

Nov. 6, 1956

L. P. EVANS
GASOLINE PREPARATION

2,769,752

Filed May 29, 1953

3 Sheets-Sheet 1

Fig. 1

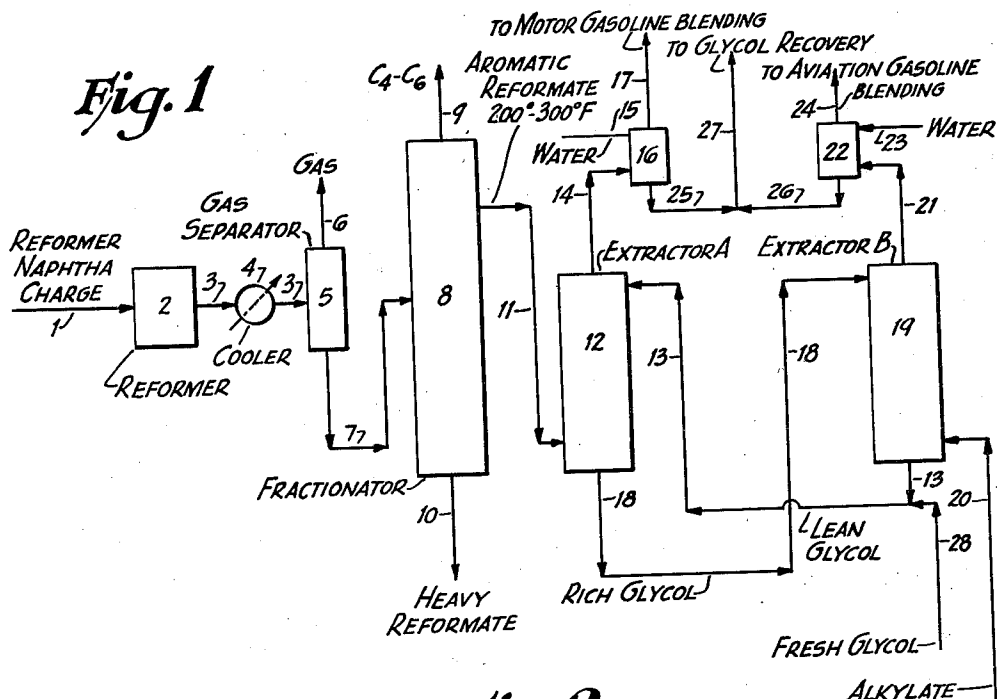
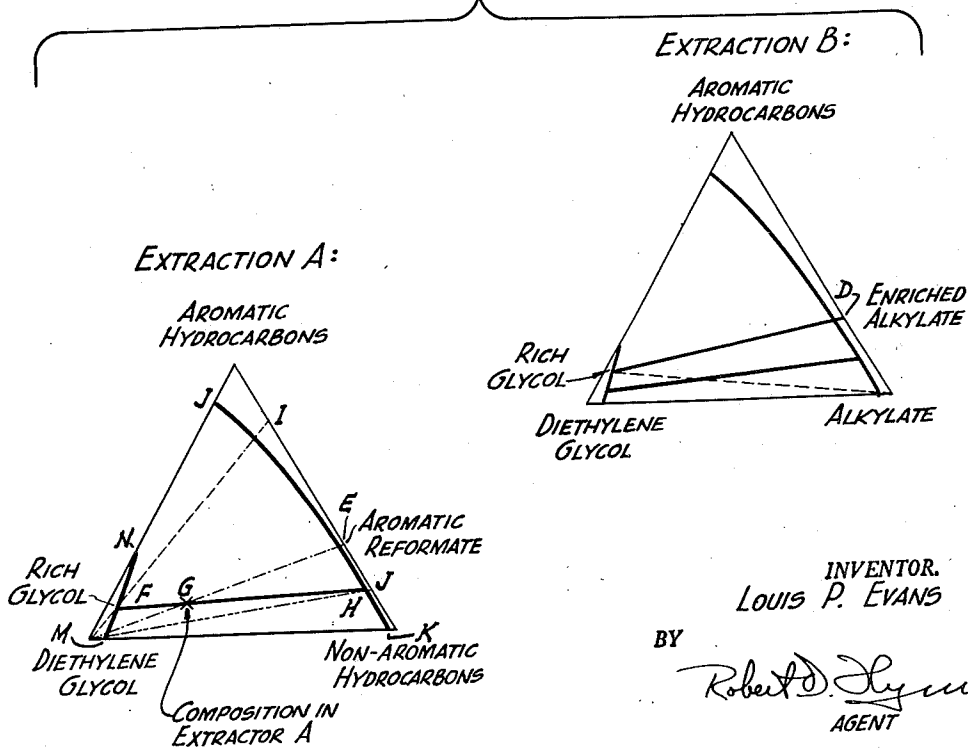


