

UNITED STATES PATENT OFFICE

2,369,554

PROCESS FOR THE PREPARATION OF
SWEET HIGH OCTANE GASOLINEHerbert G. M. Fischer, Westfield, N. J., assignor
to Standard Oil Development Company, a corporation of DelawareNo Drawing. Application September 4, 1941,
Serial No. 409,489

5 Claims. (Cl. 196—33)

The present invention relates to the art of refining hydrocarbon oils. As is generally known, a number of hydrocarbon oils such as gasoline, naphthas and gas oil contain sulfur in various forms. For example, most of the gasolines produced in this country, in the raw state, contain appreciable amounts of hydrogen sulfide, thiophenes, and mercaptans. The presence of these compounds in commercial petroleum products is objectionable due to their offensive or "sour" odor and, consequently, most refineries "sweeten" these products before release to the trade.

An ordinary method of sweetening "sour" hydrocarbon oils is to treat them by the so-called lead doctor method. Briefly, this process consists of treating the sour hydrocarbon oil with a sodium plumbite solution or, in any event, an aqueous medium containing dissolved lead oxide and sodium hydroxide. Prior to this treatment, however, the more easily removable sulfur compounds, such as H_2S , are removed by simple treatment with sodium carbonate solution, caustic soda, or the like. This preliminary treatment, however, fails to remove substantial amounts of mercaptans. It may be said that the treatment of gasoline or other hydrocarbon oil with the lead doctor solution does not generally remove the mercaptans contained in the gasoline but converts them by oxidation to a form in which they are less odoriferous and objectionable. The exact mechanism of the reaction is a subject of some dispute, but a working hypothesis, at least, of the reaction which takes place when sour gasoline containing mercaptans is treated with lead doctor solution is the explanation that lead mercaptides are first formed by interaction between the mercaptans and the sodium plumbite, followed by careful addition of sulfur, whereupon the mercaptides and the sulfur react to form lead sulfide which precipitates from the gasoline and organic disulfides. In other words, the mercaptan is oxidized to the corresponding and less objectionable disulfide.

In the sulfur addition previously referred to, emulsification frequently occurs, that is to say,

when the gasoline which has been treated with sodium plumbite is further treated with sulfur, an emulsion containing gasoline forms at the bottom of the treating zone as a distinct phase from the upper sweetened gasoline phase. The phases are separated by any conventional method such as decantation and the emulsion is frequently centrifuged in the sweetening plant to separate the components, and samples of naphtha recovered from such a process showed the following analysis:

	First sample		Second sample, as received
	As received	Rerun to 98% overhead	
Sulfur, per cent.....	0.895	0.643	0.600
Color.....	10 Tag Robinson	+18S	10 3/4 Tag Robinson
Reactive sulfur, mg./100 ml.	13		13
Octane number, A. S. T. M. clear.	52.4	58.2	54.3

It will be noted that the above gasoline or naphtha is of conspicuously poor quality, so that if it is added, after recovery from the centrifuging operation, to the remainder of the gasoline, the final product is degraded accordingly.

I have now found that the naphtha or gasoline recovered from the aforesaid centrifuging operation can be improved as to quality by a reforming operation.

The main object of the present invention, therefore, is to improve the quality of a hydrocarbon oil recovered from the emulsified portion of a doctor sweetening operation, particularly as to octane number and sulfur content, by a thermal or catalytic reforming operation.

In carrying my invention into effect, and particularly to show the utility thereof, the second sample specification above was heated to 1000° F. under a pressure of 500 lbs./sq. in. and passed through a reaction chamber at a space velocity of 6 volumes of oil per volume of chamber per

hour. The product obtained was stabilized and redistilled to recover a product having a 400° end point and a Reid vapor pressure of 10 lbs. Complete inspection of the original and reformed products are contained in the table below:

