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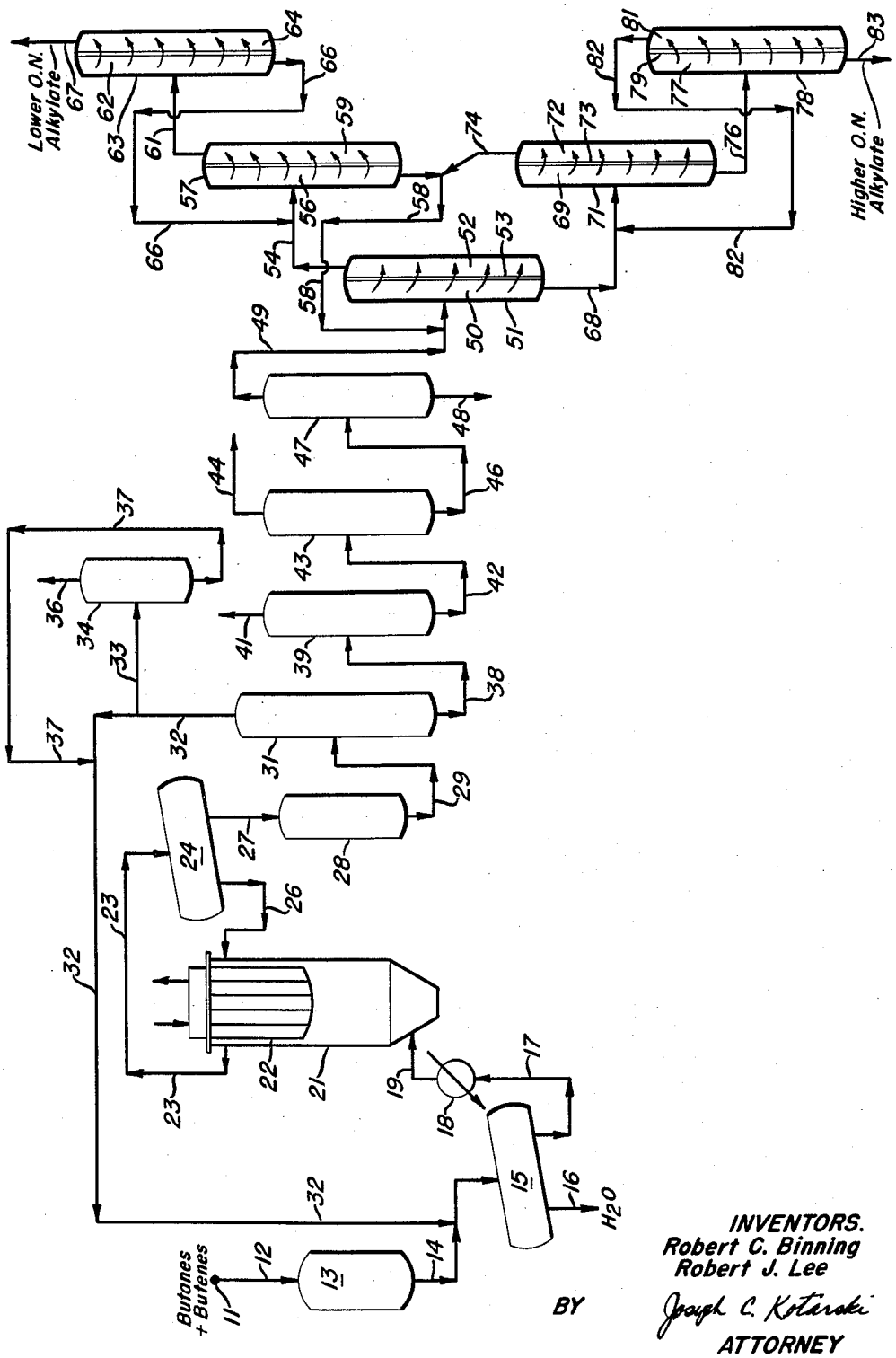

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PRODUCTION OF HIGH OCTANE ALKYLATE USING A PERMEABLE MEMBRANE SEPARATION SYSTEM

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This invention concerns a process for producing segregated portions of alkylate having differing octane numbers and in particular it concerns the combining of an alkylation process and a permeation process whereby large quantities of high octane alkylate as well as lower octane alkylate can be produced.

