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SWEETENING PROCESS

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This invention relates to a method of refining mineral oil distillates and is more particularly concerned with the step known in the industry as "sweetening", whereby a sour distillate having a positive A. S. T. M. doctor test is treated so as to give the negative test characteristic for sweet oil.

A number of oil sweetening processes are known in the oil refining industry, the most common among which is the doctor treatment. In this last treatment a sour mineral oil distillate is thoroughly contacted with an alkaline solution of lead oxide in the pressure of a small quantity of elementary sulfur; the mixture is allowed to settle, and the treated sweet oil is separated from the spent doctor solution and the sludge consisting of lead sulfide formed during the treatment. The cost of lead oxide makes this treatment rather expensive; moreover, the lead sulfide precipitated during the reaction causes gasoline losses by promoting emulsification. It was very desirable, therefore, to devise a sweetening method not requiring the use of an expensive reagent and not entailing the formation of a solid precipitate. It is an object of this invention to provide such a method.

It is another object to improve the sweetening step of my invention by addition of a corrosion-inhibitor to the treated distillate, so that any residual elementary sulfur left in the said distillate after my treatment is rendered non-corrosive. This latter point will be made more clear in the following discussion.

According to my invention a sour mineral oil distillate is sweetened by treatment with an alkali hydroxide, such as sodium and potassium hydroxide, or soda lime, in the presence of elementary sulfur dissolved in the distillate being treated. I have discovered that I can sweeten any mineral oil distillate, i. e. obtain a product giving negative A. S. T. M. doctor test, by treating said distillate with an alkali hydroxide, either in water solution or in solid form, in the presence of a sufficient quantity of elementary sulfur; I have discovered, that a certain amount of dissolved sulfur in a distillate is essential to effect the sweetening reaction; the amount of sulfur required varies for different distillates, and for the form in which the alkali is applied, and has to be carefully regulated. I have found that for any distillate the amount of elementary sulfur either added or already present, should normally not be less than about one half of the mercaptan sulfur present in the said distillate; preferably it should not be greater than about double the amount of said mercaptan sulfur. The amounts of elementary sulfur required to be dissolved in a sour oil in order to effect the sweetening reaction by my process, although being relatively small, are markedly greater than those required for an ordinary doctor treatment; in this last treatment the amounts of free sulfur normally are not required to exceed one half of the mercaptan sulfur present in the sour oil, which is to be sweetened.

A portion of the dissolved elementary sulfur usually remains in the sweet product, and as it is undesirable to have a large quantity of such sulfur left in the finished distillate on account of its corrosiveness, I prefer, in order to avoid a large excess of residual sulfur in the sweetened oil, to add gradually during my treatment small quantities of elementary sulfur to the mixture of the distillate and alkali hydroxide, while this mixture is vigourously agitated. The reaction is observed by means of doctor tests on the samples withdrawn from the mixture, and I stop adding sulfur immediately when the distillate has become sweet. The mixture is then allowed to settle, and the sweetened product is separated from the spent, or partly spent, alkali hydroxide used in the process. As has been stated above, the alkali hydroxide may be used in this process either in solution or in solid form; as a general rule, the effectiveness of the treatment increases with the concentration of the alkali hydroxide solution, so that less elementary sulfur is required to complete the sweetening reaction when more concentrated solution is used. Excellent results are produced in all cases by using a solid alkali hydroxide either as a filter bed or as a contact material suspended in the distillate while the mixture is agitated; the required elementary sulfur concentration is lower when the distillate is treated with a solid alkali hydroxide, than when the latter is used in water solution. The sulfur may be added in my process either prior to or during the step of contacting the distillate with the alkali hydroxide. In carrying out the process of my invention the elementary sulfur may be added to the distillate either as a solid, or in solution in a mineral oil distillate, or in a water soluble form, such as a polysulfide, or in any other suitable manner. In every case the essential requirement for obtaining a complete sweetening reaction is to have a sufficient quantity of sulfur dissolved in the distillate, while the latter is brought in contact with the alkali hydroxide.

