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F. W. SULLIVAN, JR

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SOLVENT FRACTIONATION

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2 Sheets-Sheet 1

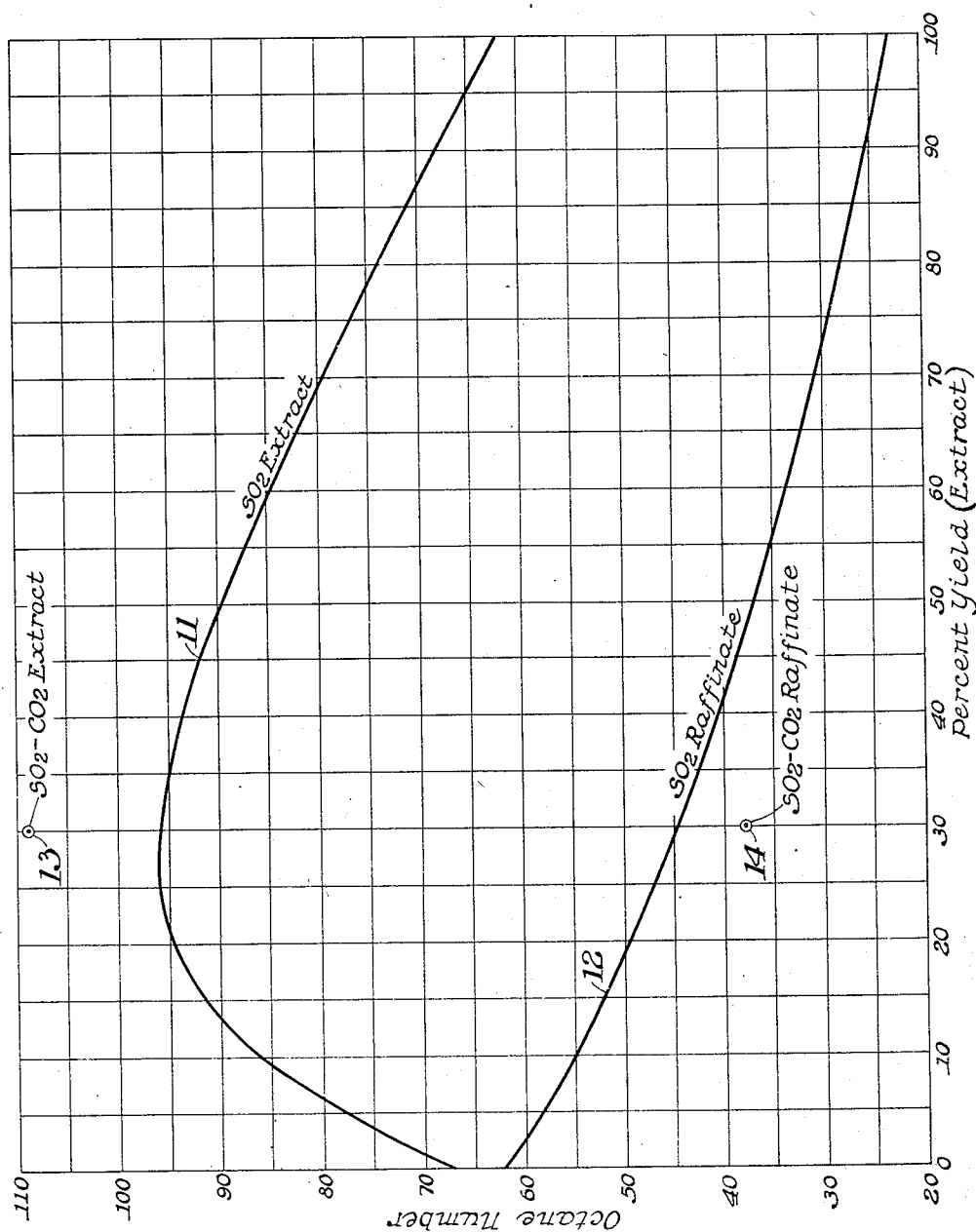


FIG. 1

INVENTOR
Frederick W. Sullivan, Jr.

BY Bruce K. Brown
ATTORNEY

March 17, 1936.