The demand for high octane number gasoline has required petroleum refiners to operate their alkylation units for the production of blending stocks for motor fuels. Alkylate has high lead susceptibility and is additionally a desirable component of motor fuels because it reduces the sensitivity of the gasolines which is ever increasing because of larger concentrations of aromatic components. While the octane number of the raw nonleaded alkylate is generally not of crucial importance to the petroleum refiner because of its excellent lead response, it is extremely important to the refiner who produces a gasoline which contains no tetraethyl lead. When petroleum refiners are producing approximately 100 octane number gasoline which contains no tetraethyl lead, the octane number of the alkylate must obviously be as high as possible. The alkylate generally produced, which has an F–1 octane number of between 85 to 96, leaves something to be desired in this respect.

It has long been appreciated that when an alkylate process is operated at maximum production rates of alkylate (and even higher than design rates), the nonleaded octane number of the alkylate is appreciably lower than if the alkylation unit were operating under conditions for the production of lesser amounts of alkylate. For example, a typical alkylation unit may be capable of producing 10,000 bbl./day of 380° F. E.P. alkylate having an F–1 octane number of 92.6, whereas when the same unit is operated so as to produce 3000 bbl./day of alkylate the F–1 octane number of the latter alkylate will be 96.8. While the advantage in octane number is highly desirable, the penalty in loss of production is very severe.

An object of this invention is to provide a process capable of producing segregated portions of alkylate which have differing octane numbers. Another object is to provide a combined alkylation and permeation process whereby maximum production rates of alkylate are possible while still producing portions thereof which have a high octane number. A further object is to provide a combined alkylation and permeation process capable of producing one portion of alkylate having a volume and an octane number at least as great as the alkylate produced at lower alkylate production rates and in addition an amount of a lower octane number alkylate. An additional object is to provide an efficient and economic

method for producing an alkylate blending stock of high octane number for a non-leaded gasoline and a lower octane number alkylate blending stock for a leaded gasoline and a lower octane number alkylate blending stock for a leaded gasoline in which the alkylation process is operated to produce maximum quantities of alkylate.

It has been found that the peculiar advantages of a permeation process can be keyed into the disadvantages of an alkylation process to overcome the undesirable features of the alkylation process and thereby yield the necessary high octane number gasoline as well as an additional quantity of a lower octane number gasoline. In our invention an alkylation process is operated at high production rates, preferably at the maximum rate of alkylate production, thus yielding a gasoline boiling range alkylate which generally has an F–1 octane number of less than 96. This alkylate is passed to a permeation process wherein it is permeated in one or more stages into segregated portions of alkylate which have octane numbers differing from each other and from the alkylate which is charged to the permeation process. While the total gasoline boiling range alkylate produced in the alkylation process may be charged to the permeation process, it is preferred to fractionate the alkylate into separate fractions which consist of hydrocarbons substantially all of which have the same number of carbon atoms in their molecule. Thus a preferred fraction of the alkylate charged to the permeation process may be the C_6, C_7 fraction or the C_8 fraction, especially the latter which boils over the range of about 205° to 260° F. In the permeation process, the alkylate is charged to a permeation vessel which may consist of one or more vessels separated by a thin plastic membrane into two sections.

The alkylate is charged into the charge section, which operates usually at a temperature of 100° to 300° F. and a super-atmospheric pressure sufficient to maintain the alkylate liquid. A portion of the alkylate, which may be as little as 10% or as high as 90% of the charge, is permeated through the plastic membrane into the permeate zone which operates generally at a sub-atmospheric pressure so that as the hydrocarbons permeate the membrane they are immediately vaporized into the permeate zone. The permeated portion of the alkylate, which has a lower octane number than the alkylate initially in contact with the membrane, is removed from the permeate zone. The remaining nonpermeated portion of the alkylate is removed from the charge zone. This portion of the alkylate has a higher octane number than the charge to the permeation step. In the permeation process the plastic membrane used should be as thin as possible e.g. 0.1 to 5 mils or even less. It may be of any type through which paraffinic hydrocarbons permeate more rapidly the less the number of methyl side chains the paraffins contain. It may be of a cellulosic type such as cellulose acetate-butyrate, ethyl cellulose, films prepared by casting from solutions containing blends of cellulose ester and ethers, etc. The process of our invention is characterized by the production of segregated portions of alkylate, one portion of which has at least as high an octane number as the similar boiling range alkylate produced when an alkylation process is operated at a lower production rate and a second segregated portion of alkylate having a lower octane number than the first segregated portion, but the

combined volume of these segregated portions being greater than that of the equivalent boiling range alkylate which is produced at the lower alkylate production rate.

