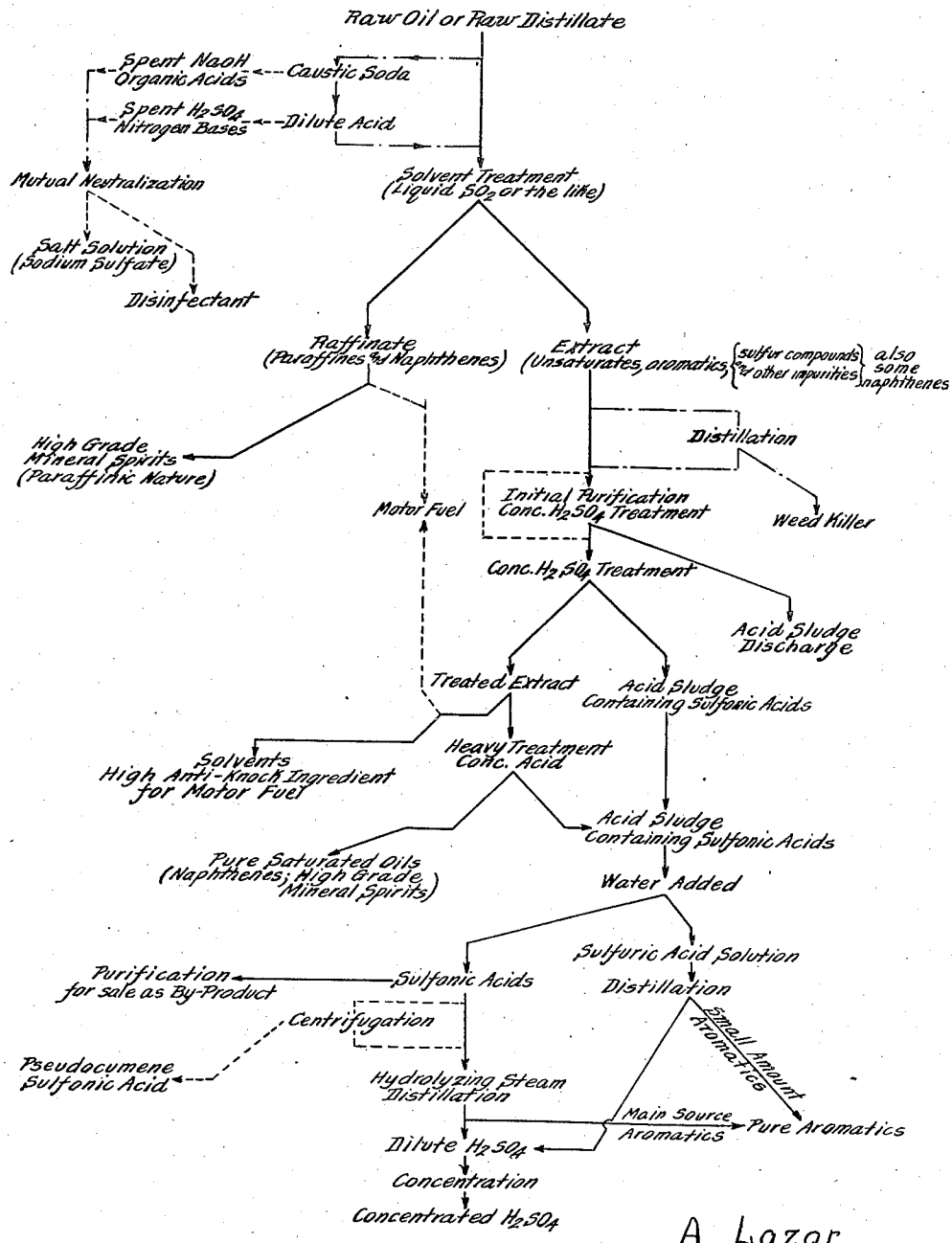
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TREATMENT OF LIGHT PETROLEUM DISTILLATES

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TREATMENT OF LIGHT PETROLEUM DISTILLATES

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3 Claims. (Cl. 196—37)

This invention relates to the recovery of by-products from the refining of petroleum which have properties making them extremely valuable for uses hereinafter described.

The principal object of this invention is to treat light petroleum distillates in such a manner that valuable by-products can be recovered in additional to normal petroleum products, thus making petroleum an entirely new source for the manufacture and recovery of a number of organic compounds.

Another object is to so treat petroleum distillates with selective solvents of various characteristics that a separation of component hydrocarbons in a distillate, (whether derived from a cracking process or not) can be effected with minimum losses.

