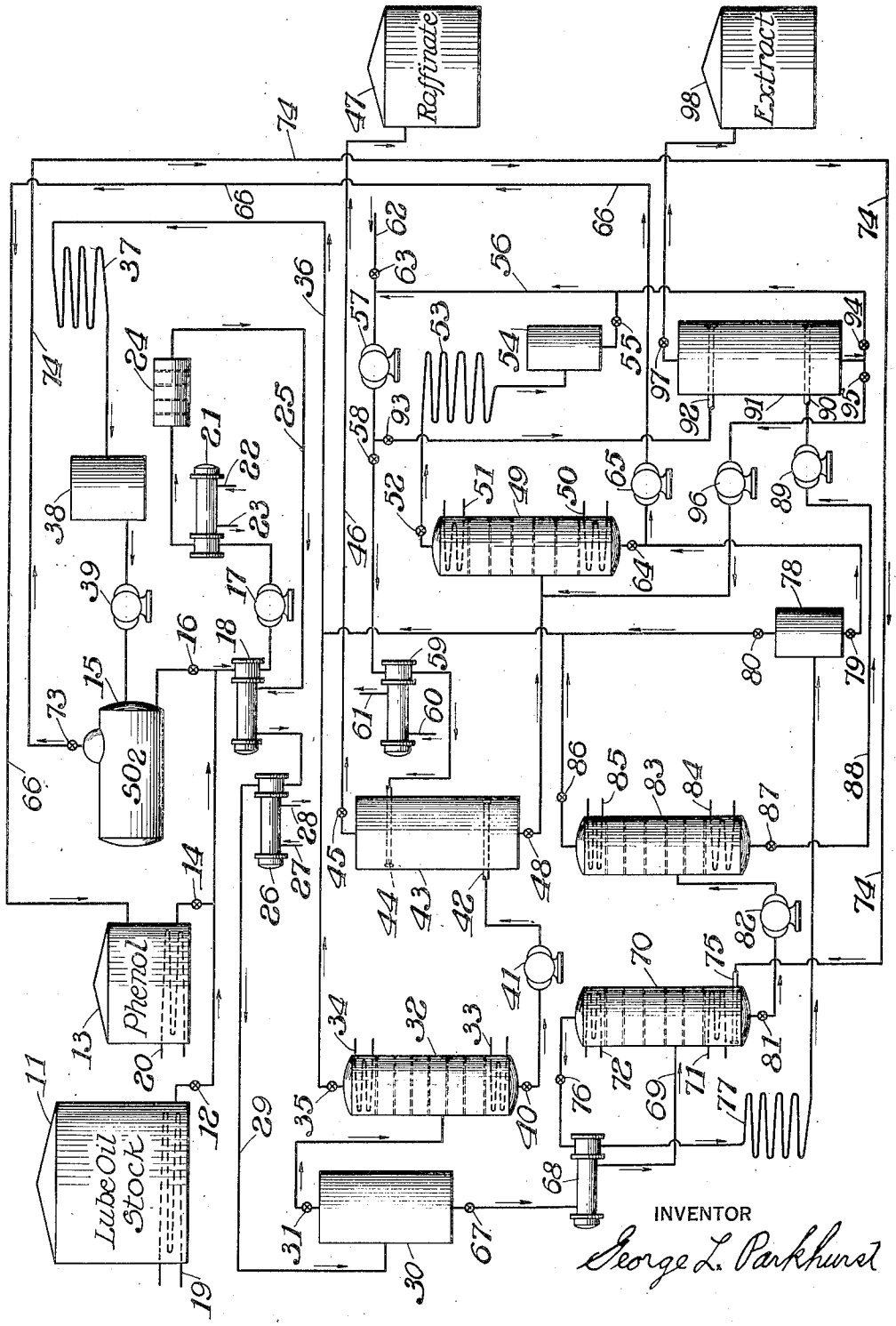
June 14, 1938. G. L. PARKHURST 2,120,810