As illustrative of our invention a preferred embodiment thereof will be described hereinafter.

Figure 1 is a diagrammatic representation of our combined alkylation-permeation process for producing alkylate at high production rates while also producing segregated portions of alkylate having high and low octane numbers respectively. Numerous valves, pumps, heaters, coolers etc. have been omitted from this diagrammatic representation for purpose of clarity.

Referring to Figure 1, the charging stock to the alkylation process consists of a depropanized refinery butanes-butenes stream from catalytic cracking. It contains about 50°% olefins and is composed essentially of isobutane, normal butane, and butenes with minor amounts of propane and pentanes. Butanes and butenes from other sources may obviously be used also. The butanes-butenes charge stock is passed under pressure from source **11** by way of line **12** into vessel **13** which contains an aqueous caustic solution for removing mercaptans and hydrogen sulfide. The caustic washed hydrocarbons are removed from vessel **13** and passed through line **14** wherein they meet recycled isobutane in an amount such that the isobutane:butene ratio is then approximately 4:1 to 10:1 e.g. 6:1. The butanes-butenes stream is passed by way of line **14** into water settler **15** from which water is removed and discarded by way of line **16**. The hydrocarbon stream is removed from settler **15** and passed by way of line **17** to chiller **18**. Thereafter the chilled hydrocarbons are passed by way of line **19** into the alkylation reactor **21**.

In alkylation reactor **21**, the liquid mixture of butanes and butenes at a temperature between about 30° and 50° F. is intimately contacted with sulfuric acid having a concentration between 90 and 100%, preferably about 95 to 98%. The ratio of acid to hydrocarbon should be between about 0.7:1 and 1:1. An internal isobutane to olefin ratio of between 25 and 1000 (the higher the internal ratio, the higher the octane number of the alkylate) is used. An olefin space velocity of 0.15 to 0.50 and a hydrocarbon-acid contact time of about 10 to 20 minutes is employed. The influence of the various operating conditions described above are well-known in the art and may be adjusted accordingly to produce the optimum results of alkylate production and octane number with minimized usage of sulfuric acid.

When the rate of production of alkylate is increased, the operating conditions are changed usually in the following manner. The external ratio of isobutane to olefins is approximately the same, the olefin space velocity is greatly increased, for example, it may be increased to 0.4 or thereabouts and the hydrocarbon acid contact time is reduced. The recycle of isobutane is constant. In such an operation, the internal ratio of isobutane to olefins is decreased (because of the constant isobutane recycle ratio and the greater throughput of olefins) and this causes the octane number of the alkylate to be reduced. The increase in the olefin space velocity and the reduction in contact time also appear to contribute to reducing the octane number of the alkylate. The alkylate product does not appear to have the more desirable higher octane number isomers, some chain breaking of the hydrocarbon occurs, and more of the higher molecular weight lower octane number components are formed. Because the alkylation units are usually designed to produce a defined quantity of a given end point alkylate having a prescribed minimum octane number, such units will be operated at less than designed capacity to produce a higher octane number alkylate or operated at greater than designed capacity to produce a lower octane number alkylate.

In the embodiment illustrated herein the design capacity of the alkylation process is about 7500 bbl./day of 94.2 F–1 octane number alkylate having an end point of 380° F. The alkylation process in this embodiment is operated at maximum throughput to produce 10,000 bbl./day of 380 E.P. alkylate having an F–1 octane number of 92.6. Thus in the embodiment illustrated herein the alkylation unit is operating in excess of the designed capacity and it produces an additional 2500 bbl./day of alkylate, but the entire alkylate has a lower octane number by 1.6 units. Although the alkylate herein has an octane number of 92.6, the alkylate may have an even lower octane number, for example, it may be between 85 and 96. In general, the lower the octane number of the alkylate charge to the permeation process, the greater the improvement in octane number of the non-permeated portion per permeation stage, and therefore it is greatly preferred to produce the largest possible volume of alkylate even though its octane number is as low as 85 F–1 or thereabouts.