Another object is to so treat and separate impurities from a petroleum distillate of definite boiling range that a motor fuel of low sulphur content and high anti-knock value is obtained.

Another object is to provide an improved process for recovering sulphonic acids from acid sludges, whether such sludges are derived from the herein described treating steps or from other treating processes.

Another object is to provide an improved process for isolating groups of aromatic hydrocarbons, or sulphonic acids derived therefrom.

Another object is to provide for the separation of a petroleum distillate so that substantially pure saturated hydrocarbons (paraffines and naphthenes) and pure aromatic hydrocarbons can be recovered.

Further objects will become apparent as the invention becomes more fully disclosed hereinafter.

Certain mineral oil distillates, such as those produced from California crudes, contain appreciable quantities of non-hydrocarbon impurities. In refining such distillates, particularly those comprising the normal boiling point range of gasoline, petroleum spirits, and kerosene, it is found that the presence of these non-hydrocarbons interferes to a certain extent with the usual treating methods applied on said distillates.

Chemically speaking these non-hydrocarbons consist of organic acids, such as naphthenic acids, phenols, and the like, sulphur compounds of acidic nature like mercaptans and thiophenols, other sulphur compounds, and nitrogen bases.

Since the organic acids and nitrogen bases are also attacked by sulphuric acid, which is the treating agent generally used for refining petroleum products, these compounds will consume a certain amount of the treating agent before the acid could have effected any action upon the undesirable hydrocarbons to be removed.

In addition it has often been found that distillates containing such impurities cause difficulties in subsequent processing. For example, if the distillates containing said non-hydrocarbons are treated with liquid sulphur-dioxide or other solvents according to the well-known Edeleanu process, it has been found that salts of nitrogen bases and resinous deposits are formed in the treating equipment. The salt crusts represent reaction products of sulphurous and sulphuric acid with nitrogen bases mixed with resinous material, which has been formed by polymerization of the phenols. Such deposits often are quite troublesome and can be the cause of the emulsions in the SO_2 or other treating process, or, when accumulated in large quantities can interfere with heat transfer in the exchangers and evaporators of the treating unit, or when accumulated in lines and pumps, can interfere with the through-put of the plant.

It is therefore an object of this invention to submit mineral oil distillates composed of a plurality of fractions to a number of treating steps in the proper sequence and thereby to split the fractions up in such a manner that valuable organic products are obtained which heretofore could not be obtained from mineral oils in any appreciable quantity.

Broadly speaking, the invention involves the treatment of a petroleum distillate (cracked or uncracked) with specific reagents in such sequence of steps that such reagents, which cannot under usual conditions exercise their function of selectivity, are enabled to be applied with complete selectivity.

This will be better understood if, for instance, the reactions of sulphuric acid with hydrocarbons is considered when a certain concentration of sulphuric acid is ineffective to dissolve, or react with, unsaturated and aromatic hydrocarbons, while other concentrations may be used to

effectively separate unsaturated and aromatic hydrocarbons from saturated hydrocarbons and from each other. In consequence, this selective action of sulphuric acid and of solvents such as liquid sulphur dioxide, benzol-sulphur dioxide, phenol, furfural, nitrobenzene, dichlorethylether, a mixture of propane and cresylic acid, and like solvents, or a combination of any of these solvents with each other or with liquid SO_2, for hydrocarbons and impurities in hydrocarbons, is so utilized herein that a refined petroleum distillate of improved qualities is obtained while pure hydrocarbons of definite characteristics and pure by-products are made available for varied uses in the arts.

More specifically, the invention is applicable to the treatment of a petroleum distillate of gasoline boiling range (whether cracked or not) to assure a highly refined motor fuel of low sulphur content and high anti-knock value.

Referring to the diagrammatic flow sheet of the drawing, a light raw distillate obtained from California crude petroleum, such as the gasoline, kerosene, or petroleum spirits fractions thereof is the original stock to be treated.

Such raw distillate may be, merely by way of illustration and not of limitation, a selected cut from a crude oil within the boiling range of a specification gasoline desired as a final product, or of any desired cut within such boiling range suitable for treatment to provide a finished cut available for blending to yield a specification gasoline.

If it be assumed that such raw distillate is from a California crude oil, the same may contain fractions of the paraffine, naphthene, olefine, diolefine, and aromatic hydrocarbons together with organic acids, nitrogenous bases, and various forms of sulphur compounds, and may have the following physical characteristics:

Gravity	A. P. I.	50.7
Initial boiling point	°F.	155
End point	°F.	470
Sulphur	per cent	0.12
Nitrogen	do	0.08
Aniline point	°F.	127

As before stated, it must be understood that steps of the process are particularly applicable to any selected overhead distillate from petroleum which ranges in volatility from the light gasoline cuts right through the various boiling ranges of petroleum spirits, kerosene, gas oil, spindle oil, and spray oils down to heavy viscous lubricating oils and the treatment of a gasoline fraction is described as being illustrative of a fuller range of operations which will include the recovery of a very superior motor fuel as well as other included purified products.

