

UNITED STATES PATENT OFFICE

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METHOD OF SWEETENING OILS

Vernon J. Loyd, East Chicago, Ind., assignor to
Socony-Vacuum Oil Company, Incorporated,
New York, N. Y., a corporation of New York

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This invention has to do with the sweetening of petroleum hydrocarbons containing "sour" sulphur constituents, as mercaptans and the like, to render the material sweet to the "doctor" test.

In treating hydrocarbons, such as straight run gasoline, natural gasoline, cracked gasoline and the like, to render them sweet to the "doctor" test, the objective is to remove materials of the nature of dissolved sulphur, hydrogen sulphide, mercaptans or the like or to convert them to innocuous compounds. Washing with aqueous solutions of strong alkalies, such as caustic soda will remove most of the hydrogen sulphide and some, but not all, of the mercaptans. Washing with aqueous caustic to which some material has been added as a "solutizer," or solubility promoter, enables the caustic to dissolve and remove more or all of the mercaptans. Butylene glycols, butyric acids, and phenolic materials are so used. Older methods make use of sodium plumbite formed by dissolving lithage in caustic soda, the effect here being to convert mercaptan to mercaptides and later to disulphides, which are innocuous to the doctor test, by addition of free sulphur.

In general, all processes of this kind leave something to be desired, and this field, one of the oldest in petroleum refining, is still the subject of active research.

The principal object of this invention is the provision of a novel process for rendering petroleum hydrocarbons sweet to the doctor test and reducing the amount of mercaptan sulphur.

This invention is based upon the discovery that effective reduction of mercaptan sulphur may be effected by treatment with aqueous caustic soda solution, containing tannic acid, in the

presence of oxygen or an oxygen containing gas, such as air.

In this operation, the reaction is apparently not parallel to the usual "solutizer" type of operation, since the reaction apparently does not take place to any great extent in the absence of oxygen.

The caustic alkali solution to be used may be any of the usual alkaline solutions normally used for these purposes, such as caustic soda, caustic potash, alkali metal carbonates, ammonia and basic ammonium compounds and the like. Usual preference is had for caustic soda, in aqueous solutions of from about 5° Baumé to 20° Baumé, the usual and preferred strength being around 10° Baumé.

The tannic acid used may be the usual commercial grade of the material.

We have found this tannic acid activator to be effective in quite small amounts, ranging from 5.0% downward to fractions of 1% with amounts of from about 0.3% to about 1.0% by weight of caustic solution being the most effective.

To avoid undue consumption of reagent it is best to caustic wash the oil, prior to this treatment, as with an aqueous alkaline reagent, to remove hydrogen sulphide and the more readily removable sulphur containing materials.

The following experimental data show the effectiveness of the process herein described. To secure this data straight run and cracked gasolines were treated with various caustic alkali solutions, with and without tannic acid, in various concentrations, with oxygen present, with air, and with nitrogen to show the effect of oxygen elimination.

TABLE I

Effect of tannic acid on removal of mercaptan sulphur from straight run gasoline by caustic solution

[Raw S. R. gasoline 0.005% RSH]

NaOH Kind °Bé.	Tannic acid	Temperature	Ratio (NaOH:Gaso.)	Gas atmosphere	Number of extractions	Mercaptan removal
	Per cent	°F.				Per cent
Fresh 10.3.....	0.3	100	1:4	Air.....	1	72.5
Do.....	1.0	100	1:4	Air.....	1	72.5
Do.....	5.0	100	1:4	Air.....	1	67.5
Do.....	0.0	100	1:4	Air.....	1	25.0
Do.....	1.0	82	1:4	Air.....	3	75.0
Fresh 11.0.....	0.0	90	1:4	N ₂	1	29.0
Do.....	0.0	90	1:4	O ₂	1	29.0
Do.....	1.0	90	1:4	N ₂	1	31.8
Do.....	1.0	90	1:4	O ₂	1	73.4
Do.....	5.0	90	1:4	O ₂	1	62.5

TABLE II

Effect of tannic acid on removal of mercaptan sulphur from cracked gasoline by caustic solution

[Thermal cracked gasoline 0.025% RSH]

NaOH kind °Bé.	Tannic acid	Temper- ature	Ratio (NaOH:Gaso.)	Gas atmos- phere	Number of ex- tractions	Mercap- tan removal
	<i>Per cent</i>	<i>° F.</i>				<i>Per cent</i>
Fresh 10.3....	0.0	100	1:4	Air....	1	59.0
Do.....	0.3	100	1:4	Air....	1	77.3
Do.....	1.0	100	1:4	Air....	1	81.8
Regeneration 17 ¹ (a p- prox.).....	0.0	95	1:4	Air....	1	60.2
Regeneration 17 ²	1.0	95	1:4	Air....	1	70.4
Do. ³	1.0	95	1:4	O ₂	1	87.1
Do. ³	1.0	95	1:4	N ₂	1	59.1
Do. ³	1.0	95	1:4	Air....	3	85.3
Fresh 11.0....	0.0	90	1:4	O ₂	1	68.6
Do.....	1.0	90	1:4	N ₂	1	67.4
Do.....	1.0	90	1:4	O ₂	1	89.0
Fresh 35.9....	0.0	90	1:4	O ₂	1	65.3
Do.....	1.0	90	1:4	O ₂	1	83.6
Regeneration Do.....	0.0	90	1:4	N ₂	1	63.1
	1.0	90	1:4	O ₂	1	83.2
KOH						
Fresh 10.....	0.0	90	1:4	O ₂	1	69.5
Do.....	1.0	90	1:4	O ₂	1	91.8
Fresh 22.5....	0.0	90	1:4	O ₂	1	73.2
Do.....	1.0	90	1:4	O ₂	1	91.8

¹ NaOH solu. boiled before using.

² Ditto.

The above data demonstrate the effectiveness of the reagent.

I claim:

1. That method of removing mercaptans from petroleum fractions comprising contacting the fraction with an aqueous alkaline reagent to which tannic acid has been added, in the presence of oxygen.

2. That method of removing mercaptans from gasoline and the like comprising contacting the oil in the presence of oxygen with an aqueous solution of caustic soda activated by the addition of a small amount of tannic acid.

3. That method of removing mercaptans from gasoline and the like comprising contacting the oil in the presence of oxygen with an aqueous solution of caustic soda activated by the addition of a small amount, less than about 5%, of tannic acid.

4. That method of removing mercaptans from gasoline and the like comprising contacting the oil in the presence of oxygen with an aqueous solution of caustic soda activated by the addition of a small amount, from about 0.3% to about 1.0%, of tannic acid.

VERNON J. LOYD.