Fig. 2



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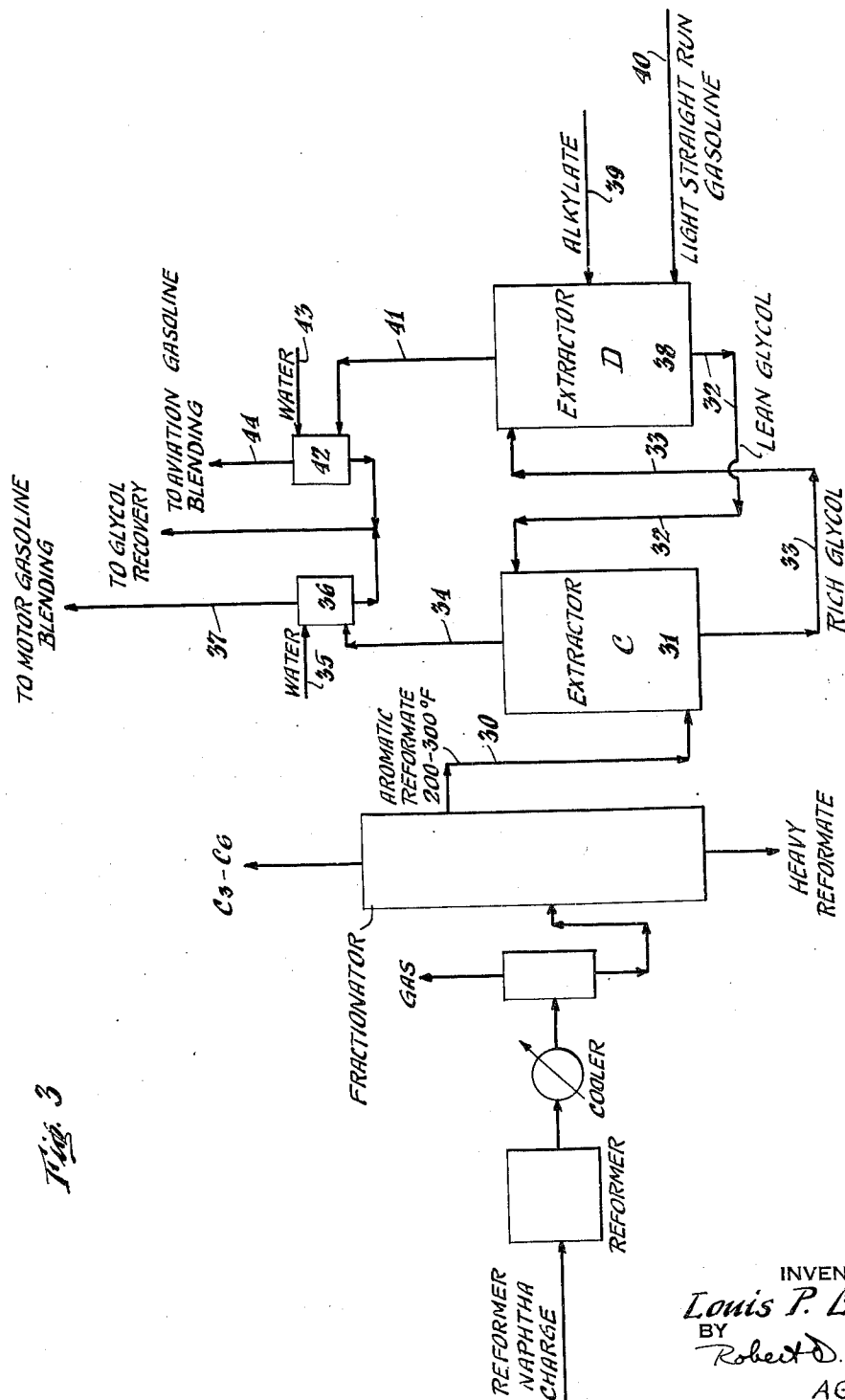
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3 Sheets-Sheet 2



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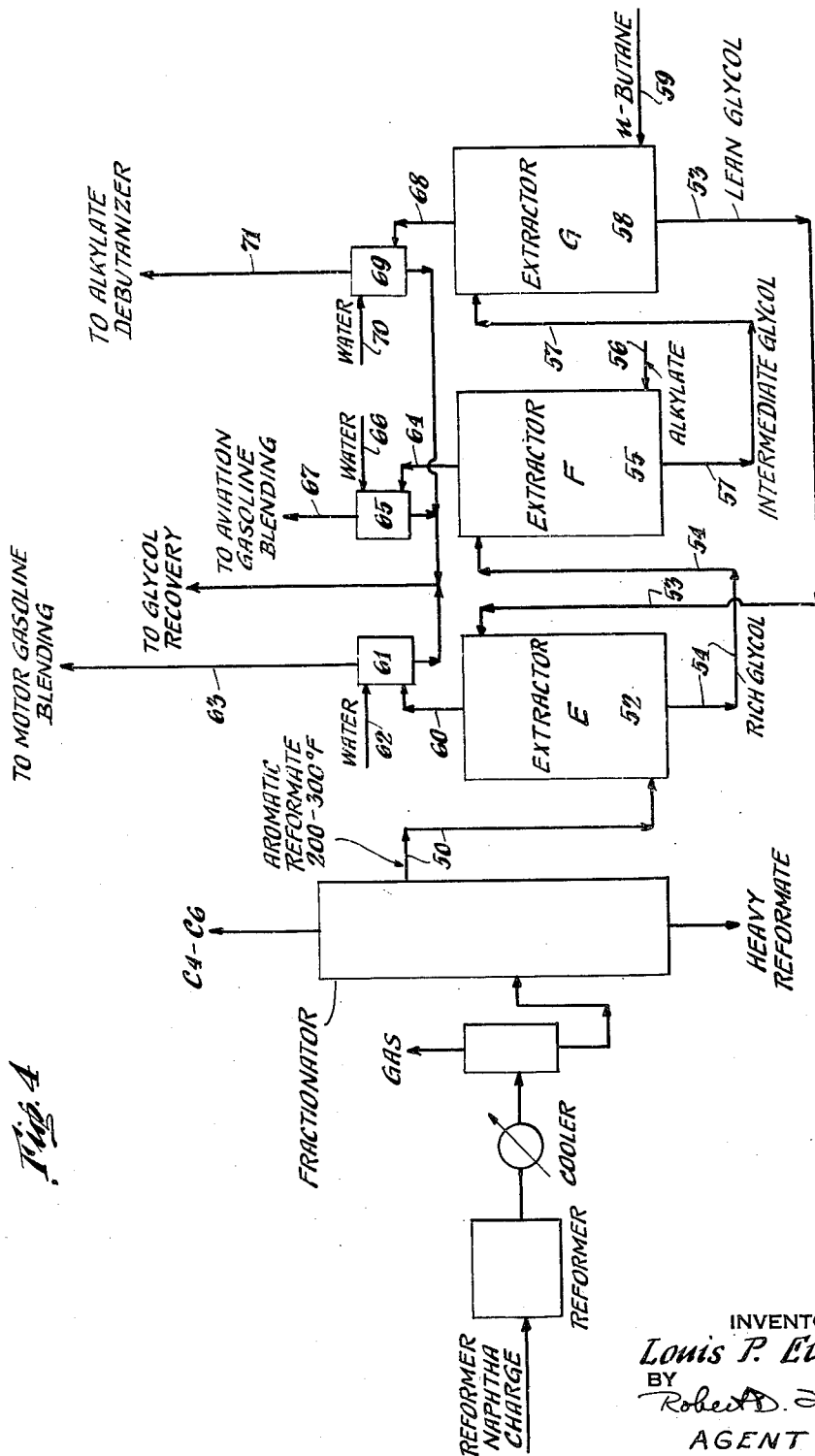
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3 Sheets-Sheet 3