Alkylation reactor **21** may be any of a number of varied types such as the impeller type reactor system as is diagrammatically indicated herein, the jet type, time-tank system or others. Reactor **21** is provided with a bayonet tube cooling bundle **22** through which refrigerant flows to remove the heat of reaction liberated in the process. The hydrocarbon-acid emulsion leaves reactor **21** and is passed by way of line **23** into an acid settler **24**. The settled acid is removed and recycled by way of line **26** into reactor **21**. To maintain the desired strength of the acid, a portion thereof may continuously be withdrawn and replaced with higher strength acid or an entirely fresh batch of acid may be charged batchwise as is necessary. The hydrocarbon layer from settler **24**, which consists of alkylate, excess isobutane, and the inert diluents introduced with the feed, is passed by way of line **27** into vessel **28** which contains an aqueous caustic solution for removing components such as SO_2 which are formed in small quantities by catalyst degeneration. The caustic washed hydrocarbons are then removed from vessel **28** and passed by way of line **29** into the fractionation section of the alkylation plant. While a sulfuric acid catalized butene alkylation process has been described, a different catalyst such as HF, $AlCl_3$ or complexes thereof, or an ethylene alkylation process may be substituted therefor.

The caustic washed product is passed by way of line **29** into deisobutanizer **31** from which an overhead stream of recycle isobutane is taken and passed by way of line **32** into line **14** for the purpose of fortifying the butanes-butenes stream with respect to isobutane. A slip-stream portion of the isobutane recycle is removed from line **32** and passed by way of line **33** into depropanizer **34** from which an overhead stream of propane is removed by way of line **36** and sent to storage means not shown, and a stream of purified isobutane is removed by way of line **37** and returned to isobutane recycle line **32**. A bottoms stream is removed from deisobutanizer **31** and passed by way of line **38** into debutanizer **39** from which an overhead stream of n-butane is removed by way of line **41** and sent to storage means not shown. A bottoms stream from fractionator **39** is removed and passed by way of line **42** into fractionator **43** from which an overhead stream of about 2550 bbl./day containing substantially all of the pentanes, hexanes, and heptanes is removed and passed by way of line **44** to storage means not shown. A bottoms fraction of about 7450 bbl./day is removed from fractionator **43** and passed by way of line **46** into fractionator **47**. From fractionator **47** a bottoms fraction of about 2250 bbl./day which boils at 260° F. and higher is removed and sent by way of line **48** to storage means not shown. The overhead stream from fractionator **47**, which amounts to about 5200

bbl./day, has an F–1 octane number of 94, and consists almost exclusively of branched chain paraffins having 8 carbon atoms in their molecule. This octane fraction, which boils between about 205° and 260° F., is passed by way of line 49 into the permeation plant.

The permeation process which segregates the alkylate into portions having differing octane numbers can be described, in its simplest form, as a single stage operation using a single closed vessel which is separated into two sections by a thin plastic membrane. The two sections formed by the dividing membrane are termed a charge section and a permeate section. The alkylate, which consists almost exclusively of branched chain paraffins, is charged to the charge zone and a portion of the alkylate is permeated through the membrane. The paraffinic hydrocarbons which have a lesser degree of branching, i.e. those having fewer methyl side chains permeate the membrane more rapidly than do the branched chain paraffinic hydrocarbons having a greater number of methyl substituents. Fortuitously the paraffinic hydrocarbons in alkylate which have fewer methyl side chains also have a lower octane number than the paraffins having a greater number of methyl side chains. Consequently the permeated portion of alkylate will have a lower octane number than the charge and the non-permeated portion will have a higher octane number than the charge. The fraction of the charge which is permeated through the membrane may be between 10% and 90% thereof, for example about 50% of the charge may be permeated. The permeation process may be carried out in a batch-type operation wherein the charge is introduced into the charge section and permeated without adding additional charge thereto until the desired fraction of the charge has been permeated. When the charge is a fraction of alkylate (substantially all of the hydrocarbons having the same number of carbon atoms per molecule) the first portion of permeate will have the lowest octane number and successive incremental portions of the permeate will have progressively higher octane numbers. Or, the process may be operated in a continuous fashion by continuously introducing alkylate into the charge section while continuously withdrawing the permeated portion from the permeate section and the non-permeated portion from a point in the charge section which is remote from the point of introduction of the charged alkylate.