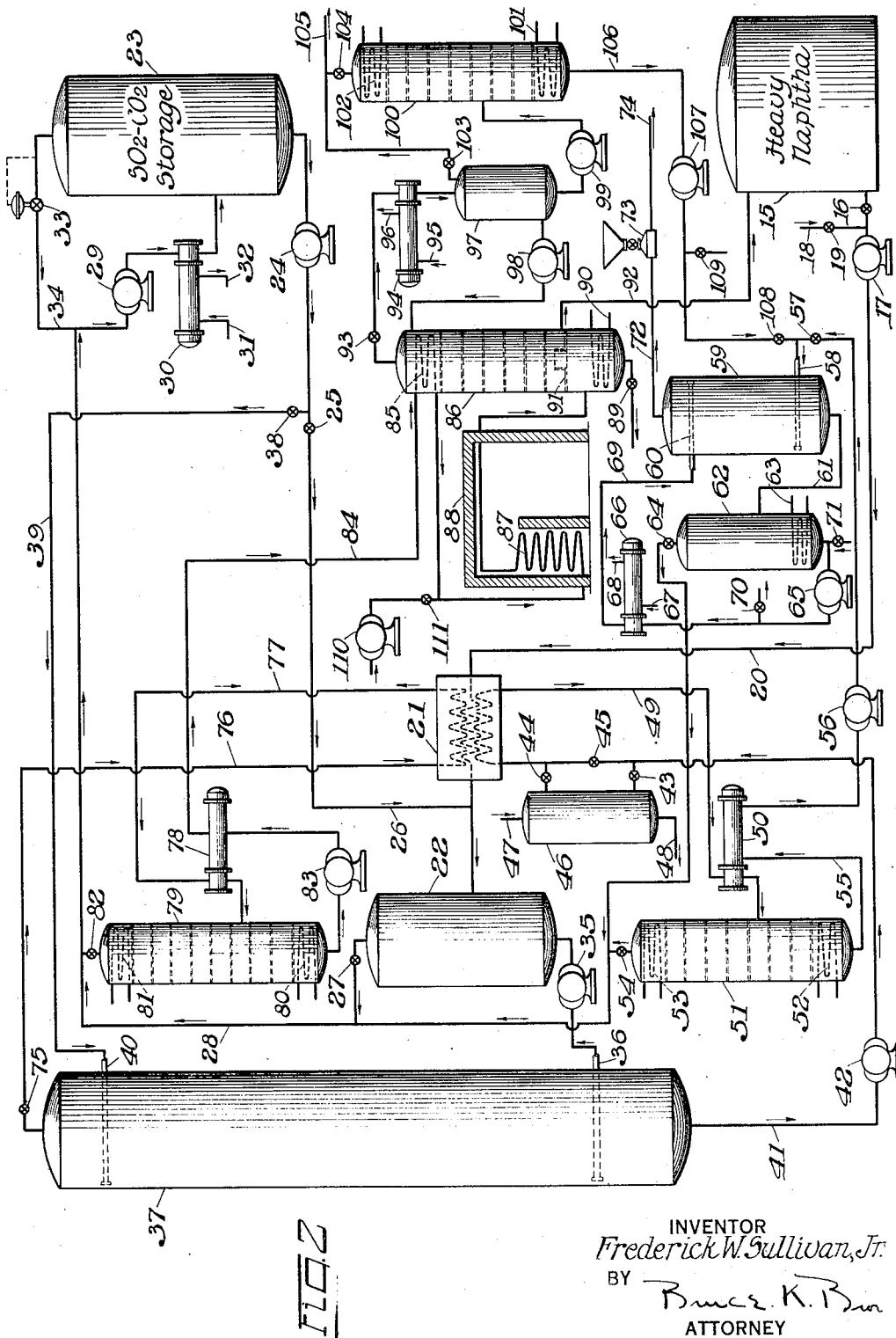
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INVENTOR
Frederick W. Sullivan, Jr.
BY Bruce K. B. *B. B.*
ATTORNEY

UNITED STATES PATENT OFFICE

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SOLVENT FRACTIONATION

Frederick W. Sullivan, Jr., Hammond, Ind., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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6 Claims. (Cl. 196—37)

This invention pertains to the solvent fractionation of motor fuel stocks to form a relatively high octane number fraction and a relatively low octane number fraction. It also pertains to certain new combinations of cracking and solvent fractionation steps.

It is an object of the invention to provide a solvent fractionation process for motor fuel stocks utilizing a new mixed solvent having improved properties. A further object is to provide a process of this type which will produce a higher octane number fraction than is produced by prior art processes under comparable conditions. Another object is to provide a process in which, by a combination of cracking and solvent fractionation, large yields of a very high octane number motor fuel can be produced. Other and more detailed objects of the invention will become apparent as the description thereof proceeds.

