

ALIEN PROPERTY CUSTODIAN

SOLVENT TREATMENT OF NAPHTHAS AND THE LIKE

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This invention relates to improvements in the Edeleanu process for producing motor fuels, especially gasolines, of a high anti-knock value, described in United States Patents No. 1,585,473, dated May 18, 1926, and No. 1,661,566, dated March 6, 1928, and also to the production of improved lacquer solvents.

The patents describe processes of refining gasolines and kerosenes by splitting the crude distillate into a lower boiling and a higher boiling fraction, treating the latter with liquid sulphur dioxide and reblending the extract obtained by such treatment with the non-treated lighter fraction. This extract has a considerably higher content of aromatic and unsaturated hydrocarbons than the original stock and, since the presence of these constituents in the motor fuel is chiefly responsible for its anti-knock quality, it is apparent that by adding the extract obtained from the higher boiling fraction to the lower boiling one the anti-knock value of the latter is increased.

The anti-knock quality of a motor fuel is expressed by its "octane number", the anti-knock value being higher the higher the octane number. By employing the processes described in the above cited patents it has been possible to produce gasolines having octane numbers of 70 to 75. Sulphur dioxide treatment of the higher boiling fraction of a gasoline, as described in said patents, has been customarily done at temperatures between +14° F. and +20° F., the extract obtained in this manner having an average concentration of aromatic and unsaturated constituents of 35 to 40 percent.

New developments in the design of internal combustion engines, especially for aeroplanes, make it desirable to refine the gasoline to such an extent that the octane number is raised above the limit of 75 mentioned above.

We have found that such first grade gasolines may be produced by refining the higher boiling cut of the gasoline crude to such a degree that the extracts from this refining step have a very high content of aromatic and unsaturated hydrocarbons and are largely free of saturated hydrocarbons. By blending such extracts with the untreated gasoline fraction of lower boiling range, a gasoline is obtained, the octane number of which may be as high as 85 and above. With the methods employed for refining motor fuel so far, it has not been possible to commercially produce such a gasoline.

For producing extracts of the specification given above it is necessary to employ a solvent of excellent selectivity. Unfortunately any solvent is only slightly selective on low boiling petroleum fractions such as gasoline. However, we have found that liquid sulphur dioxide exerts a very high selective solvent action at temperatures substantially below zero degrees Fahrenheit, and that, if the extraction temperature is chosen suf-

ficiently low, the liquid sulphur dioxide splits the gasoline fraction into a raffinate being practically free of unsaturated hydrocarbons and an extract containing practically only unsaturated and aromatic hydrocarbons. This split will be sharper and the more complete the lower the temperature of extraction, and there is no technical but only an economical limit to reducing the extraction temperature.

Two factors are of chief importance for fixing the temperature of treatment with liquid sulphur dioxide, the one being the boiling range of the gasoline cut to be refined and the other its original content of aromatic and unsaturated hydrocarbons. The lower the boiling range of the gasoline fraction is and the higher its content of aromatic and unsaturated components the more advisable will it be to employ a very low temperature in extracting. Temperatures as low as -60 to -70° F. are still allowable for technical reasons as well as from an economical viewpoint.

According to our invention the following different steps may be employed for producing an extract of the specification given above:

(a) The naphtha fraction is treated with liquid sulphur dioxide at the conventional temperature of +14 to +20° F. in an extraction tower of conventional type. The extract layer obtained thereby by settling is further cooled down to about -60° to -70° F., whereby this extract layer is again split in two phases, an upper raffinate layer that has practically the same characteristics as the raffinate obtained in the first extraction step, and a new extract layer, which we may call second extract and which contains in some instances more than twice as much aromatic and unsaturated components as the extract obtained in the first step of extraction.

(b) Refining of the naphtha fraction is done in one single step, whereby the naphtha is cooled down to -60 to -70° F. and continuously introduced into the base of a conventional extraction tower which liquid sulphur dioxide of substantially higher temperature, for instance 14 to 20° F., is charged to the upper part of the tower. In continuous operation a temperature gradient will result from this method, the temperature of the liquid gradually decreasing from the top to the base of the extraction tower. The extract withdrawn from the base of the tower will be superior to that obtained in the first step of the method described under (a).

(c) Refining of the naphtha fraction is done in a single step as described under (b), but both stock and liquid sulphur dioxide are charged to the extraction tower with a temperature of -60 to -70° F. The extract obtained in this way will have a concentration of unsaturated and aromatic hydrocarbons equal to or even surpassing that of the extract produced by method (a), but requires somewhat more refrigeration.

In each of the three methods described above a series of mixers and settlers combined to make a unit that is conventionally called multi-stage mixing-settling equipment may be used in lieu of the vertical single extraction tower. It is further understood that the process described herein is not restricted to operation upon gasoline fuel nor to the temperature specified above.