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1

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GASOLINE PREPARATION

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Application May 29, 1953, Serial No. 358,392

8 Claims. (Cl. 196—14.17)

This invention has to do with the preparation of gasoline and, more specifically, has to do with the preparation of motor and aviation gasolines with high-octane blending stocks.

As is well known in the art, aviation gasoline blends comprise alkylate and aromatic blending stocks prepared by severe cracking or reforming operations. During World War II, the aromatic blending stocks were produced by catalytic re-cracking of first-pass catalytic naphthas or of selected straight run fractions; unfortunately, these re-cracking operations are relatively expensive and involve considerable degradation of non-aromatic hydrocarbons. Current methods for producing aromatic blending stocks—such as grade 100–130 and the more recent super-fuel, grade 115–145 aviation gasoline—involve catalytic reforming of select straight run gasoline fractions to produce products (reformates) containing aromatics in the aviation gasoline boiling range (167° F. (10%) to 307° F. (90%)) (MIL-F-5562). However, such reforming operations call for expensive pre-fractionation of a hydrocarbon stock in order to prepare the select straight run gasoline fractions; and in many cases this requires stock segregation. Moreover, excessive severity of the reforming operation is responsible for loss of excessive quantities of non-aromatic gasoline fractions.

A more recent development employs selective extraction of aromatics from the aforesaid highly reformed fractions to further concentrate the aromatics, particularly for grade 115–145 aviation gasoline. This development involves the use of a solvent having a high selectivity for aromatics and having a low solubility for non-aromatic hydrocarbons. This procedure is quite expensive in both investment and operating requirements, because large volumes of solvent must be circulated, because the solvent must be heated and the aromatics must be distilled from the solvent.

OUTLINE OF INVENTION

I have now discovered a new method for producing blending or base stocks for preparing gasolines. This novel method eliminates the aforementioned disadvantages of pre-fractionation and excessive stock degradation attending catalytic reforming, and also eliminates the high investment and operating costs involved in the solvent recovery operation of the above-mentioned solvent extraction procedure.

I have discovered that gasoline blending stocks can be obtained by the following sequence of operations:

(1) Contacting a gasoline fraction containing at least about 22 percent by volume and preferably in the range of 35 and 50 volume percent, of aromatic hydrocarbons boiling predominantly in the aviation gasoline range (170° F. to 400° F.) with a selective solvent for said aromatic hydrocarbons,

(2) Contacting said solvent associated with said aromatic hydrocarbons, with a non-aromatic hydrocarbon fraction with which said aromatic hydrocarbons are ultimately to be blended, whereby said aromatic hydrocar-

bons are extracted from said selective solvent by said non-aromatic hydrocarbon fraction.

OBJECTS

It is an object of this invention, therefore, to prepare gasoline blending stocks. It is also an object of this invention to prepare such stocks without the need for pre-superfractionation of the hydrocarbon fractions from which they are prepared to obtain narrow boiling range aromatic fractions, without severe catalytic reforming of the said hydrocarbon fractions, and without conventional distillation means for solvent recovery.

Other objects and advantages of the invention will be apparent from the following description.

DEFINITIONS

In order that the terminology used herein be free from misinterpretation, several definitions are provided.

The term "alkylate" denotes a paraffinic hydrocarbon fraction obtained by condensation of one or more isoparaffins with one or more olefins. Such fractions are composed essentially of branched-chain isomers of paraffinic hydrocarbons, and are generally prepared by condensing said isoparaffins and olefins in the presence of such catalysts as sulfuric acid, phosphoric acid, hydrofluoric acid, aluminum chloride, etc.

The term "reformate" broadly denotes a hydrocarbon product obtained by rearranging hydrocarbons to more highly branched paraffins and/or to more aromatic hydrocarbons and/or to more naphthenic hydrocarbons. Such products are obtained by a number of conversion processes well known in the hydrocarbon art, among which are thermal reforming, polyforming, hydroforming, Thermoform Catalytic Reforming (TCR), platforming and houdriforming. Thus, the sub-generic term "aromatic reformate" means an aromatic hydrocarbon product containing a substantial quantity of aromatic hydrocarbons and obtained by rearranging other less aromatic hydrocarbon fractions by a process of the character referred to, and particularly by such a process as Thermoform Catalytic Reforming (TCR), platforming, houdriforming and the like.

The term "light straight run gasoline" connotes a gasoline which boils from about 100 to 250° F., which is present in a crude oil, and which is obtained directly from such crude oil by distillation.