SOLVENT FRACTIONATION

Filed July 31, 1933



Patented June 14, 1938 2,120,810

UNITED STATES PATENT OFFICE

2,120,810

SOLVENT FRACTIONATION

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Application July 31, 1933, Serial No. 682,919

2 Claims. (Cl. 196—13)

This invention relates to the solvent fractionation of hydrocarbon mixtures. It is an object of the invention to provide a process for the solvent fractionation of hydrocarbon mixtures which will give either higher yields of the desired fraction or a greater "spread" in properties between the two fractions produced than has been the case with previously known processes. In some cases both of these advantages can be secured simultaneously. Further objects will become apparent as the description of my invention proceds.

Liquid sulfur dioxide (SO_2) and phenol have been used separately as selective solvents for the fractionation of lubricating oil stocks. Each of these selective solvents has, however, certain disadvantages and inadequacies. Thus liquid sulfur dioxide is not highly selective. In other words, the "spread" in properties between the two fractions produced by its use is relatively small as will be pointed out in a specific instance below. This "spread" can be increased by operating at higher temperatures but this involves the use of high pressures with consequent expensive equipment and high compression costs. Furthermore when the operating temperature is raised the yield of the desirable raffinate fraction is very markedly decreased.

On the other hand, when using phenol as a selective solvent, for instance, in the fractionation of lubricating oil stocks, the yield of the desirable raffinate fraction is relatively low. This can be increased by lowering the operating temperature but concomitantly there is a distinct decrease in the quality of the raffinate or in other words a decreased "spread" between the properties of the two fractions produced.

I have found that a mixture of liquid sulfur dioxide and phenol is very greatly superior as a selective solvent to either sulfur dioxide or phenol alone. If sulfur dioxide, phenol and a mixture of the two are compared as selective solvents under conditions such that the yields of raffinate and extract are the same in all three cases, it will be found that the raffinate and extract produced by the use of a mixture of the two solvents have a greater "spread" in properties than the fractions produced by either solvent alone. In other words, the raffinate produced with sulfur dioxide plus phenol will in the case of lubricating oil extraction be more "paraffinic" and have a higher viscosity index, greater stability, etc. than is the case with the raffinates produced by either solvent alone. In the case of gasoline or naphtha extraction, for another example, the extract fraction will have a higher antiknock rating (octane number) and the raffinate fraction a lower antiknock rating than the corresponding fractions produced by the use of liquid sulfur dioxide or phenol alone under conditions adapted to produce the same yields of the two fractions.

If instead of operating under conditions (temperature, ratio of volume of solvent to volume of stock, etc.) adapted to produce identical yields, the comparative tests are conducted under conditions adapted to give, for instance, a lubricating oil raffinate of a given viscosity index (Dean and Davis, Chemical and Metallurgical Engineering, v. 36, page 618—1929) or a gasoline extract of a given octane number (National Petroleum News, June, 1930; page 35), it will be found that the yield of the desired fraction will be markedly higher in most cases when a mixture of sulfur dioxide and phenol is used than when either sulfur dioxide or phenol is used alone. In some cases both a higher yield and an improved product can be secured simultaneously by the use of the mixed solvent.

These facts can be illustrated by the following data relating to the solvent fractionation of lubricating oil stocks. The particular stocks used where lubricating distillates from midcontinent crude. The method of test was to agitate the stock and solvent together until equilibrium was attained at the optimum temperature for the particular solvent being used, separate the raffinate and extract, and remove the solvent from both fractions by fractional distillation and water and caustic washing. After percolation of the raffinate fraction through clay its viscosity in seconds Saybolt at 210° F. and Dean and Davis viscosity index were determined and compared with those of the original stock. The results are tabulated below:

Solvent per 1 vol. of stock	Yield of raffinate	Fractionation temperature	Loss in viscosity raffinate vs. stock	Gain in viscosity index raffinate vs. stock
	Percent	*° F.*	*Percent*	*Percent*
1 vol. SO_2	76	70	21.8	20.5
1 vol. of phenol				
2 vols. of phenol	67	145	28.3	19.5
2 vols. SO_2	85	8	12.1	12

The SO_2-phenol mixture thus gives a 9% higher yield with less loss in viscosity and a slightly greater increase in viscosity index as compared with an equal volume of phenol alone. A 9% increase in yield will in many cases make all the difference between commercial success and commer-

cial failure. The yield with phenol can be increased, to be sure, by lowering the fractionation temperature but if this is done the viscosity index of the raffinate drops very rapidly, the loss in viscosity increases, the sludge and oxidation stabilities deteriorate rapidly, etc. so that if one operates with phenol at a temperature which will give the same yield of raffinate as with SO_2-phenol the raffinate produced will be very inferior.

Sulfur dioxide alone on the other hand gives a high yield and a small loss in viscosity but the raffinate is, relatively speaking, but little better than the original stock. The best measure of the improvement in a lubricating oil raffinate is probably the viscosity index. It will be noted that the improvement in viscosity index when using SO_2 alone was only slightly more than half that secured by the use of the SO_2-phenol mixture. By raising the fractionation temperature more improvement could be obtained with SO_2 alone but it is found that although the yield drops off rapidly as the temperature is raised, the improvement in the raffinate is only slight. Moreover the use of high temperatures with SO_2 alone involves the use of pressure equipment, high compression costs, etc. This is avoided when using SO_2-phenol since the phenol tends to keep the SO_2 in the liquid phase and greatly reduces its partial vapor pressure.

In general, I prefer to use from 0.5 to 10.0 volumes of my mixed solvent to each volume of the hydrocarbon mixture or stock to be fractionated. The solvent mixture may suitably comprise from 20% to 75% of phenol by volume and from 25% to 80% of sulfur dioxide by volume. The optimum fractionation temperature will vary with the stock to be fractionated, the results desired, the composition of the solvent mixture, etc. and can be determined readily by experiment in each case. For the solvent fractionation of lubricating oil stocks, I prefer in general to fractionate at from 50° F. to 100° F.

It is highly preferable that the phenol used be substantially anhydrous since the presence of any substantial amount of water decreases yields markedly and has other undesirable results.

Although I can utilize my new mixed solvent efficiently in a batch process such as is described with regard to the above experiments or in a batch process wherein the solvent and hydrocarbon mixtures are heated to a temperature at which they are completely miscible and then cooled to a temperature at which the desired raffinate and extract fractions separate, I prefer to utilize a continuous process in which a much better fractionation can be accomplished and in which provision is made for the continuous recovery of the components of the solvent mixture and in which they are returned to the process.

One such continuous process is shown in the drawing which is a conventionalized flow diagram. The hydrocarbon mixture to be fractionated, for instance a lubricating oil stock, is removed from storage tank **11** through valve **12**. Simultaneously anhydrous phenol is removed from storage tank **13** through valve **14** and sulfur dioxide, preferably liquid sulfur dioxide, is removed from tank **15** through valve **16**. All of this is accomplished by means of pump **17** and the various materials are pumped through heat exchanger **18** in which their temperature is raised. If the lubricating oil stock is too viscous to flow readily, its temperature can be raised by means of steam coil **19**. Similarly the phenol can be heated by means of steam coil **20** if necessary. The various materials then pass through heater **21** where they come in contact with an indirect heating medium introduced through line **22** and withdrawn through line **23**. The heated materials pass through mixer **24**, wherein homogeneity is obtained, and through line **25** to heat exchanger **18** where they are cooled by contact with the incoming materials and thence to cooler **26** where they come in indirect contact with cooling medium introduced through line **27** and withdrawn through line **28**. The purpose of the steps thus far is to heat the two solvent components and the stock to a temperature at which they can be homogenized and then cool them to a temperature at which the desired fractionation will occur. This insures complete contact between the stock and the solvents prior to fractionation. This is not essential, however, and alternatively the stock and the solvent mixture can merely be agitated together at the desired temperature and then separated or they can be passed in countercurrent relationship to each other, for instance, in a vertical tower.