A wide variety of operating conditions may be employed in the permeating process. To achieve high rates of permeation through the membrane it is desirable to employ as high a temperature as is possible since the rate of permeation increases with increasing temperature. A temperature of from 100 to 300° F. may conveniently be used. The alkylate in the charge zone should be maintained in the liquid state. Because at least a portion of the alkylate charge may boil at the operating temperatures used, the charge zone should be operated at a super-atmospheric pressure sufficient to maintain the charge in the liquid state. Pressures of from 5 to 50 or even 100 p.s.i.g. may be used. The permeate zone should be operated at a sub-atmospheric pressure such that as the hydrocarbons are permeated through the membrane they are immediately vaporized from the permeate side of the membrane into the permeate zone and then rapidly removed from the permeate zone. Absolute pressures in the permeate zone of from 10 to 400 mm. Hg may be used. The plastic membrane used should be as thin as possible because the permeation rate increases as the thickness of the membrane is diminished. It may be between 0.1 and 5 mils or thereabouts, preferably less than one mil in thickness. The plastic membrane may be composed of a cellulosic material such as a cellulose ester or a cellulose ether. Cellulose acetate-butyrate (having an acetyl content of 5–15% by weight and a butyryl content of 35–50% by weight) ethyl cellulose (having an ethoxyl content of about 40–50% by weight) and films which are formed by casting from a solution containing cellulose esters and/or ethers such as cellulose acetate-butyrate and ethyl cellulose are very satisfactory, although of course membranes composed of other plastic materials may be used provided they allow the less highly branched paraffins to permeate more rapidly than the more highly branched paraffins. It should be understood however that membranes composed of different materials will have different permeation rates and also may exhibit a different selectivity for permeating the less highly branched in preference to the more highly branched paraffins and therefore achieve different amounts of octane number improvement.

In the embodiment of the permeation process illustrated herein, the process consists of five permeation stages (which are represented herein as five permeation vessels), each stage being operated at a temperature of about 230° F. with a pressure in the charge zone of about 1 p.s.i.g. and an absolute pressure in the permeate zone of about 30 mm. Hg. Thus the charge is maintained in the liquid state and the permeated hydrocarbons are recovered from the permeate zone in the vapor state. The membrane used is one mil in thickness and is a film prepared by casting from a solution of ethyl acetate, ethylene dichloride, and cyclohexanone containing ethyl cellulose (having an ethoxyl content of 45 weight percent) and cellulose acetate-butyrate (having an acetyl content of 6% and a butyryl content of 41% by weight) in a weight ratio of 5 parts of the former per 3 parts of the latter. Approximately one-half of the charge to each of the stages is permeated through the membrane and one-half of the charge is recovered as the nonpermeated portion.

The octane fraction, in the amount of about 5200 bbl./day, from the alkylation process is passed by way of line 49 into the charge zone 50 of permeation vessel 51 which constitutes the first permeation stage. Permeation vessel 51 is divided into a charge zone 50 and a permeate zone 52 by plastic membrane 53. While the first stage is illustrated herein as consisting of one permeation vessel, obviously a number of separate permeation vessels may be used. A portion of the octane fraction charged is permeated through the membrane at the rate of approximately 30 gallons of permeate/hour/1000 sq. ft. of membrane surface. This permeated portion has an F–1 octane number of about 92.2. It is removed from permeate section 52 and passed by way of line 54 into the charge zone of the second permeation stage i.e. into charge zone 56 of permeation vessel 57. Approximately one-half of the charge introduced into charge zone 56 is permeated through the membrane, the non-permeated portion having an F–1 octane number of about 94.4 and the permeated portion having an F–1 octane number of about 90.1. The non-permeated portion is recycled by way of line 58 into line 49 whereby it is recycled as a part of the charge to the first stage of the permeation process. The permeated portion is removed from permeate zone 59 and passed by way of line 61 as charge to the third permeation stage i.e. into charge zone 62. In this third permeation stage the plastic membrane 63 separates the charge zone 62 from the permeate zone 64. The non-permeated portion, which has an F–1 octane number of 92.9, is recycled by way of line 66 into line 54 whereby it is recycled as a portion of the charge to the preceding (second) permeation stage. The permeated portion is removed from permeate zone 64 by way of line 67 and passed to storage means not shown. This permeate fraction, which in the continuous process described will amount to approximately 2600 bbl./day, has an F–1 octane number of about 89.3. It may be blended with the stored fraction of alkylate boiling below 205° F. and with the stored fraction boiling above 260° F. to form a balanced alkylate which can be used for blending with a leaded gasoline, the alkylate fraction

responding excellently to the tetraethyl lead which is added.