The term "extractant" is used herein in a broad sense, connoting a material having the capacity to withdraw one or more substances from a mixture of substances. The extractant is preferably a selective solvent such as diethylene glycol.

INVENTION IN DETAIL

In order that this invention may be more readily understood, typical separations are described below with reference being made to the drawings attached hereto. Figures 1, 3 and 4 are flow sheets, simplified diagrammatic illustrations, of the invention.

In Figure 1, a reformer naphtha charge such as a hydrocarbon fraction having the following properties, is taken through line 1 to reformer 2 wherein it is reformed:

Hydrocarbon fraction

Boiling range, °F. (ASTM)	237–399
Gravity, °API	50.6
Aromatics, percent volume	3.3
Aromatics, percent weight	—
Octane rating, research clear	62.7

Reformer 2 is generally operated at a temperature of about 1000° F. to 940° F., 175 p. s. i., contact time of 8–10 seconds, with a typical reforming catalyst such as chromia-alumina being used; such operation is well known

in the art. It is preferred herein that reformer 2 be operated as required for normal motor gasoline production, that is, a temperature of 960° F., pressure of 175 p. s. i., contact time of 8.6.

The product produced in reformer 2 is generally known as the "reformate" and this is taken through line 3 and cooler 4 to a gas separator 5. Gases such as hydrogen, methane, ethane and ethylene are removed from separator 5 through overhead line 6. Gas-free reformate is taken from separator 5 via line 7 to a fractionator 8. The latter is so operated that a C₄-C₆ fraction is taken as an overhead product via line 9, and a heavy reformate product, boiling above about 300° F., is removed as a bottoms product via line 10. An aromatic reformate fraction having a boiling range from about 200° F. to about 300° F. is removed from an intermediate section of fractionator 8 through line 11.

The aromatic reformate fraction in line 11 is within the aviation boiling range and contains appreciable quantities of toluene and xylenes, in addition to aliphatic hydrocarbons. The aromatic reformate has the following properties:

Boiling range, °F. (ASTM) -----	200-300
Gravity, °API -----	50.2
Aromatics, percent volume -----	32.0
Aromatics, percent weight -----	29.3
Octane, rating, research clear -----	80.5

This fraction is introduced into a lower section of extractor 12, also referred to herein as extractor A, wherein it is in countercurrent relation with lean diethylene glycol, which is introduced via line 13 into an upper section of extractor A. The conditions maintained in extractor A are those favorable for a selective solution of some or most of the aromatics present in the 200-300° F. fraction. As a guide, from about 3 to about 15 volumes and preferably 4-8 volumes of diethylene glycol are used to contact one volume of 200-300° F. fraction, at temperatures of about 60 to about 200° F., and preferably at 80-110° F. A partially de-aromatized fraction, associated with a minor quantity of diethylene glycol, is removed as a raffinate through line 14, and is washed with water, from line 15, in washer 16. Water removes diethylene glycol from the partially de-aromatized fraction in 16, and the latter fraction is removed through line 17 to a motor gasoline blending operation (not shown). In general, the partially de-aromatized fraction is blended with motor gasoline stocks so as to upgrade the latter. It will be understood that the partially de-aromatized fraction is dried before use as a gasoline; any conventional drying operation (not shown) can be used.

The extract taken from extractor A via line 18 is termed "rich glycol," inasmuch as the diethylene glycol is associated with the aromatics extracted from the 200-300° F. reformate fraction (from line 11). The extract in line 18 is fed to an upper section of extractor 19, also referred to herein for convenience as extractor B, wherein it is in countercurrent contact with an alkylate fraction, flowing from inlet line 20. The alkylate fraction, or a light straight run gasoline, or blend of the two, is capable of dissolving an appreciable quantity of aromatics, such that the resulting solution of aromatics and alkylate fall within gasoline blending requirements. Generally, from about 0.2 to about 0.04 volume of the alkylate is used in contact with one volume of rich glycol (from line 18), at temperatures of the order of about 60 to about 200° F. and preferably 80-110° F. An extract comprising aromatics and alkylate and a minor quantity of diethylene glycol is taken from extractor 19, through line 21 to washer 22 wherein it is washed with water from line 23 to effect removal of the minor amount of diethylene glycol. A blend of aromatics and alkylate, free from diethylene glycol, and suitable as an aviation blending stock is removed from the system via line 24. The blend in line 24 is taken to an aviation gasoline blending

operation (not shown), where it is blended with light straight run gasoline or isopentane.

A raffinate stream comprising diethylene glycol, some alkylate and some aromatics, referred to as a "lean glycol" in contrast to the rich glycol in line 18, is taken from extractor B and is recycled to extractor A via line 13. The minor quantity of alkylate present in the lean glycol is in contact with the 200-300° F. aromatic reformate in extractor A and a major portion of such alkylate goes into the raffinate phase which issues through line 14.

Diethylene glycol removed by water-washing in washers 16 and 22 is withdrawn from the washers via lines 25 and 26, respectively, to removal line 27. Diethylene glycol can be recovered in concentrated form (not shown) by distillation. Fresh or make-up diethylene glycol can be added to the system through inlet line 28.

It is to be noted that there is need for little, if any, heating or cooling of the various solutions in contact in extractors A and B or transferred therebetween. These extraction operations can be conducted in either single stage, multistage or countercurrent tower type equipment.

An important feature of the system illustrated by Figure 1 is that the alkylate fraction has a sufficiently low solubility in the diethylene glycol solution (since it is non-aromatic), such that substantially all of the alkylate will be recovered in the aromatic blend issuing from the second extraction effected in extractor B. Conversely, a sufficient transfer of aromatics from the rich glycol solution to the alkylate to provide a satisfactory aviation gasoline blending stock, results because of the specific solubility relationships involved and the relative volumes of the rich glycol and alkylate streams.