Normally, the total sulfur content of the distillate is increased by this process rather than reduced. However, I have observed that when I use soda lime with the elementary sulfur, in sweetening mineral oil distillates by my process, a slight but noticeable reduction of the total

sulfur content of the distillate is produced in certain cases. For example, a sour cracked gasoline containing .34% S was sweetened with .5% by weight soda lime and .05% elementary sulfur; the sweetened product contained .31% S; the removed sulfur was apparently free sulfur originally present in the distillate; its quantity would not have been sufficient, however, to complete the sweetening and the .05% more sulfur had to be added.

More often, however, when using elementary sulfur and an alkali other than soda lime, an increase in the elementary sulfur content is observed in the distillates sweetened by my process. In the past such effect was considered to be quite detrimental on account of the corrosive action of this form of sulfur. It has been found possible, however, to counteract this corrosive action of free sulfur by the addition of relatively small quantities of chemical compounds which apparently inhibit the corrosive activity of the sulfur. Various unsaturated hydroaromatic compounds such as cyclohexene, dipentene, pinene, tetrahydronaphthalene, or hexahydronaphthalene, have the desired effect. In no case is it necessary to add the compound for inhibiting free sulfur corrosion in quantities greater than about four times the amount of the elementary sulfur present in the distillate.

If, however, the excess of elementary sulfur would be objectionable, even though made harmless by adding, for instance the tetraline, means may be resorted to, which reduce the elementary sulfur content of the distillate. For this purpose for instance compounds may be added which are capable of binding elementary sulphur. For instance, the removal of elementary sulfur could also be effected by treating the sweetened product with alkali polysulfide; for example, two sour gasolines with .34% and .15% S contents, respectively were sweetened by my process, using a caustic soda solution and solid sulfur, whereafter the sulfur contents increased to .40% and .21%; these sweet gasolines were next contacted with a 5% solution of technical sodium polysulfide, and after this treatment were found to contain only .30% and .08% S, or almost 10% and 50% respectively less sulfur than the original sour gasolines.

This behaviour of an alkali polysulfide may appear unexpected in view of the statement made above that the addition of a polysulfide is a means for introducing the elementary sulfur required for my sweetening process. This apparently inconsistent behaviour of alkali polysulfides has been confirmed, however, by additional experiments in which sour distillates containing free sulfur in quantities below those required for my sweetening reaction have been sweetened with a concurrent removal of elementary sulfur when treated with solid, powdered sodium hydroxide and sodium polysulfide. In these treatments sodium polysulfide acted both as a source of elementary sulfur and as a desulfurizing agent.

Other substances which have the effect of removing the sulfur from the sweetened distillate are for instance solid potassium hydroxide or finely divided metals, such as copper, or sulfides.

Having thus set forth the object and substance of my invention, and various means for carrying out same in the actual refining practice, I do not intend to limit myself to the particulars described in this specification, but desire to claim as new and useful the general method of sweetening a mineral oil distillate with an alkali hydroxide in solid form or in solution in the presence of elementary sulfur. The following claims are appended to recite more fully the scope of my invention.

I claim as my invention:

1. A process for producing a sweet non-corrosive mineral oil distillate, comprising: treating said distillate solely with an alkali hydroxide and elementary sulfur and adding to the resulting product a small quantity of an unsaturated hydroaromatic compound which is capable of inhibiting the corrosive action of sulfur.

2. A process for producing a sweet non-corrosive mineral oil distillate comprising treating said distillate solely with an alkali hydroxide and elementary sulfur and adding to the resulting product a small quantity of tetrahydro naphthalene.

3. A process for producing a sweet non-corrosive mineral oil distillate comprising treating said distillate solely with an alkali hydroxide and elementary sulfur and adding to the resulting product a small quantity of pinene.

4. A process for producing a sweet non-corrosive mineral oil distillate comprising treating said distillate solely with an alkali hydroxide and elementary sulfur and adding to the resulting product a small quantity of cyclohexene.

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