The non-permeated portion from the first permeation stage (permeation apparatus **51**) is removed from charge zone **50** and passed by way of line **68** into charge zone **69** of permeation apparatus **71** (which is the fourth permeation stage and which operates on the non-permeated portions of the fraction of original alkylate charged). The permeation apparatus **71** is divided into charge zone **69** and permeate zone **72** by membrane **73**. Approximately one-half of the charge is permeated through the membrane, the permeated portion having an F–1 octane number of about 93.7 and the non-permeated portion having an F–1 octane number of about 96.9. The permeated portion is removed from permeate zone **72** and passed by way of line **74** into line **58** by which it is recycled as a portion of the charge to the first permeation stage. The non-permeated portion is removed from permeation vessel **71** and passed by way of line **76** into the charge zone **77** of permeation vessel **78** (which is the fifth permeation stage and which operates on the non-permeated portion of the original alkylate charged to the permeation plant). In permeation vessel **78** plastic membrane **79** separates the charge zone **77** from the permeate zone **81**. The permeated portion is removed from permeate zone **81** and passed by way of line **82** into line **68** by which it is recycled as a part of the charge to the preceding permeation stage. This permeated portion has an F–1 octane number of about 96.2. The non-permeated portion, which in the continuous operation described herein amounts to about 2600 bbl./day, is removed from permeation vessel **78** and passed by way of line **83** to storage means not shown. This non-permeated portion has an F–1 octane number of about 97.5. Because of its very high octane number it is an excellent stock for blending to produce a high octane number non-leaded premium gasoline.

A number of examples were carried out which demonstrate methods of carrying out the process of this invention. In the first example an alkylate (380° F. E.P.) having an F–1 octane number of 92.6 was produced by the sulfuric acid catalytic alkylation of isobutane with butenes (using the butane-butenes streams from catalytic cracking plus additional high purity isobutane) at the rate of 10,000 bbl. of alkylate/day. This rate of production was higher than the designed capacity of the alkylation unit by about 2500 bbl./day. A portion of the depentanized alkylate boiling between about 120° and 260° F. was then charged to a permeation apparatus. The amount charged to the apparatus was about 13 liters. The permeation apparatus was operated in a batch fashion and three permeation stages were employed.

The permeation apparatus used consisted of a sealed chamber in which was suspended a box like membrane holder. The sealed chamber was the charge zone into which the alkylate was introduced. The membrane holder had five open faces which were tightly covered (leakproof) with a membrane consisting of ethyl cellulose having an ethoxyl content of about 45% by weight and which was one mil in thickness. The total amount of membrane surface effective for permeation was 22 sq. in. The chamber was maintained at atmospheric pressure and at a temperature of 212° F. The membrane holder, into which hydrocarbons could not pass from the charge chamber except by permeation through the membrane, constituted the permeate zone. A sub-atmospheric pressure of 30 mm. Hg was maintained within the membrane holder by a vacuum pump. The permeation apparatus was operated until approximately half of the alkylate charged was permeated through the membrane and recovered as vapors of permeated hydrocarbons withdrawn from the membrane holder. The unpermeated portion of the hydrocarbons was then segregated. Thereafter the one-half of the alkylate which was permeated in the first stage was permeated through the membrane holder which constituted a second permeation stage and the permeated hydrocarbons were separately recovered. These permeated hydrocarbons which were the remaining one-fourth of the alkylate charged to the permeation apparatus were then permeated in what constituted the third permeation stage and approximately 50% thereof was removed as a permeated portion. The F–1 octane numbers of the permeated and the non-permeated portions from each individual stage were determined. The F–1 octane numbers of these portions are shown in the following table:

Table I

Portion of the Alkylate	Octane Number
Alkylate charged to first stage	94.0
Permeate from first stage (and charged to second stage)	92.9
Non-permeated portion from first stage	95.3
Permeate from second stage (and charged to third stage)	91.8
Non-permeated portion from second stage	94.0
Permeate from third stage	90.9
Non-permeated portion from third stage	92.7

From the above table it is apparent that the permeated portion has a lower octane number than the charge and the non-permeated portion has a higher octane number than the charge to the permeation stage. By this batchwise operation it is possible to segregate permeate fractions having incrementally different octane numbers. Thus the permeate from the third stage could be discarded and the remaining portions of permeated and non-permeated alkylate could be blended to produce an alkylate having a higher octane number than the original alkylate charged to the first stage, i.e. 94.0, and which blend would constitute about 90% of the original alkylate.