Reference is now made to Figure 2 which contains two charts or ternary diagrams representative of the extractions effected in extractors A and B of Figure 1. These diagrams can be used to determine: The suitability of a selective solvent for a desired separation; the approximate selectivity of the solvents; the range of compositions of solvent, aromatic hydrocarbons and alkylate; the approximate number of stages or extractions necessary to effect a separation of desired degree; etc.

The diagrams in Figure 2 represent the systems: diethylene glycol, aromatic hydrocarbons (e. g., xylenes) and non-aromatic hydrocarbons (e. g., n-heptane); and diethylene glycol, aromatic hydrocarbons and alkylate. It is to be understood that in Figure 2, the phase boundaries are necessarily approximate since the hydrocarbons and alkylate are not pure compounds.

Figure 2 reveals that the diethylene glycol, and the aromatic hydrocarbons are incompletely miscible, that diethylene glycol and the non-aromatic hydrocarbons are incompletely miscible, and that the aromatic and non-aromatic hydrocarbons are completely miscible. When one volume of a hydrocarbon mixture containing 32 volume percent of aromatics and 68 volume percent of non-aromatics (point E), is mixed with approximately four volumes of diethylene glycol, the material balance composition of the resulting mixture is represented by point G. Diagrammatically,

E G (DEG)
G B (Hydrocarbon)

is equal to the 4:1 ratio of the two feeds to extractor A. At equilibrium, this mixture settles to form two phases of a composition represented by the points of intersection F and H of the solid tie lines with the two equilibrium lines KL and MN. The glycol phase composition (point F) comprises 91 percent of diethylene glycol, 7.2 percent of aromatics and 1.8 percent of non-aromatics. (The glycol free composition is shown as 80 percent of aromatics and 20 percent of non-aromatics, by point I.) The raffinate phase from extractor A is represented by point H of Figure 2. Point 4 represents the composition of the raffinate phase from extractor A after diethylene

glycol removal (glycol-free raffinate), 85.8 percent of non-aromatics and 14.2 percent of aromatics.

As shown by the ternary diagram representative of extraction B, in extractor B the aromatic content of the alkylate is increased from zero percent (volume) to 19.0 percent (volume), as contrasted with the results in extractor A, when the aromatic content of the hydrocarbon fraction is reduced from 32.0 percent (volume) to 14.4 percent (volume).

Another advantage of the instant process resides in the fact that only a portion of the aromatics available in the feed stock to the first extraction (extractor A) is normally required for the volume of aviation blend stock produced. Thus, it is contemplated herein that the first extraction (extractor A) can be quite inefficient such that it can be conducted in a single stage unit, and the second extraction (extractor B) can be conducted in a countercurrent tower unit. However, it is preferred that two or more countercurrent stages be used in the first extraction (extractor A), in order to increase the efficiency of that operation. As a consequence, less alkylate is lost to motor gasoline.

To further illustrate the invention, 251 parts by volume of a 200–300°F. boiling range aromatic reformat, containing 32.0 percent by volume of aromatics, were charged through line 11 to extractor A of Figure 1. The extraction in extractor A was a single stage contact of the aromatic reformat with 1000 parts by volume of diethylene glycol (DEG), from line 13, at 85–90°F. The extract or rich glycol phase formed in extractor A was withdrawn via line 18 to extractor B wherein it was washed countercurrently in a three-stage multicontact process at 85–90°F. with a total of 251 parts by volume of an alkylate (aviation grade, 118/137 octane) obtained by HF alkylation, such as described in United States Letters Patent 2,431,500. In extractor B, an extract of lean glycol and a raffinate of aromatics and alkylate were formed. The raffinate, 298 parts by volume, was withdrawn from extractor B, as through line 21, and washed with 30 parts by volume of water. The water-washed, glycol-free raffinate so obtained comprised 296 parts by volume and contained 19.0 percent of aromatics. This raffinate had a fuel rating of 106/141.

The raffinate obtained in the initial extraction in extractor A was removed via line 14 and washed with 20 parts by volume of water. The water-washed, glycol-free raffinate obtained here was a motor gasoline blend, 206 parts by volume, and had an octane rating of 76.2 clear (3 cc. TEL, 90.5).

Results of the foregoing illustration are tabulated below, in order to reveal the improvement realized by the process of this invention:

	Charge					Raffinate			
	Deg. Parts by Vol.	Parts by Vol.	Octane No. (Research Method)	Aromatics		Parts by Vol.	Octane No. (Research Method)	Aromatics	
				Per-cent Vol.	Per-cent Wt.			Per-cent Vol.	Per-cent Wt.
Extractor A.....	1,000	251	80.5 (92.8 with 3 cc. TEL ^a).	32.0	29.3	206	76.2 (90.5 with 3 cc. TEL ^a).	14.2	13.3
Extractor B.....		251	118/137 ^b	0.0	0.0	296	106/141 ^b	19.0	15.8

^a Tetraethyl lead.

^b Performance Number.

Although the solubility of alkylate in the rich glycol solution is generally low, it can, nevertheless, be sufficient in some cases to warrant an additional modification of the second extraction (extractor B), in order to minimize any loss of alkylate to motor gasoline (line 17) through the first extraction (extractor A). For this purpose, I contact the diethylene glycol solution issuing from the

second extraction (extractor B) with an additional solvent which would also be included in the final aviation gasoline blend and which has the capacity to extract substantially all of the dissolved alkylate, thus permitting the latter to be recovered with the main alkylate stream from the second extraction. The additional solvent can be isopentane, or a light straight run gasoline (boiling range, 100 to 250°F.) suitable for aviation blending, whichever is more available or less expensive at the time needed. A schematic diagram of this processing scheme is illustrated in Figure 3.