It is old to fractionate a motor fuel stock by the use of liquid sulfur dioxide (SO_2) alone but the process suffers from the fact that the octane number (antiknock rating) of the motor fuel produced by its use is unsatisfactorily low and from the fact that the yields of extract obtained are low, necessitating the use of large quantities of SO_2 . I have found that greatly improved results can be obtained by incorporating a secondary selective solvent with the sulfur dioxide. This secondary selective solvent is liquid carbon dioxide (CO_2).

Although the CO_2 used in my process may serve an incidental purpose as a refrigeration medium, its principal function is to increase greatly the selectivity of the SO_2 for the high octane number constituents of the motor fuel stock. This is particularly true with highly olefinic motor fuel stocks such as are produced by vapor phase cracking processes. This will be brought out more fully below.

Referring now to the drawings:

Figure 1 shows data on the use of my mixed solvent compared with data on the use of SO_2 alone, and Figure 2 shows a conventionalized flow diagram of a preferred embodiment of my process.

In Figure 1, curve 11 illustrates the relationship between the yield of extract motor fuel fraction and the octane number of the extracted material when a motor fuel stock is treated with various volumes of liquid SO_2 at -90°F . Curve 12 gives corresponding data for the raffinate fraction. The "yield" figures in Figure 1 refer to the extract and the corresponding raffinate yields are, of course, 100% minus the extract yield. If an

amount of SO_2 is used which will produce 50% extract and 50% raffinate the octane numbers will be 89 and 37 respectively. If less SO_2 is used and only 25% is extracted the extract will have an octane number of 97 and 75% of a raffinate having the exceedingly low octane number of 47 will be produced simultaneously. Since -90°F is about the lowest temperature which can be reached with SO_2 alone in a practical process and since the use of lower temperatures does not materially improve the octane number of the extract it is apparent that the highest octane number extract which can be reached with this particular stock using SO_2 alone is about 97.

Points 13 and 14 represent corresponding data using an SO_2 - CO_2 mixture on this same stock. The temperature of the solvent fractionation in this case was -115°F but this temperature can be reached easily by evaporating a portion of the CO_2 and almost equally superior results can be obtained at higher temperatures.

The motor fuel stock used in these experiments was a heavy naphtha boiling between 250°F and 460°F obtained by fractionally distilling a pressure distillate from a vapor phase pyrolytic cracking process. The octane number of the stock was 62 (after redistillation to a 400°F end point) and the composition, determined by sulfuric acid absorption and polymerization was as follows: olefines 52%, aromatics 1%, paraffins and naphthenes 47%.

The method of treating was to coagitate the motor fuel stock and the solvent very vigorously and then separate an extract fraction and a raffinate fraction. The solvent was then removed from the extract fraction by fractional distillation followed by water and caustic washing and the octane number was then determined by the Cooperative Fuel Research engine test after redistillation to a 400°F end point. In the SO_2 - CO_2 experiment the composition of the system immediately prior to separation of the two fractions was: 2 volumes SO_2 , 0.8 volume CO_2 , 1 volume heavy naphtha.

It is to be noted that an extract having the exceedingly high octane number of 109 was obtained as compared with 97 for SO_2 alone.

Liquid carbon dioxide alone is not at all effective as a selective solvent for motor fuel stocks. Thus in an experiment using the above-described motor fuel stock and an equal volume of liquid carbon dioxide it was found that only 4% of the stock was extracted even at the relatively high temperature of -40°F . It therefore appears that mixtures of SO_2 and CO_2 have very differ-

ent and highly superior properties as solvents for the fractionation of motor fuel stocks as compared with either constituent alone.

Although my improved mixed solvent can be used in a batch process such as that used in the laboratory tests referred to above, I prefer to utilize a countercurrent process not only because of the efficiencies well known to be inherent in such processes but also because the first portions of the motor fuel stock dissolved in the solvent have a relatively low octane number. By countercurrent extraction the fresh stock comes in contact only with solvent which is already nearly saturated with olefinic constituents and the low octane number materials are not extracted to the extent they would be in a batch process. The result is an even higher octane number extract than is indicated by the above data.

One countercurrent process which I may use is shown in Figure 2 together with the cracking equipment and other equipment used in my complete process for the production of high octane number motor fuels.