In another example of the manner in which the permeation of the alkylate may be carried out, a portion of the depentanized alkylate produced in the manner previously described was fractionated in a three foot hypercal column at a reflux ratio of 10:1 and four fractions were collected as follows: (1) a C_6 fraction boiling between 122° and 165° F, (2) a C_7 fraction boiling between 165° and 205° F, (3) a C_8 fraction boiling between 205° and 260° F, and (4) a C_9 and higher fraction boiling between 260° and 380° F. Each of the individual fractions of alkylate was then employed separately as the charge to the permeation process using the previously described permeation apparatus. The pressure in the charge zone and the temperature during the permeation of each fraction were as follows: fraction (1), 30 p.s.i.g. and 175° F.; fraction (2), 0 p.s.i.g. and 185° F.; fraction (3), 0 p.s.i.g. and 230° F.; and fraction (4), 0 p.s.i.g. and 240° F. An absolute pressure in the permeate zone of 30 mm. Hg was used in each case. The membrane employed was approximately one mil in thickness. It was prepared by casting the film from a solution of 5 grams of ethyl cellulose (having an ethoxyl content of about 45% by weight) and 3 grams of cellulose acetate-butyrate (having an acetyl content of 6% and a butyryl content of 41% by weight) in a solvent consisting of 41 grams ethyl acetate, 41 grams ethylene dichloride, and 10 grams cyclohexanone. The permeation procedure consisted of permeating approximately 20% of the alkylate fraction charged, segregating this permeated portion, separately recovering the next 20% of the alkylate permeating the membrane, then separately recovering the third 20% portion of the alkylate permeated, and then removing a non-permeated portion which approximated

40% of the original fraction of the alkylate charged to the permeation apparatus. The F–1 octane number of each of the three permeated portions and the non-permeated portions was then determined. This procedure was used for the separate permeation of each of the four fractions of alkylate. The octane numbers of the permeated and non-permeated portions of the various fractions of alkylate are shown in Table II which follows:

Table II

Portion of Alkylate	Octane Numbers, F–1			
	C_6	C_7	C_8	C_9
Total	94.2	89.6	94.0	76.2
1st 20% Permeated	91.5	86.1	91.4	75.7
2nd 20% Permeated	93.4	87.8	92.6	79.4
3rd 20% Permeated	92.3	88.3	93.7	78.0
40% Non-permeated	95.9	92.9	96.1	76.1

It is evident from the above table that fractions of alkylate which consist of hydrocarbons substantially all of which have the same number of carbon atoms in their molecule can be segregated by permeation into portions having differing octane numbers. The first portion permeated will generally have the lowest octane number and the portion last to be permeated will generally have the highest octane number. By combining various permeated and non-permeated portions of the various boiling range fractions, a very high octane number alkylate can be produced which is highly desirable for blending with non-leaded premium gasolines, and a low octane number alkylate satisfactory for blending into leaded gasolines can be made.

While the invention has been described in detail with reference to specific operating examples, other modifications will be apparent therefrom to those skilled in the art.

What is claimed is:

1. A process which comprises contacting under permeation conditions an isobutane-butene alkylate boiling in the gasoline boiling range which has an F–1 octane number of less than 96 with one side of a permeable plastic membrane and thereby permeating a portion of the alkylate through the membrane, separately recovering a portion of the alkylate which permeates the membrane and a portion of the alkylate which has not permeated the membrane, the non-permeated portion having a higher octane number than the permeated portion.