The raw distillate, depending on its boiling range, is subjected to a series of steps for the removal of impurities and recovery of finished products.

Preferably the raw distillate is first treated with a solution of alkali, such as caustic soda solution of a concentration of about from 15° Bé. to 30° Bé. which serves with proper agitation to combine with the organic acids in the distillate and to break up the combination between the organic acids and nitrogen bases in the distillate while polymerizing certain unstable resinous compounds therein and the thus reacted caustic with absorbed material is removed from the distillate.

The distillate is then agitated with sufficient quantity of dilute sulphuric acid, which is of a concentration less than 90% acid and preferably of about 50% to 60% acid, which serves to react with nitrogenous bases in the distillate and the spent acid is then withdrawn to leave the distillate free from organic acids and nitrogenous bases.

The spent acid may be separated by gravity settling or the settling can be accelerated by centrifugal action. Any of the well known methods can be used for removing the spent acid in order to prepare the distillates for solvent refining. In commercial operation certain stocks may require the neutralization of the last traces of sulphuric acid with caustic soda or other alkalies before solvent refining.

The thus withdrawn caustic solution may be acidified with fresh acid which serves to throw the absorbed organic acids out of solution for recovery as such, while the spent dilute acid may be causticized with fresh caustic soda solution to throw out the nitrogenous bases for recovery as such.

If separate recovery of the organic acids and nitrogenous bases is not desired, the thus spent caustic solution and spent dilute acid may be mixed to effect mutual neutralization which yields two layers of liquids, the upper layer comprising an oily mixture of the abstracted organic acids and nitrogenous bases very valuable as a disinfectant oil, while the lower water layer represents substantially a solution of sodium sulphate.

It must be understood that while the above described removal of organic acids and nitrogenous bases is preferably done as the first step of the process so that the remaining steps of the process may be more clearly illustrated and facilitated, such removal is not essential as a first step but may be performed as a later step as will be later more fully described.

The thus purified distillate is then subjected to treatment with a solvent such as liquid sulphur dioxide, or any of the other described and well known selective solvents, in a well known manner to separate the distillate into two portions or layers.

The upper layer is known as the raffinate composed of the paraffine and naphthene series of hydrocarbons and the lower layer (termed the extract) consists mainly of the olefine, diolefine, and aromatic series of hydrocarbons together with a certain percentage of saturated hydrocarbons of the paraffine and naphthene series and certain sulphur compounds.

The raffinate comprising a purified motor fuel of definite boiling range but of relatively low anti-knock value may be then used as such after the usual removal, or neutralization, of contained SO_2, but the invention comprehends its blending with products later derived from the extract to form a finished motor fuel of satisfactory ignition and detonation characteristics.

Depending on required uses, the extract after removal of SO_2 therefrom may either be used as is or first subjected to treatments in certain steps to derive certain products or to leave a fraction of high anti-knock value to be added to said raffinate.

The extract of gasoline boiling range is first treated with sulphuric acid of a concentration from 90% H_2SO_4 up to a fuming acid containing 20% SO_3, depending on the action desired on the extract, and all treatments of the distillate or extract with the reagents described and used

herein are preferably conducted for the fullest contact efficiency as for example in accordance with the method disclosed in a co-pending application of Edwards and Stark, Serial No. 532,000 filed April 22, 1931, the range of temperatures used therewith being regulated from below 0° F. up as high as 80° F., depending on the solvent or sulphonating effect required from the sulphuric acid.

If organic acids and nitrogenous bases have already been removed from the extract of definite boiling range, the extract will be contacted with sulphuric acid of 90% concentration, or greater, in such quantity and at such temperature as to leave an extract composed mainly of hydrocarbons of a cyclic structure, such as aromatics and hydroaromatics.

The acid treated extract, as such, or fractions of the same have unique properties which make them suitable as a varnish and lacquer diluent in place of the commonly used coal tar diluents. It shows a high compatibility for nitro-cellulose and synthetic resin solutions which are used in the manufacture of lacquers and enamels. On account of its high solvency power for resins, gums, rubber and the like, it can also be used in place of the high priced turpentine. Furthermore, due to its aromatic nature it has a higher affinity for vapors of a low boiling range than ordinary petroleum distillates and therefore can advantageously be used as an absorption oil in vapor recovery plants of all kinds.