Stock and procedure	Naphtha from Laughlin centrifuge (as received)	Reformed product
Operating conditions:		
Temperature.....° F		1,000
Pressure.....#/sq. in.		500
Feed rate.....v./v./hr.		6
Gasoline inspections:		
Color, Tag, Rob	10%	
Color, Saybolt		+10
Doctor test	(1)	(2)
Mg. reactive S/100 ml. oil	13	Trace
Sulfur.....wt. per cent	0.600	0.119
Octane No.:		
A. S. T. M.—clear	54.3	79.7
A. S. T. M.—+1½ ml. tetraethyl lead/gal.	60.4	82.5
C. F. R. R.—clear	61.5	92.2
C. F. R. R.—+1½ ml. tetraethyl lead/gal.	65.1	95.3
Reid vapor pressure.....#/sq. in.		9.4
Gravity.....° A. P. I.	50.5	47.4
Distillation of naphtha:		
I. B. P.....° F	158	121
Per cent at—		
158° F		6.0
212° F	7.0	31.0
257° F	28.5	51.0
302° F	57.0	74.5
356° F	86.0	91.5
392° F	96.0	97.0
F. B. P.....° F	411	405
Per cent recovery	98.0	98.5
Per cent loss	0.9	0.2
Dry gas analysis ³ from reforming operation:		
Hydrogen.....volume per cent		7.0
Methane.....do		35.0
Ethane.....do		24.7
Ethylene.....do		5.1
Propane.....do		16.7
Propylene.....do		11.5

¹ Passed.

² Did not pass.

³ Corrected to O₂, H₂, CO free basis.

By performing the operation, it will be noted that the sulfur content was reduced from 0.6 to 0.119%, and that the octane number was increased from 54.3 to 79.7 (American Society for Testing Materials Method and without lead tetraethyl addition) and from 65.1 to 95.3 by the Committee on Fuel Research Method, with 1½ cc. of tetraethyl lead per gallon added.

As to operating conditions during the reforming operation of the naphtha recovered from the emulsion resulting from the centrifuging operation, the following give good results:

Temperature 900–1050° F.
Pressure 200–1,000 lbs.
Feed rate 5–15 volumes of oil per volume of reaction space per hour

To recapitulate, the present invention relates to improvements in the treatment of gasoline, naphthas, or any other hydrocarbon oil which has been sweetened by the usual lead doctor method. As is known, following the addition of

sulfur in this operation, the sweetened mixture is settled and an emulsion phase is formed at the oil-doctor solution interface. This emulsion may contain from 5% to 70% of hydrocarbon oil.

The hydrocarbon oil, say gasoline recovered by centrifuging this emulsion is generally of inferior quality and cannot be added, after its recovery from the emulsion, to the main body of the sweetened gasoline without seriously degrading the latter. I have found that by reforming this recovered gasoline according to the details hereinbefore set forth, that I may improve the quality of this gasoline so that it may be added to the main body of the sweetened gasoline without causing degradation of the latter.

Good yields of improved gasoline or naphtha may be recovered from the aforesaid emulsion.

While I have illustrated my invention by means of the foregoing specific example describing a thermal reforming operation, it is pointed out that any of the known reforming catalysts may be employed; or, in other words, that the reforming operation may be carried out catalytically, using as a catalyst say 10% by weight of molybdenum oxide and 90% activated alumina. Hydrogen may also be employed, say 10 to 90 mol per cent.

The term "reforming" as employed herein means the heat treatment of naphthas for the purpose of improving the octane number thereof without materially changing the boiling range of said naphthas.

Many modifications falling within the spirit of my invention may be made by those familiar with this art.

What I claim is:

1. An improved process for the preparation of sweet high octane gasoline which comprises treating sour gasoline with aqueous sodium plumbite, thence adding sulfur, whereby two liquid phases consisting of an upper sweetened gasoline phase and a lower emulsion phase are formed, separating the two phases, centrifuging the emulsion phase to recover low grade gasoline therefrom, subjecting said low grade gasoline to a reforming operation at elevated temperatures to recover a product low in sulfur and having a high octane number, and adding the product to said sweetened gasoline.

2. The process set forth in claim 1 in which the reforming operation is carried out at a temperature within the range of from about 900 to 1050° F.

3. The process set forth in claim 1 in which the reforming operation is performed thermally.

4. The process set forth in claim 1 in which the reforming operation is carried out catalytically.

5. The process specified in claim 1 in which the reforming operation is carried out under superatmospheric pressure

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