The motor fuel stock which may suitably be a heavy naphtha produced by a vapor phase cracking process as hereinafter described is removed from tank 15 through valve 16 by means of pump 17. Additional motor fuel stock from a source not shown may be introduced from line 18 through valve 19. The stock passes through line 20 to heat exchanger 21 where it is cooled by indirect contact with the cold extract fraction and/or raffinate fraction from the solvent fractionation step. The cooled stock passes into chilling chamber 22 where its temperature is lowered to the temperature desired for the solvent fractionation step. This may suitably be accomplished by introducing a portion of the mixed SO_2 - CO_2 solvent from storage tank 23 by means of pump 24 through valve 25 and line 26 into chilling chamber 22. In chilling chamber 22 at least the greater part and preferably all of the solvent is removed through valve 27 and line 28 by means of compressor 29, is cooled in heat exchanger 30 by means of a refrigerating medium introduced through line 31 and removed through line 32 and passes back to solvent storage tank 23. The temperature and pressure in tank 23 are controlled by means of pressure release valve 33 and recycle line 34. The chilled stock is withdrawn from the bottom of chilling chamber 22 by means of pump 35 and passes to upwardly directed spray 36 located in countercurrent fractionation tower 37.

Simultaneously with the introduction of motor fuel stock into upwardly directed spray 36, mixed solvent from tank 23 is withdrawn by means of pump 24 and passed through the valve 38 and line 39 into downwardly directed spray 40 also located in tower 37. The solvent passes downward in tower 37 in countercurrent to the rising stream of motor fuel stock from spray 36. The solvent dissolves out the more olefinic constituents of the motor fuel stock to form the extract fraction and is removed from the base of tower 29 through line 41 by means of pump 42. At this point it may be desirable to treat the cold solution of motor fuel constituents with sulfuric acid in order to remove sulfur compounds since at the prevailing temperature this can be accomplished with little or no loss of the valuable olefinic hydrocarbons. This acid treating can be accomplished by means of valves 43 and 44 (valve 45 being closed) whereby the extract fraction is

passed through tower 46 where it comes in contact with sulfuric acid introduced and removed by means of lines 47 and 48. If this treatment is not desired it is merely necessary to close valves 43 and 44 and open valve 45. The refrigerating value of the motor fuel stock is utilized by passing it through heat exchanger 21 where it comes in indirect contact with the incoming motor fuel stock and thence through line 49 and heat exchanger 50, where its temperature is again raised by indirect contact with the hot bottoms to be described hereafter, to stripping tower 51 which is equipped with reboiling coil 52 and dephlegmating coil 53. The temperature at the top of tower 51 is controlled so as to remove all of the solvent, which passes off through valve 54 into line 28 and thence back to solvent storage tank 23. The bottoms from tower 51 constituting the extract constituents of the motor fuel stock is removed through line 55 by means of pump 56 and passes through heat exchanger 50 as previously described. It is then introduced through valve 57 into upwardly directed spray 58 located in scrubbing tower 59 where it meets a downward stream of water, or other suitable wash fluid such as caustic, from spray 60. The purpose of this step is to remove any residual SO_2 and/or CO_2 . The wash fluid descends to the bottom of tower 59 and is removed through line 61 and introduced at an intermediate point into tower 62 which is heated at the bottom by means of coil 63. The SO_2 and CO_2 picked up by the caustic in tower 59 are thereby boiled off and passed through valve 64 into line 28 and thence back to storage tank 23. Revivified wash fluid is removed from the bottom of tower 62 by means of pump 65, passes through cooler 66 where it comes in indirect contact with a cooling medium introduced through line 67 and removed through line 68 and thence passes by means of line 69 back to spray 60. The wash fluid can be used for a long period but ultimately it may have to be withdrawn through valve 70 and fresh wash fluid introduced through valve 71. It will be understood that a second tower can be used in series with tower 59 for water washing if desired. The purified extract fraction passes from the top of tower 59 through line 72. Since the oxidation stability of this type material is generally not high, it is desirable to add an antioxidant and this can be done by means of mixing device 73. Suitable antioxidants are pyrogallol, catechol, para-benzyl aminophenol, etc. They can be introduced in dry form or in solution in benzene, ether, etc. The finished product passes through line 74 to storage.