As illustrations of the improvement, which may be obtained in treating light oils at temperatures substantially below zero degrees Fahrenheit, we mention the following examples:

Example 1

A naphtha cut with 57.9° A. P. I. gravity and a boiling range from 152 to 252° F. was treated in the countercurrent manner with 65% liquid SO₂ at +14° F. in one case and with 60% liquid SO₂ at -22° F. in another case. The yields of raffinate and extracts and their specifications are shown in comparison with the original naphtha in the following table:

	Original naphtha	Raffinate at +14° F.	Extract at +14° F.	Raffinate at -22° F.	Extract at -22° F.
Yield per cent by vol.....	100	62	38	80	20
° A. P. I.....	57.9	63.0	49.4	63.0	40.1
Per cent aromatic and unsaturated hydrocarbons.....	16	2.1	38.4	2.0	65.9
Saybolt color..	+17	+23	+10	+23	+4

The content of aromatic and unsaturated hydrocarbons was determined by means of sulphuric acid of 100% strength.

A comparison of the figures shows that the raffinate yield is increased from 62% to 80% by carrying out the extraction at -22° F. instead of at +14° F., and that the concentration of the aromatic and unsaturated components in the extract was raised from 38.4% to 65%.

Example 2

A cracked naphtha with a 46.4° A. P. I., boiling range from 195 to 286° F. and containing as much as 50% aromatic and unsaturated hydrocarbons could not be extracted at all with liquid SO₂ at +14° F. because of entire miscibility at this temperature. However, by reducing the temperature to -22° F. a separation into raffinate and extract phase took place and the treatment could be carried out in the normal way. For comparison the cracked naphtha was treated with 100% SO₂ followed by two treatments with 50% SO₂ at -22° F. and in another case the same stock was similarly treated at -60° F. The latter treatment resulted in a greatly improved raffinate yield and in a higher concentration of aromatic and unsaturated components in the extract, indicating the advantage of extremely low treating temperatures in some instances. The results may be seen in detail from the following table:

	Original cracked naphtha	Raffinate at -22° F.	Extract at -22° F.	Raffinate at -60° F.	Extract at -60° F.
Yield percent by vol.....	100	19	81	40	60
° A. P. I.....	46.4	59.0	43.1	58.3	37.8
Percent aromatic and unsaturated hydrocarbons.....	50	6	61	6	80
Saybolt color..	+23	+25	Dark	+25	Dark

The two fractions of the original naphtha from which the higher boiling one had been extracted with the result mentioned above had the following specifications:

Lower boiling fraction

Boiling range ----- 100-180° F.
Amount----- 93 vol. % of original stock

Higher boiling fraction

Boiling range ----- 170-250° F.
Amount----- 7 vol. % of original stock

The octane number of the untreated lower boiling fraction was 78.

The yield of extract from the higher boiling fraction was 60%, and this extract contained 80% aromatic and unsaturated compounds. The extract was rebled with the whole untreated lower boiling fraction with the result that the octane number was raised to 84.

The extraction of naphtha fractions at such low temperatures as mentioned above can be avoided when using an auxiliary solvent, which increases the selectivity of liquid sulphur dioxide. In this case extraction temperatures as low as 14° F. are sufficient to obtain extracts with higher contents of aromatic and unsaturated compounds.

Example 3

The naphtha fraction used in this example had the following boiling range:

I. B. P.....	220
10.....	229
20.....	232
30.....	236
40.....	240
50.....	244
60.....	249
70.....	255
80.....	263
90.....	276
End pt.....	304

The A. P. I. gravity of this untreated fraction was 49.0.

This naphtha fraction was extracted with sulphur dioxide and several mixtures of the latter with an auxiliary solvent, such as ethylene glycol, diethylene glycol and trimethylene glycol. All extractions were carried out at 14° F. and the extracts showed the following specifications:

	Extraction with sulphur dioxide	Extraction with sulphur dioxide plus ethylene glycol 20:80	Extraction with sulphur dioxide plus diethylene glycol 20:80	Extraction with sulphur dioxide plus trimethylene glycol 20:80
° A. P. I.....	44.5	39.1	38.4	38.7
Per cent aromatic unsaturated hydrocarbons.....	48	68.7	70.7	69.3
Saybolt color.....	+9	0	10	Dark

Other extractions were carried out with a similar favorable effect with mixtures of sulphur dioxide and the following auxiliary solvents: benzylalcohol and diacetone alcohol. The separation of these auxiliary solvents from the raffinates and extracts was effected with the first one by means of distillation and with the second one by means of washing out the solvent with water.

As auxiliary solvents suitable for use in accordance with this invention, there can be used any solvent miscible with liquid sulphur dioxide and selective against saturated low boiling hydrocar-

bons, which has a suitable boiling point in comparison with the naphtha fraction or which can be washed out of the raffinates and the extracts by means of other solvents easy to separate from the naphtha hydrocarbons.

