which comprises as the first step intimately contacting the oil in a non-oxidizing atmosphere at substantially atmospheric temperature with an aqueous solution consisting of sodium hydroxide and sodium polysulphide higher than the trisulphide, and separating the oil from the treating solution.

6. A method of sweetening sour gasolines which comprises as the first step agitating the gasoline without the aid of lead compounds, while at substantially atmospheric temperatures with a solution of sodium hydroxide and sodium polysulphide higher than the trisulphide in an aqueous solvent containing about 1 to 15 per cent of a saturated aliphatic alcohol, and then separating the gasoline from the treating solution.

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