In Figure 3, all operations are the same as described above in connection with Figure 1, except for the operation effected in the second extraction. For this reason, reference is made to only those portions of Figure 3 which differ from corresponding portions of Figure 1.

In Figure 3, an aromatic reformat having a 200–300°F. boiling range is taken through line 30 and is fed to a lower section of extractor 31 (extractor C for convenience). The reformat is contacted countercurrently in extractor C with lean diethylene glycol, introduced via line 32. Aromatics in the reformat are extracted preferentially by the diethylene glycol, and a rich glycol extract is removed from the bottom of extractor C through line 33. Raffinate comprising non-aromatics and a minor quantity of diethylene glycol is withdrawn from extractor C through line 34, and is then washed with water, from line 35, in washer 36. Non-aromatics are removed from washer 36 through line 37; these non-aromatics are suitable for motor gasoline blending.

The rich glycol solution comprising diethylene glycol, aromatics and some non-aromatics in line 33 is contacted countercurrently in extractor 38 (extractor D), with alkylate from line 39. The alkylate is introduced at an intermediate section of extractor D, below the rich glycol feed. Also introduced into extractor D, but at a section below the alkylate feed, is light straight run gasoline, which is brought in through line 40. Thus, in an intermediate section of extractor D, aromatics are removed preferentially from the rich glycol stream (from line 33) by the alkylate, and some alkylate goes into solution with the diethylene glycol; in short, a displacement of aromatics by alkylate. In turn, at a lower section of extractor D, the light straight run gasoline goes into solution preferentially with the diethylene glycol, and the alkylate which had been in solution with diethylene glycol is released; here, a displacement of alkylate by light straight run gasoline. The bottoms product from extractor D is primarily a solution of diethylene glycol and light straight run gasoline with only a minor proportion of alkylate. This bottoms product is taken from extractor D through

line 32 to extractor C. The light straight run gasoline and alkylate so circulated to extractor C is removed in the raffinate in line 34 and becomes a part of the motor gasoline blend stock removed from the system via line 37. Thus, the motor gasoline blend stock contains little of the relatively expensive alkylate, instead containing substantially more of the much less expensive light

straight run gasoline. In this respect, the procedure of Figure 3 is more advantageous than Figure 1.

Returning now to extractor D, a raffinate stream comprising aromatics and minor quantities of alkylate, light straight run gasoline and diethylene glycol is removed through line 41 to washer 42 wherein it is washed with water from line 43. Aromatics, alkylate and light straight run gasoline, constituting aviation blend stock, are removed from the system via line 44. It should be noted here, however, that the quality of the aviation blend stock taken from line 44, is somewhat lower than the corresponding base stock taken from line 24 of Figure 1, inasmuch as the light straight run gasoline, present in line 44 and absent in line 24, has a lower octane or power value than the alkylate.

Diethylene glycol is recovered from the system shown by Figure 3 in the same manner as described earlier in regard to Figure 1.

As indicated above in describing the procedures illustrated by Figures 1 and 3, some high quality alkylate is lost to motor gasoline blend stocks, in the streams of lines 17 and 37, respectively, rather than being available in the aviation gasoline blend stocks of the streams of lines 24 and 44, respectively. This loss can be reduced substantially or even nullified by operating in the manner illustrated by Figure 4. Here again, only those operations of Figure 4 which differ from operations of Figures 1 and 3 are referred to; it will be understood, therefore, that all other operations are carried out in the manner recited earlier in conjunction with Figure 1.

Referring now to Figure 4, three extraction units are used to produce three individual raffinates: motor gasoline blend stock, aviation-grade super fuel and a butane solution of alkylate. Line 50 carries aromatic reformat, boiling range 200–300° F., to a lower section of extractor 52 (extractor E), wherein it is contacted countercurrently with lean diethylene glycol fed to an upper section of extractor E via line 53. Aromatics are extracted from the reformat, with a resulting rich glycol being withdrawn through extract line 54 to an upper section of extractor 55 (extractor F). The rich glycol is in contact with alkylate, introduced countercurrently at a lower section of extractor F through line 56. Alkylate extracts aromatics from the diethylene glycol-aromatic reformat fed from line 54, such that an extract of intermediate glycol is formed, the intermediate glycol being comprised of diethylene glycol, alkylate and a substantially lesser quantity of aromatic reformat. The intermediate glycol is conducted from extractor F through line 57 to an upper section of extractor 58 (extractor G). Normal butane is brought into extractor G via line 59, connecting with a lower section of extractor G, such that normal butane and the intermediate glycol are contacted countercurrently. In extractor G, n-butane extracts alkylate from the intermediate glycol stream such that an extract of lean glycol is formed; the lean glycol comprises diethylene glycol, n-butane and minor quantities of alkylate and aromatics. The lean glycol is taken from extractor G through line 53 for return to extractor E.

Attention is now given to the three raffinates produced in extractors E, F and G. The raffinate formed in extractor E is comprised principally of non-aromatics from the aromatic reformat charged via line 50, and n-butane from the lean glycol introduced through line 53; minor quantities of diethylene glycol and alkylate are also present in the raffinate. The raffinate is taken from extractor E through line 60 to washer 61 wherein it is washed with water from line 62. Diethylene glycol is removed from this raffinate, and a motor gasoline blend of non-aromatics and n-butane, with a small amount of alkylate, is withdrawn through line 63 for final blending (not shown) to motor gasoline.