Naphtha extracts produced by means of liquid sulphur dioxide at the normally employed extraction temperatures of +14 and +20 degrees Fahrenheit have also been used as lacquer solvents. The kauri gum number is an indication of the amount of naphthenic constituents present in a lacquer solvent, and a good solvent should have a kauri gum number of not less than 70.

Example 4

A naphtha from Gulf Coast crude was treated with sulphur dioxide at temperatures between -40°F. and +14°F. Four treatments with 37.5% of SO₂ by volume were given at each temperature, and the kauri gum number of the extract determined.

Treatment with SO ₂ in batch volume, percent	Original (untreated)	1	2	3	4
		4×37.5	4×37.5	4×37.5	4×37.5
Temperature, °F		+14	0	-14	-40
Extract yield, volume percent		47	45	39	32
Kauri gum No.	46.5	61	65	71	77

It can be seen from the table that a satisfactory lacquer solvent cannot be obtained from a naphtha distillate with a naphthenic base by treat-

Methods (a) and (b), above described, as compared with treating the entire volume of naphtha at low temperatures. The following examples are illustrative.

Example 5

(a) A naphtha sample was treated at 0°F. with 70% by volume SO₂. The extract solution, instead of charging it directly to the solvent recovery still, was first cooled to -60°F. which resulted in the separation of an intermediate oil. The three products, raffinate, intermediate oil and extract, were freed from SO₂ and analyzed, the results being as shown in the table below.

(b) The same naphtha was extracted counter-currently at a temperature decreasing from 0°F. to -60°F. with 70% by volume SO₂, the conditions being such that the SO₂ was admitted at the top of the extraction tower at a temperature of 0°F. and the naphtha stock at the bottom at a temperature of -60°F. By suitable cooling arrangements the temperature at the top of the extraction tower was held at 0°F., in the middle of the tower at -30°F. and at the bottom at -60°F. The results are shown in the table below.

(c) For purposes of comparison, the same stock was treated under the same conditions as in (b) excepting that a temperature of -60°F. was maintained in the whole tower. The results of these treatments are shown in the following table:

	Original oil	Treatment						
		(a)			(b)		(c)	
		70 vol. percent SO ₂ at 0° F. extract cooled to -60° F. to reject intermediate oil			70 vol. percent SO ₂ gradient 0° F. to -60° F.		70 vol. percent SO ₂ -60° F.	
		Raf.	Int. oil	Extr.	Raf.	Extr.	Raf.	Extr.
Yield	100	53.5	13.6	32.9	66.0	34.0	66.0	34.0
° A. P. I.	46.8	53.7	50.8	34.0	54.0	33.6	53.9	33.7
Vol. percent aromatics+olefines	20.8	2.0	9.5	82.0	0.8	84.0	0.8	83.3
Kauri gum No.	46.1	32.7	38.3	81.9	32.4	82.4	32.5	82.4
Octane No. C. F. R.	57.9	Below 41	46.2	91.1	Below 41	90.8	Below 41	91.1

ment at 14°F (the usual treating temperature of solvent refining by the Edeleanu method) nor even at 0°F., but that it is possible to produce superior lacquer solvents by treating at -14°F. and lower temperatures.

Naphtha extracts which are manufactured in accordance with this invention by treating the stocks with sulphur dioxide at substantially below +14° Fahrenheit, that is down to -70° Fahrenheit, are superior to the normal extractions inasmuch as they have a higher solubility for lacquer because of the higher percentage of aromatic and unsaturated components present. One of the great advantages of naphtha extracts over other lacquer solvents consists in that their boiling range increases gradually and evenly without showing breaks in the distillation curve. Consequently the formation of streaks, after applying the lacquer solution, is eliminated. The extraction may be carried out in the same manners as specified above in reference to motor fuels under (a), (b) and (c).

A substantial improvement in results and saving may be obtained by following the steps of

It is evident from these data that the temperature gradient extraction, Example 5(b) gives the same yields and qualities of raffinates and extracts as the normal treatment (Example 5(c)). The extract obtained by rejection of the intermediate extract in Example 5 (a) has almost the same quality as the extracts obtained in Examples 5 (b) and 5 (c), but the yield is somewhat lower, the reason for this lower yield being that the intermediate oil which was obtained by cooling the original extract solution from zero to -60° F. still contains substantial amounts of aromatics and olefines. The intermediate oil may, of course, be recycled into the extraction tower, thereby raising the extract yield.

The invention is not restricted to motor fuels and lacquer solvents, but relates to the process of producing improved extracts and blends thereof suitable for these and other purposes; and where motor fuels and lacquer solvents are referred to in the claims, it is to be understood that we intend thereby to include any use to which the product is adapted.

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