Returning now to the raffinate fraction, this is removed from the top of tower 37 through valve 75 and passes through line 76 to heat exchanger 21 where its refrigerating value is utilized, through line 77 to heat exchanger 78, where its temperature is again raised by contact with the hot bottoms as described hereafter, and thence to stripping tower 79 which is similar to tower 51 and is equipped with reboiling coil 80 and dephlegmating coil 81. The solvent is removed through valve 82 and passes by means of pump 29 back to storage tank 23. The bottoms from tower 79 constitute the raffinate portion of the motor fuel stock and are removed by pump 83, passed through heat exchanger 78, as previously described, and thence through line 84 to dephlegmating coil 85 and tower 86. This raffinate fraction then passes through heating coil 87 located in pipe still 88 whereby its temperature is raised to vapor phase cracking conditions and is

then introduced into bubble tower 86 equipped with reboiling coil 90 and trap-out plate 91. A soaking drum may be placed in line between furnace 88 and tower 86. Tar is removed from the bottom of tower 86 through valve 89. A heavy naphtha fraction is removed by means of trap-out plate 91 and passes through line 92 back to storage tank 15. A light naphtha fraction passes overhead through valve 93 and condenser 94, where it comes in indirect contact with a cooling medium introduced through line 95 and removed through line 96, and then passes to separator 97. A portion of the condensed light naphtha is re-introduced into the top of tower 86 by means of pump 98 in order to supply reflux. The remainder is removed by means of pump 99, passes into tower 100 equipped with reboiling coil 101 and dephlegmating coil 102. Vapors from tank 97 are removed through valve 103 and from tower 100 through valve 104 and pass through line 105 for use as fuel or to an absorption plant. The light naphtha bottoms from tower 100 are removed through line 106 by means of pump 107 and pass through line 108 to spray 58 in caustic tower 59. In this way the light naphtha fraction from the cracking step is blended with the extract heavy naphtha fraction. If, however, the light naphtha fraction is available in proportions greater than those desired for the preparation of the final product passing off through line 74 the excess can be removed through valve 109 for other use as desired.

Instead of introducing fresh motor fuel stock into the process by means of line 18 and valve 19 it will very often be preferable to introduce the fresh material to the process as charging stock to the cracking step. This can be accomplished by means of pump 110 and valve 111. This charging stock may be naphtha bottoms, gas oil, crude oil or any other suitable pressure still charging stock.

By means of this combination of cracking and solvent fractionation steps it will be noticed that a charging stock is broken down into a highly olefinic heavy naphtha and an antiknock light naphtha fraction. The heavy naphtha is split by means of solvent fractionation with my improved solvent mixture into an extract fraction of very high antiknock value and a raffinate fraction of low antiknock value. The latter is recycled at least in part to the cracking step whereby its antiknock value is raised and the former is blended with the light naphtha constituents to produce a highly superior final motor fuel.

I find that my new mixed solvent comprising sulfur dioxide and carbon dioxide is highly superior of the extraction of the high antiknock olefinic constituents present in motor fuel stocks and particularly the olefinic constituents existing in fractions boiling between about 250° F. and 400° F. The most suitable motor fuel stocks for my process are produced by pyrolytic cracking and particularly by cracking in the vapor phase whereby large percentages of olefines are formed with very small proportions of aromatics.

In the solvent fractionation of lubricating oils the purpose is to extract the naphthenic hydrocarbons, leaving as a raffinate the more desirable paraffinic hydrocarbons (Industrial and Engineering Chemistry, July, 1931, page 753). In the solvent fractionation of kerosene, burning oils, etc. the principal object is to extract the smoky aromatic hydrocarbons, again leaving a paraffinic raffinate (Petroleum Zeitschrift, January 8, 1930, page 47). My process, on the other hand, is

found to be particularly suitable for the extraction of low boiling olefinic hydrocarbons such as are found in cracked motor fuel stocks.

I have found that my mixed solvents are peculiarly advantageous in the solvent fractionation of highly olefinic motor fuel stocks, particularly those containing at least 30% of olefinic hydrocarbons and which do not normally contain substantial amounts of aromatics. By the term motor fuel stock I refer to any petroleum distillate lying predominantly within the gasoline boiling point range. Motor fuel stocks from vapor phase cracking processes contain very high concentrations of olefinic hydrocarbons; those produced from liquid phase cracking processes contain somewhat lower concentration; virgin or uncracked motor fuel stocks contain relatively little of these desirable constituents. Since I find that my mixed solvents are peculiarly adapted to the selective extraction of these olefinic hydrocarbons it is desirable to select a motor fuel stock containing a high percentage of them and therefore my process is peculiarly applicable to motor fuel stocks such as pressure distillates, naphthas, and refined or unrefined gasoline produced by cracking processes and particularly vapor phase cracking processes. The content of olefinic hydrocarbons seems to be roughly measured by the octane number of the motor fuel or motor fuel stock and since this is also a measure of the antiknock characteristics of the fuel it is apparent that it is desirable in the production of a high grade antiknock fuel to start with a motor fuel stock having a fairly high octane number, which is indicative of a fairly high concentration of olefinic hydrocarbons, and then selectively fractionate to segregate an extract having as high an octane number as may be consistent with reasonably high yields. This, I find, can be accomplished with unprecedented efficiency by the use of the mixed solvents which I have discovered. In general, I find it desirable to start with a motor fuel stock having an octane number of at least 50 and preferably 55 to 70 and obtain an extract motor fuel having an octane number of 75 or better and preferably 80 or better.