The raffinate formed in extractor F is comprised of aromatics from the aromatic reformat, carried into ex-

tractor F via line 54, and alkylate from line 56. This raffinate also contains a small amount of diethylene glycol. Removal of the raffinate from extractor F is through line 64 which is connected with washer 65. Diethylene glycol is removed from the raffinate by water, fed through line 66. The water-washed raffinate, free from diethylene glycol, is withdrawn from the system via line 67 for blending (not shown) to aviation gasoline. The aviation gasoline stock in line 67 is comprised of aromatics and alkylate.

Raffinate formed in extractor G is made up of diethylene glycol, alkylate and a minor quantity of aromatic reformat (all introduced via line 57) and a substantial quantity of n-butane (from line 59). This raffinate is withdrawn from extractor G via line 68 to washer 69. Diethylene glycol is removed from this raffinate by water brought through line 70, and a water-washed, glycol-free raffinate is withdrawn from the washer (69) through line 71. The raffinate in line 71 is taken to an alkylate debutanizer (not shown) such as described in United States Letters Patent 2,471,211, wherein alkylate is recovered and is returned to the process through line 56, and wherein n-butane can be recovered for return to the process via line 59.

Diethylene glycol is recovered from washers 61, 65 and 69 in the same manner as indicated above in regard to Figure 1.

As indicated earlier, the system or process illustrated by Figure 4 is particularly meritorious in that aviation blend stock (taken from line 67) is produced with little or no loss of high quality alkylate to motor gasoline blend stock (taken from line 63).

Selective solvents

With regard to solvents having preferential selectivity for aromatic hydrocarbons, such as diethylene glycol illustrated above, it is to be understood that all such solvents are contemplated herein, although diethylene glycol is preferred. Typical of solvents having selectivity for aromatic hydrocarbons are: ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, furfural, tetrahydrofurfuryl alcohol, nitrobenzene, chlorex (B,B'-dichlorodiethyl ether), cresylic acid, phenol, aniline, quinoline, ethylene carbonate and mixtures of the various polyethylene glycols, and these glycols admixed with small amounts of water which increase their selectivity for aromatics. However, in order to eliminate the necessity for solvent recovery by distillation and to minimize alkylate losses, the selective solvent should also exhibit a low capacity for non-aromatic hydrocarbons. Therefore, of the numerous solvents mentioned above, the following are more desirable: tetrahydrofurfuryl alcohol, diethylene glycol, triethylene glycol, mixtures of these solvents and also such solvents admixed with small amounts of water.

Extraction factors

In connection with diethylene glycol (DEG) as the selective solvent, it is preferred that approximately four volumes of the same be used for each volume of aromatic reformat containing from thirty to forty volume percent of aromatics. However, the volume ratio of DEG to aromatic reformat can vary widely, as from about 3:1 to about 15:1. It will be understood that the optimum ratio will vary with the selective solvent used; however, the broad operative range will generally be of the order of about 3:1 to about 15:1.

The volume ratio of the aromatic reformat charge to extractor A, to the alkylate charge to extractor B, in processes typified by Figure 1, should be at least about 1:1 so as to produce an aviation grade gasoline; whereas, this volume ratio should normally be greater than about 5:3 in order to produce super-fuel grade aviation blending stocks. It will be apparent that in connection with Figure 3, and extractors C and D, these same volume ratios

are involved; the volume ratio of alkylate (charged to extractor D) to light straight run gasoline (also charged to extractor D) is of lesser import, generally about 2:1. Correspondingly, the volume ratio primarily involved in systems illustrated by Figure 4 is that of aromatic reformat (charged to extractor E) to alkylate (charged to extractor F), about 5:3; the ratio of alkylate to n-butane, is of secondary importance, again being about 2:1.

A further observation is that operable feed ratios, solvent dosage and number of extraction stages required to produce super-fuel aviation blend stocks, all increase as the aromatic concentrations in the aromatic reformat feed stream decreases. Furthermore, as the ratio of aromatic reformat to alkylate approaches unity, the number of stages required for extraction with the alkylate increases.

Hydrocarbon charges

As indicated above, the aromatic reformates can be obtained as products from any one of a number of reforming procedures, such as Thermoform Catalytic Reforming, which is described in the May 1952 issue of the Petroleum Refiner. The aromatic reformates herein are generally within the boiling range of about 170° F. to about 400° F., and preferably within the 200–300° F. boiling range. The aromatic content of such reformates should be greater than about 22 percent by volume, with no limit being placed upon the maximum aromatic content. As a rule, however, such reformates will contain from about 30 to about 50 percent by volume of aromatics.

Alkylates used herein are, as indicated above, paraffinic in character and boil within the range of about 170° F. to about 400° F. Or, in other words, the paraffinic alkylates fall within the molecular weight range of about 72 to about 170, preferably 80 to 128. The alkylates can be prepared by any number of alkylation processes, one excellent source being HF alkylation. A straight run gasoline can be used in place of an alkylate in preparing a motor gasoline, or can be blended therewith for use in the second extraction stage. Suitable straight run gasoline are within the 100° F. to 250° F. boiling range. Isopentane can be used in place of the alkylate or together therewith.

With respect to using a light straight run gasoline with alkylate, in a technique such as that shown by Figure 3, attention is called to the definition of such a gasoline as recited above in the section concerned with "Definitions." Any of such gasolines can so serve herein, as can the following individual hydrocarbons or mixtures thereof: mixed butanes, mixed pentanes, and a mixture of butanes and hexanes.

As was mentioned above in connection with the technique illustrated by Figure 4, n-butane is used in extractor G to aid in the recovery of alkylate from the intermediate glycol (in line 57). It is to be understood, however, that other light hydrocarbons or light hydrocarbon fractions can be used in place of or together with n-butane. Typical of such hydrocarbons or hydrocarbon fractions are: propane, pentane or mixture thereof.