The materials passing out through cooler **26** pass through line **29** and enter separator **30** at an intermediate level therein. In separator **30** raffinate and extract fractions separate, the former passing upward and the latter passing downward continuously. The raffinate fraction is removed continuously from the top of separator **30** through valve **31** and enters fractionating column **32** at an intermediate point. Fractionating column **32** is provided with re-boiling coil **33** and dephlegmating coil **34** which are used to adjust the temperatures at the bottom and top of the tower so that at least the greater part of the sulfur dioxide passes overhead and substantially all of the hydrocarbons and phenol pass out at the bottom of the tower. The sulfur dioxide vapors leave tower **32** through valve **35** and pass through line **36**, condenser **37**, surge chamber **38** and compressor **39** back to storage tank **15**. Simultaneously, the bottoms from tower **32** pass out through valve **40** by means of pump **41** and enter upwardly directed spray **42** located near the bottom of scrubbing tower **43**. In this tower the raffinate fraction comes in contact with a downwardly flowing stream of water, preferably hot water under pressure, from spray **44**. This scrubbing removes the phenol and any residual sulfur dioxide. The purified raffinate passes out from the top of the tower through valve **45** and, if necessary to remove residual phenol, can again be scrubbed in a second tower similar to tower **43**. It then passes through line **46** to storage tank **47** from which it can be removed for further treatment for use as desired.

Simultaneously, the aqueous materials from tower **43** pass out of the tower through valve **48** and are introduced into fractionating tower **49** at an intermediate level therein. Tower **49** is provided with reboiling coil **50** and dephlegmating coil **51** which are used to control the bottom and top temperatures so that water will pass overhead and phenol will be removed at the bottom. The water vapor passes out of tower **49** through valve **52**, condenser **53**, separator **54**, valve **55**, line **56**, pump **57**, valve **58** and heater **59** back to spray **44**. Heater **59** is operated by means of a heating medium introduced through line **60** and removed through line **61**. Any sulfur dioxide or phenol passing out of the top of tower **49** is thus recycled with the water back to the process and is not lost. Fresh makeup water can be introduced through line **62** by means of valve **63**.

While water vapor is being withdrawn through valve 52, phenol is withdrawn through valve 64 by means of pump 65 and passes through line 66 back to storage tank 13. Instead of recycling the phenol and sulfur dioxide back to their respective storage tanks it is, of course, possible to recycle them back to heater 18, mixer 24 or some other point in the process.

Returning now to separator 30, the extract fraction is withdrawn from the base of the separator through line 67 and is passed through heat exchanger 68 where its temperature is raised, as will be described hereafter. It then passes through line 69 into tower 70 at an intermediate point therein. It will be found in general that the extract fraction contains considerably more phenol than does the raffinate fraction and it is, therefore, desirable to provide somewhat more efficient means for its removal. This is done in tower 70 and the subsequent apparatus now to be described. Tower 70 is provided with reboiler coil 71 and dephlegmating coil 72 used to control the bottom and top temperatures in such manner that a maximum amount of the phenol and sulfur dioxide will pass overhead and the hydrocarbons will pass out of the base of the tower in liquid form. Sulfur dioxide vapors are removed from the dome of tank 15 through valve 73 and line 74 and are introduced into fractionating column 70 by means of a perforate pipe 75 located near the bottom of the tower. Sulfur dioxide vapors carrying with them the great bulk of the sulfur dioxide and phenol present in the material introduced through line 69 pass out of tower 70 through valve 76 and give up a portion of their heat to the incoming material. These vapors are then further condensed by means of condenser 77 and passed to trap 78. Phenol is removed from the base of this trap through valve 79 and passes back to storage tank 13 by means of pump 65 and line 66. This phenol will in most cases contain some sulfur dioxide, but since it is recycled to the process this is not a matter of importance. The bulk of the sulfur dioxide passes off from trap 78 in vapor form through valve 80 to line 36, condenser 37, surge chamber 38 and compressor 39 back to storage tank 15.