Although it is quite possible to use a complete pressure distillate or gasoline as a stock for my process I find that it is often preferable to use a heavy naphtha such as can be produced by the fractional condensation or fractional distillation of a pressure distillate. Such a heavy naphtha may suitably have an initial boiling point of from 200° F. to 300° F. and a maximum boiling point of from 350° F. to 500° F. Any material present having a boiling point in excess of about 400° F. will, in general, be removed by redistillation following the solvent fractionation. The elimination of the light constituents, boiling below 200° F. to 300° F. is highly advantageous since it greatly reduces vapor losses, enhances the separation of the solvent from the motor fuel fractions produced by the process and permits the production of a higher octane number extract fraction. The light constituents are normally of high octane number and can be blended with the high octane number material recovered from the extract fraction to give a maximum yield of a highly superior antiknock motor fuel.

My new and improved mixed solvent can vary greatly in the proportions of its constituents, but in general, the sulfur dioxide should not be present in lesser proportions by volume than the carbon dioxide. Proportions ranging from one part sulfur dioxide to one part carbon dioxide up

to five parts sulfur dioxide to one part carbon dioxide are preferred. These proportions are, of course, the proportions actually present in the solvent fractionation step and do not take into account the fact that additional carbon dioxide may often be used for refrigeration purposes, being removed by evaporation prior to the solvent fractionation operation. The ratio of mixed solvent to motor fuel stock to be extracted can range from 50 volumes of solvent per 100 volumes of motor fuel stock up to 1000 volumes of solvent per 100 volumes of motor fuel stock or even higher, but, in general, I prefer to use 100 to 500 volumes of my solvent mixture per 100 volumes of motor fuel stock. The temperature of the solvent fractionation step can also be varied, within wide limits, but, in general, I prefer to operate at a temperature at least as low as -50°F. and not lower than -150°F. Satisfactory operations can, however, be conducted at somewhat higher temperatures.

Although I have described my invention in terms of certain specific embodiments thereof, numerous modifications will be apparent in the light of my specification to those skilled in the art and I do not desire to limit my invention except to the scope of the appended claims. I have also mentioned certain theories in connection with my invention but it is to be understood that the invention is a matter of fact and is not dependent on the theories advanced.

I claim:

1. A process for the solvent fractionation of a cracked motor fuel stock falling predominantly within the gasoline boiling point range, which comprises contacting 100 volumes of said stock at a low temperature with from about 50 to about 1000 volumes of a liquefied solvent mixture, said

solvent mixture containing sulfur dioxide and carbon dioxide in the ratio of one part by volume of carbon dioxide to from one to five parts by volume of sulfur dioxide, whereby an extract phase and a raffinate phase are formed, each in substantial amount, said extract phase containing a motor fuel fraction having a substantially higher octane number than said stock and said raffinate phase containing a motor fuel fraction having a substantially lower octane number than said stock, and separating said phases at said low temperature.

2. A process according to claim 1 in which said stock is produced by vapor phase cracking.

3. A process according to claim 1 in which said stock is a cracked heavy naphtha having an initial boiling point of from about 200°F. to about 300°F. and a maximum boiling point of from about 350°F. to about 500°F.

4. A process according to claim 1 in which said low temperature falls within the range from about -50°F. to about -150°F.

5. A process according to claim 1 in which said low temperature is obtained by the evaporation of an additional quantity of carbon dioxide in direct contact with said stock and said solvent mixture.

6. A process for the solvent fractionation of a cracked motor fuel stock falling predominantly within the gasoline boiling point range, which comprises contacting 1 volume of said stock with about 2 volumes of sulfur dioxide and about 0.8 volumes of carbon dioxide at a temperature of about -115°F. , whereby two liquid phases are formed, each in substantial amount, and separating said phases at about said temperature.

FREDERICK W. SULLIVAN, JR.