2. A process for producing segregated portions of isobutane-butene alkylate having differing octane numbers which process comprises operating an isobutane-butene alkylation process under conditions of high production rates whereby an alkylate boiling in the gasoline boiling range which has an F–1 octane number of less than 96 is produced; contacting a fraction of the alkylate under permeation conditions with one side of a permeable plastic membrane and permeating a portion of the alkylate through the membrane; separately removing from opposite sides of the membrane a portion of the alkylate which permeated the membrane and a portion of the alkylate which has not permeated the membrane, the permeated portion having a lower octane number than that of the alkylate initially contacting said membrane and the non-permeated portion having a higher octane number than that of the alkylate initially contacting the membrane; which process is characterized by the production of segregated portions of alkylate, a first segregated portion having at least as high an octane number as does the similar boiling range alkylate produced when the alkylation process is operated at a lower production rate and a second segregated portion of alkylate having a lower octane number than said first segregated portion, the combined volume of the segregated portions produced in the combination process of alkylation and permeation exceeding the volume of equivalent boiling range alkylate produced at the lower alkylate production rate.

3. The process of claim 2 wherein the first segregated portion has an octane number at least as high as does the corresponding boiling range alkylate which is produced at the lower alkylate production rate and the volume of the first segregated portion is at least as large as the volume of the equivalent boiling range alkylate produced at the lower alkylate production rate.

4. The process of claim 2 wherein the alkylate contacted with the membrane under permeation conditions contains hydrocarbons substantially all of which have between 6 and 8 carbon atoms, inclusive, in their molecules.

5. The process of claim 2 wherein the membrane is a plastic cellulosic material.

6. The process of claim 2 wherein a number of permeation stages are used and wherein permeated and non-permeated portions of alkylate which have approximately the same octane number are combined and used as the feed in the later permeation stages.

7. The process of claim 2 wherein the alkylate which is contacted with the membrane under permeation conditions consists of hydrocarbons substantially all of which have the same number of carbon atoms in their molecule.

8. The process of claim 7 wherein the fraction of alkylate which is contacted with the membrane consists of hydrocarbons substantially all of which have 8 carbon atoms in their molecule.

9. A process for producing segregated portions of isobutane-butene alkylate having differing octane numbers which process comprises operating an isobutane-butene alkylation process under conditions of high production whereby an alkylate boiling in the gasoline boiling range which has an F–1 octane number of less than 96 is produced, fractionating said alkylate and recovering an octane fraction thereof consisting of hydrocarbons substantially all of which have 8 carbon atoms in their molecule, contacting the octane fraction under permeation conditions in five separate permeation stages with one side of a permeable plastic membrane and permeating about one-half of the charged octane fraction through said membrane in each stage and recovering permeated portions from each permeation stage which have a lower octane number than the feed to the particular permeation stage and also recovering non-permeated portions from each permeation stage which have a higher octane number than the feed to the particular permeation stage, wherein the permeation stages are carried out in the following manner: (1) permeating the octane fraction in a first stage and recovering a permeated portion and a non-permeated portion therefrom; (2) permeating the permeated portion from (1) in a second stage and recovering a permeated and a non-permeated portion therefrom, the latter non-permeated portion being recycled as a part of the charge to the first permeation stage of (1); (3) permeating the permeated portion from the second permeation stage in a third permeation stage and recovering a permeated and a non-permeated portion, the permeated portion being recycled as a part of the charge to the second permeation stage of (2), and the permeated portion being a segregated portion of the octane fraction of alkylate which has a substantially lower octane number than the charge to the first permeation stage of (1); (4) permeating the non-permeated portion from (1) in a fourth permeation stage and recovering a permeated and a non-permeate portion therefrom, the permeated portion being recycled as a part of the charge to the first permeation stage of (1); (5) permeating the non-permeated portion

from (4) in a fifth permeation stage and recovering therefrom a permeated and a non-permeated portion, the permeated portion being recycled to the fourth permeation stage of (4) as a part of the charge stock thereto, and the non-permeated portion being a segregated portion of the octane fraction of alkylate which has an octane number substantially higher than the charge to the first permeation stage of (1).

10. The process of claim 1 wherein a plurality of permeation stages are used and wherein non-permeated portions of selected stages are blended to produce an alkylate

having a higher octane number than the original alkylate charged to the first stage.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,923,751 February 2, 1960

Robert C. Binning et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, lines 4 and 5, strike out "and a lower octane number alkylate blending stock for a leaded gasoline"; column 3, line 16, for "50°% read -- 50% --; column 4, line 11, after "alkylate" insert -- produced --.

Signed and sealed this 16th day of August 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents