

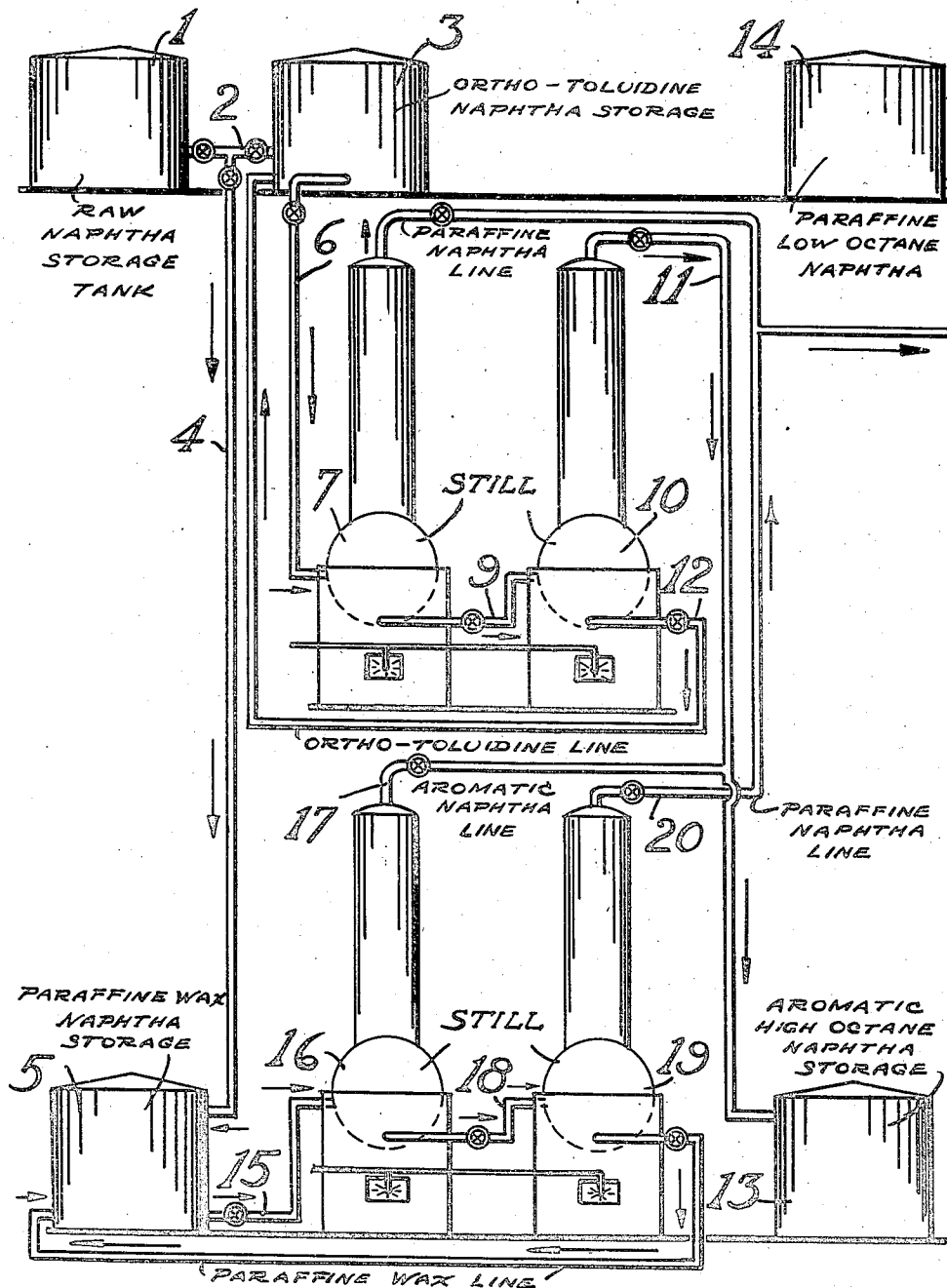
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J. M. SMITH

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METHOD FOR IMPROVING THE KNOCK RATING OF MOTOR FUEL BY DISTILLATION

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Joshua M. Smith Inventor
By *P. Young* Attorney

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METHOD FOR IMPROVING THE KNOCK
RATING OF MOTOR FUEL BY DISTIL-
LATIONJoshua M. Smith, Houston, Tex., assignor to
Standard Oil Development Company, a cor-
poration of Delaware

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The present invention is directed to a method for improving the knock rating of motor fuel. It has particular application to those naphthas which are rich in aromatics and already have a good knock rating but in which an improvement to the extent of a few octane numbers is desired.

Various methods have been proposed for improving the knock rating of motor fuels. The most common of these methods are thermal treatments conducted under pressure, which serve the purpose of increasing the light ends in the motor fuel and in this manner improving knock rating, thermal treatments in the presence of catalysts, which have the effect of converting many compounds of lower octane rating into compounds of higher octane rating and in this manner improving octane number, and solvent extraction with solvents which exhibit a preferential solubility for hydrocarbons of a certain type. The first two methods are accompanied by considerable losses of initial material, as permanent gas and resin or coke. The third method involves several procedural steps including layer separation, solvent recovery both from extract and raffinate, fractionation and blending for proper distillation curves.

According to the present invention, the desired improvement in knock rating is effected in a simple manner by distillation of the naphtha in the presence of selected vapor pressure depressants. For the improvement of the knock rating of such a naphtha, according to the present invention, it may be distilled in the presence of a high boiling substance which exerts an influence on the nature of the distillate. The employment of a high boiling straight chain compound as the depressant tends to increase the octane number of the first overhead fractions. Conversely, the employment of a high boiling aromatic hydrocarbon as the vapor pressure depressant tends to decrease the octane number of the first overhead and increase the octane number of the last overhead fractions.

It is not to be assumed that the present invention provides a method for the clean separation of a naphtha into constituents of different molecular structure. Rather, it is to be understood that the method according to the present invention affords a simple solution to the problem of increasing octane number in the upper range, that is, above 70, where increases are difficult to obtain except by methods which involve extensive plant equipment and heavy treating losses.

The depressant employed according to the present invention must have a boiling point substantially above that of the highest boiling constituent of the naphtha. As aromatic vapor pressure depressants, compounds, such as triortho-cresyl phosphate, cracking coil tar, ortho-tolui-

dine, and similar high boiling compounds containing the aromatic nucleus, may be employed. As open chain vapor pressure depressants higher paraffins, paraffin wax, high boiling paraffinic oils, and similar paraffinic materials may be employed. As will be apparent from the following discussion, the manner in which the vapor pressure depressant is employed is such that it necessitates no recovery of the depressant in a substantially pure state after it has performed its function.

The accompanying drawing is a front elevation, in diagrammatic form, of a plant suitable for carrying out the process according to the present invention. The plant illustrated is adapted for the operation of the process of the present invention in its preferred embodiment. It will be understood from the description of this plant that various changes may be made therein to modify the flow plan of the process without departing from the scope of this invention.

Referring to the drawing in detail, 1 represents a storage tank for the naphtha to be improved. A line 2 conducts the naphtha to a tank 3 in which it is mixed with an aromatic vapor pressure depressant, ortho-toluidine being designated in the drawing. A line 4 conducts the raw naphtha to a tank 5 in which it is mixed with an open chain vapor pressure depressant, paraffin wax being mentioned in the drawing. The mixture of naphtha and ortho-toluidine, the latter being employed in any desired amount varying from about one-third to twice the volume of the naphtha, is conducted through line 6 to a still 7 from which a first fraction, amounting to about one-half the naphtha fed in, is taken off through line 8. The residue from still 7 is conducted through line 9 to still 10 from which the remainder of the naphtha is taken off through line 11.

The naphtha taken off from the second still will be of higher octane number than the naphtha recovered from the first still. The distillation can be broken up into as many stages as desired, whereby fractions of successively higher octane number are recovered. The ortho-toluidine, together with whatever residues of the naphtha it may contain, is recycled through line 12 to storage tank 3. The high octane number naphtha fraction is led to a storage tank 13. The lower octane naphtha fraction is led to a storage tank 14. A low boiling fraction of improved octane number can be obtained from the lower octane number naphtha fraction by mixing with the latter, paraffin wax, subjecting the mixture to distillation, and recovering the light fraction of improved octane number as overhead. A somewhat higher boiling fraction of still higher octane number can be obtained by mixing the high octane number naphtha fraction with paraffin wax and distilling, whereby the first overhead cut

will have a higher octane number. The octane number of the naphtha fraction can also be increased by again subjecting it to distillation in the presence of an aromatic vapor pressure depressant whereby a material of poorer octane number will be obtained as an overhead initially, leaving a stock of higher octane number in the still.

The mixture of naphtha and paraffin wax in tank 5 is fed thru line 15 to a still 16 from which a fraction of the naphtha is taken overhead through line 17. The remainder of the mixture is conducted through line 18 to still 19 from which the remainder of the naphtha is recovered as an overhead through line 20. The overhead in line 17 will be of higher octane number than the initial stock and is conducted to storage tank 13. The overhead in line 20 will be of lower octane number than the initial stock and is conducted to storage tank 14. By reason of the commingling of the distillates in this manner the naphtha in storage tank 13 will have approximately the same distillation curve as the initial naphtha. The same is true of the naphtha in storage tank 14. Where more than two stages of distillation are employed, the overhead from the first two stages of the distillation in the presence of the aromatic vapor pressure depressant, is mixed with the overhead from the latter stages of the distillation in the presence of the paraffinic vapor pressure depressant.

As in the case of the first distillation, a fraction of higher octane number can be recovered from the overhead in line 17 by distillation in the presence of an aromatic vapor pressure depressant, the first overhead of such a distillation being of lower octane number and the residue being of increased octane number. Likewise a fraction of better octane number can be recovered from the overhead in line 20 by further distillation in the presence of paraffin wax, a narrow cut taken as an overhead having an improved octane number. To illustrate the process according to the present invention the stock selected was a finished aviation gasoline representing a 7.6% yield from Conroe crude. Inspection data on this aviation gasoline were as follows:

Gravity ° A. P. I.	60.7
I. B. P. ° F.	110
F. B. P. ° F.	246
5%	142
10%	150
20%	160
30%	168
40%	175
50%	182
60%	187
70%	194
80%	201
90%	213
95%	224
Recovery, %	98.0
Residue, %	0.4
Loss, %	1.6
Octane number, C. F. R.	72.1

A mixture was made consisting of 1200 cc. of the above aviation naphtha and 1400 cc. of ortho-toluidine (B. P. 392° F.) and distilled under atmospheric pressure with good reflux to prevent carrying over of any ortho-toluidine, taking 300 cc. condensate fractions. A second distillation was made on a mixture of 1200 cc. of aviation gasoline and 1400 cc. of commercial paraffin wax, under the same conditions, taking four 300 cc.

overhead cuts. A blend was made of the last overhead cut from the distillation over ortho-toluidine and the first overhead cut from the distillation over paraffin wax. Inspection data on this blend were as follows:

Gravity ° A. P. I.	62.4
I. B. P. ° F.	105
F. B. P. ° F.	264
5%	130
10%	140
20%	153
30%	164
40%	175
50%	185
60%	193
70%	201
80%	209
90%	221
95%	236
Recovery, %	97.0
Residue, %	0.9
Loss, %	2.1
Octane number, C. F. R.	76.3

A second blend was made of the last two overhead cuts from the distillation over ortho-toluidine and the first two overhead cuts from the distillation over paraffin wax. The C. F. R. octane number on this blend was 74.9.

A third blend was made up on the first overhead cut from the ortho-toluidine distillation and the last overhead cut from the paraffin wax distillation. The C. F. R. octane number on this blend was 70.5.

It will be noted that in the procedure followed in this run separate stills were not employed, the same effect having been obtained by collecting successive condensates from the single still.

It is not to be assumed that the improved knock rating of the last fraction of the distillation in the presence of ortho-toluidine can be attributed to the presence of ortho-toluidine in the distillate. Any ortho-toluidine in the distillate would raise the end point of the distillate over the 264° F. which was shown by the inspection. An amount of ortho-toluidine, sufficient to increase the octane number of the initial naphtha from 72.1 to 76.3, would raise the end point of the naphtha far above the 264° F. end point possessed by the blended fractions. This is illustrated in the following table:

Composition of blend:			
o-Toluidine, percent	0	0.3	0.6
Aviation gasoline, percent	100.0	99.7	99.4

Gravity, ° A. P. I.	60.9	60.8	60.4
I. B. P., ° F.	112	120	130
F. B. P., ° F.	256	269	291
5%	144	146	150
10%	152	154	157
20%	163	165	167
30%	170	175	176
40%	179	182	182
50%	186	188	189
60%	191	195	195
70%	200	202	201
80%	203	210	210
90%	216	223	223
95%	234	247	246
Recovery, %	98.0	96.5	97.0
Residue, %	1.0	1.0	1.0
Loss, %	1.0	2.5	2.0
Octane No., C. F. R.	73.5	74	75.0

As previously stated, the function played by the ortho-toluidine and the paraffin wax respectively in the above specific illustration could be performed equally as well by a number of other substances of similar character. This is particularly true because in performing its function the vapor pressure depressant exerts a physical action and does not enter into the final product. It is to be understood, therefore, that wherever ortho-toluidine has been mentioned, any high boiling aromatic non-reactive substance is contemplated and wherever paraffin wax has been mentioned, any high boiling open chain hydrocarbon is contemplated.

The nature and objects of the present invention having thus been set forth and specific illustrative embodiments of the same having been given, what is claimed as new and useful and desired to be secured by Letters Patent is:

1. A process for improving the knock rating of a naphtha containing aliphatic and aromatic constituents, which comprises adding to a portion of said naphtha a substance containing an aromatic nucleus and having a boiling point substantially above the highest boiling constituent of said naphtha, subjecting the mixture to distillation, taking off as overheads in said distillation a series of fractions of successively higher octane numbers, adding to another portion of said naphtha an open chain organic compound having a boiling point substantially above that of the highest boiling constituent of said naphtha, subjecting this mixture to distillation, taking off in said distillation a series of fractions of successively smaller octane numbers, and blending a sufficient number of the last overheads of the first distillation with the first overheads of the

second distillation to produce a mixture having a suitable distillation curve for motor fuel purposes.

2. A process according to claim 1 in which the substance added in the first distillation is ortho-toluidine and the substance added in the second distillation is paraffin wax.

3. A process according to claim 1 in which in each distillation the naphtha is divided into two fractions and in which the first fraction of the second distillation is blended with the second fraction of the first distillation.

4. A process according to claim 1 in which in each distillation the naphtha is divided into four fractions and in which the first two fractions of the second distillation are blended with the last two fractions of the first distillation.

5. A process for the recovery from a naphtha of a fraction having a higher octane number than said naphtha, which comprises distilling said naphtha in the presence of a substance containing an aromatic nucleus and having a boiling point substantially above the highest boiling constituent of said naphtha, and separating the overhead into a series of fractions and recovering from the last portion of the overhead a fraction having improved octane number.

6. A process for the recovery from a naphtha of a fraction having a higher octane number than said naphtha, which comprises distilling said naphtha in the presence of an open chain organic compound having a boiling point substantially above that of the highest boiling constituent of said naphtha, and recovering from the first overhead a fraction of improved octane number.

JOSHUA M. SMITH.