I claim:

1. The process for preparing a gasoline blending stock having an octane value above about 80, which comprises: contacting a hydrocarbon fraction containing at least about 22% by volume of aromatic hydrocarbons, which boil predominantly in the range of about 170° F. to about 400° F., and containing other hydrocarbon types, with a selective non-aqueous solvent having a preferential selectivity for aromatic hydrocarbons, whereupon an extract phase comprising solvent and aromatic hydrocarbons and a raffinate phase comprising said other hydrocarbons and solvent are formed; separating said extract and raffinate phases; contacting said extract phase with a paraffinic alkylate having a boiling range from

about 170° F. to about 400° F., whereby said aromatic hydrocarbons are disassociated from said extract phase and associate with said paraffinic alkylate to form said gasoline blending stock.

2. The process of claim 1 wherein said hydrocarbon fraction is an aromatic reformat having a boiling range from about 200° F. to about 300° F.

3. The process of claim 1 wherein said paraffinic alkylate is one having a boiling range from about 200° F. to about 300° F. and has an octane value of at least about 100.

4. The process of claim 1 wherein said selective solvent is diethylene glycol.

5. The process for preparing a gasoline blending stock having an octane value above about 80, which comprises: contacting a hydrocarbon fraction containing at least about 22% by volume of aromatic hydrocarbons, which boil predominantly in the range of about 200° F. to about 300° F., and containing other hydrocarbon types, with a selective solvent having a preferential selectivity for aromatic hydrocarbons, whereupon an extract phase comprising solvent and aromatic hydrocarbons and a raffinate phase comprising said other hydrocarbons and solvent are formed; separating said extract and raffinate phases; contacting said extract phase with a paraffinic alkylate having a boiling range from about 200° F. to about 300° F., and then contacting the resulting mixture with a straight run gasoline having a boiling range from about 100° F. to about 250° F., whereby said aromatic hydrocarbons are disassociated from said extract phase and associate with said paraffinic alkylate to form said gasoline blending stock.

6. The process for preparing an aviation blending stock (I) having an octane performance value from about 100/130 and a motor gasoline blending stock (II) having an octane value above about 80, which comprises: contacting a hydrocarbon fraction containing at least about 22% by volume of aromatic hydrocarbons, which boil predominantly in the range of about 200° F. to about 300° F., and containing other hydrocarbon types, with a selective non-aqueous solvent having a preferential selectivity for aromatic hydrocarbons, whereupon an extract phase comprising solvent and aromatic hydrocarbons and a raffinate phase comprising said other hydrocarbons and solvent are formed; separating said extract and raffinate phases; contacting said extract phase with a paraffinic alkylate having a boiling range from about 100° F. to about 250° F., whereby said aromatic hydrocarbons are disassociated from said extract phase and associate with said paraffinic alkylate to form said aviation gasoline blending stock (I); and removing solvent from said raffinate phase to obtain said motor gasoline blending stock (II).

7. The process for preparing an aviation gasoline blending stock (I) having an octane performance value above about 100/130 and a motor gasoline blending stock (II) having an octane value above about 80, which comprises: contacting a hydrocarbon fraction containing at least about 22% by volume of aromatic hydrocarbons, which boil predominantly in the range of about 200° F. to about 300° F., and containing other hydrocarbon types, with a selective solvent having a preferential selectivity for aromatic hydrocarbons, whereupon an extract phase comprising solvent and aromatic hydrocarbons and a raffinate phase comprising said other hydrocarbons and solvent are formed; separating said extract and raffinate phases; contacting said extract phase with a paraffinic alkylate having a boiling range from about 100° F. to about 250° F., and then contacting the resulting mixture with a straight run gasoline having a boiling range from about 100° F. to about 250° F., whereby said aromatic hydrocarbons are disassociated from said extract phase and associate with said paraffinic alkylate to form said aviation gasoline blending stock (I), and whereby said straight run gasoline forms a solution with said solvent; contacting said

raffinate phase with said solution of straight run gasoline and solvent, and removing solvent from the raffinate so contacted to form said motor gasoline blending stock (II).

8. The process for preparing an aviation blending stock (I) having an octane performance value above about 100/130, a motor gasoline blending stock (II) having an octane value above about 80, and a paraffinic alkylate solution (III), which comprises: contacting a hydrocarbon fraction containing at least about 22% by volume of aromatic hydrocarbons, which boil predominantly in the range of about 200° F. to about 300° F., and containing other hydrocarbon types, with a selective solvent having a preferential selectivity for aromatics, whereupon an extract phase (A) comprising solvent and aromatic hydrocarbons and a raffinate phase (B) comprising said other hydrocarbons and solvent are formed; separating said extract phase (A) and contacting it with a paraffinic alkylate having a boiling range from about 100° F. to about 250° F., whereby said aromatic hydrocarbons are disassociated from said extract phase to form a raffinate phase (C) comprising said aromatic hydrocarbons, paraffinic alkylate and a minor amount of solvent, and whereby said solvent of extract phase (A) associates with a portion of said paraffinic alkylate to form an extract phase (D) comprising solvent, paraffinic

alkylate and a minor quantity of aromatic hydrocarbons; separating said extract phase (D) and contacting it with a light hydrocarbon having from about three to about five carbon atoms per molecule, whereby are formed a raffinate phase (E) comprising paraffinic alkylate, said light hydrocarbon, solvent and a minor quantity of aromatic hydrocarbons, and an extract phase (F) comprising solvent, said light hydrocarbon and minor quantities of aromatic hydrocarbons and paraffinic alkylate; returning said extract phase (F) to contact with said raffinate phase (B); removing solvent from said raffinate phases (B), (C) and (E) to form, respectively, said motor gasoline blending stock (II), said aviation gasoline blending stock (I) and said paraffinic alkylate solution (III).

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