Simultaneously, the extract hydrocarbons removed from the base of tower, 70 through valve 81 by means of pump 82, are introduced at an intermediate level into fractionating tower 83 provided with reboiling coil 84 and dephlegmating coil 85. The residual sulfur dioxide is removed in vapor form through valve 86, passes into line 36 and thence back to storage tank 15. At the same time, the hydrocarbon material containing some residual phenol is removed from the base of tower 83 through valve 87 and line 88 by means of pump 89 and is introduced into upwardly directed spray 90 located near the bottom of scrubber 91 where it comes in contact with hot water under pressure introduced through downwardly directed spray 92 by means of valve 93 and the water circulating system previously described in the case of scrubbing tower 43. The aqueous extract passes out from the base of tower 91 through valve 94 and/or valve 95. Valve 94 leads by way of line 56 back to the water circulating system. By this method phenol is only indirectly removed after passing through scrubbing tower 43 and into fractionating tower 49 and it should therefore not be used unless the phenol content of the aqueous material leaving the base of tower 91 is low. If the phenol content is high, valve 95 should be used and the aqueous material then passes through pump 96 to fractionating tower 49 where water and phenol are separated and recycled to the system.

The purified extract material is removed from tower 91 through valve 97 and passes to storage tank 98 for further treatment or use as desired. Although different systems for the recovery of solvents have been shown for the extract and raffinate fractions, it will be understood that either can be used in either case. In general, I prefer, however, to use the recovery system shown with reference to the extract fraction since it is the more efficient of the two.

Although I have described the use of my process and of my new solvent mixture with particular reference to the fractionation of the hydrocarbon mixtures present in lubricating oil stocks and although it is particularly useful in that regard, it will be understood that the process and the solvent mixture can be used for the removal of "smoky" materials from kerosenes and burning oils, for the solvent fractionation of motor fuel stocks to produce an extract fraction having a high antiknock rating (octane number), etc.

Furthermore, although I have described my invention with particular reference to the use of phenol and sulfur dioxide, other phenolic compounds such as cresol, the ortho, meta and para cresylic acids, wood tar creosotes such as beechwood cresote, etc. can be used to replace all or part of the phenol. The phenolic compound used should be substantially anhydrous. Liquid carbon dioxide can be used to replace all or part of the liquid sulfur dioxide.

In the appended claims I have set forth the novelty residing in my invention.

I claim:

1. A process for the solvent fractionation of hydrocarbon mixtures comprising contacting 100 volumes of said mixture with from 50 volumes to 1000 volumes of a solvent mixture comprising from about 20% to about 75% of phenol by volume and from about 25% to about 80% of liquid sulfur dioxide by volume, separating a raffinate fraction and an extract fraction and removing solvent from at least one of said fractions by stripping with sulfur dioxide gas.

2. A process for the solvent fractionation of hydrocarbon mixtures comprising contacting said mixture with a solvent mixture comprising at least 20% phenol and at least 25% liquefied sulfur dioxide, separating said solvent and hydrocarbon mixture into a raffinate fraction and an extract fraction and removing solvent from at least one of said fractions by stripping with said sulfur dioxide in gaseous form.

GEORGE L. PARKHURST.

CERTIFICATE OF CORRECTION.

Patent No. 2,120,810. June 14, 1938.

GEORGE L. PARKHURST.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 12, for "proceds" read proceeds; and second column, line 45, in the table, strike out the word "Percent" over last column; and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 19th day of July, A. D. 1938.

Henry Van Arsdale,
Acting Commissioner of Patents.

(Seal)