In contradistinction to SO_2 extracts removed from distillates such as cracked distillates or pressure distillates, an extract derived as described from straight run distillates shows entirely different behavior during treatment with sulphuric acid. Treating losses are relatively insignificant with straight run extracts in comparison to pressure distillate extracts, and the products obtained by the same degree of treatment are much superior in quality to those obtained from pressure distillate extracts.

When a pressure distillate is treated with strong sulphuric acid (95% or more) for the purpose of removing sulphur compounds the acid chemically attacks the unsaturated hydrocarbons present in the cracked distillate. A large percentage of the sulphuric acid is therefore used up in this reaction and not for the removal of sulphur compounds. This involves a well known conversion of valuable hydrocarbons, as can be seen from the following laboratory data on acid treatment of a typical California pressure distillate. This hydrocarbon conversion involves polymerization of lighter hydrocarbons to heavier hydrocarbons and to remove these undesirable polymers it is usually necessary to follow acid treatment of the pressure distillate with neutralization and redistillation.

When an acid treatment of a fraction from an SO_2 extract obtained from a California oil is compared with acid treatment of a California pressure distillate derived from the same stock, there is a marked difference in the chemical action and the properties on the finished product resulting therefrom. Moderate quantities of sulphuric acid which would be used for desulphurization of a fraction from an SO_2 extract does not appreciably attack the hydrocarbons present in the extract fraction.

The following tabulation shows that the acid removes the sulphur compounds almost completely without attacking desirable hydrocarbons of high anti-knock qualities.

	Pressure distillate	SO_2 extract
Acid rate, lbs./bbl. 98% acid	30	30
Treating loss:		
By acid absorption (sludge)	4.7	3.5
By polymerization	5.0	None
Percent by volume, total	9.7	3.5

Properties

	As is	After acid treat	After redistilling	As is	After acid treat	After redistilling
Gravity A. P. I.	52.7	49.3	52.0	33.5	34.5	No redistillation necessary.
Sulphur, percent cwt.	0.36	0.35	0.15	0.68	0.10	
Antiknock value	−15	−40	−15	+14	+18	
Aniline point, °F.	115	125	115	46	52	
Distilling range:						
I. B. P.	114	136	120	280	285	
5%	150	186	154	316	315	
25%	230	268	235	345	347	
50%	306	356	300	370	372	
75%	367	411	365	395	393	
95%	420	500	400	420	423	
E. P.	444	530	440	434	435	

The antiknock values shown above are based on the Secondary standard of the Ethyl Gasoline Corporation, of July, 1930. The plus values signify the tenths of cc.'s of lead tetraethyl required per gallon to make the standard equal the sample. The negative values signify the tenths of cc.'s required per gallon for the sample to equal the Secondary standard.

With the above distinctions in mind, it will be seen that the extract thus treated with sulphuric acid up to 30 pounds per barrel or more, after the usual neutralization with alkali and washing with water is an oil of low sulphur content having a sweet odor and high anti-knock value.

Furthermore, when of proper boiling range, it is especially valuable to be added in the right proportions to a raffinate or to straight run gasoline, or pressure distillate fractions, to form the heavy ends of the distilling range, the light ends being the aforesaid raffinate, gasoline, or pressure distillate fractions, for the purpose of obtaining a combination fuel which has high B. t. u. values combined with good anti-knock properties and a satisfactory volatility.

The importance of this anti-knock function will be more appreciated when it is considered that the higher boiling point fractions in an ordinary gasoline have higher aniline points than the lower boiling point fractions, and that the anti-knock value of its higher boiling fractions is lower than that of the lower boiling fractions.

The reverse of this occurs with fractions derived from the treated extract inasmuch as with increasing boiling point the aniline point decreases and the anti-knock value increases since the miscibility of hydrocarbons with aniline is directly proportional to the anti-knock value of the hydrocarbons, and thus a very important fact is observed, i. e., that both constants for SO_2 extract show just the reverse of those found for ordinary mineral oil fractions. The aniline point of an oil is defined as the critical temperature of solubility of equal volumes of oil and C. P. aniline. By substituting for such higher boiling fractions of gasoline, the treated SO_2 extract as described, or fractions thereof, due to their low aniline points, combine the highest possible anti-knock value with the desired balance in the distillation curve and thus makes an ideal fuel for internal combustion engines.

In addition to the many functions already de-

scribed the practically complete removal of active sulphur compounds is desired during the acid treatment of sulphur dioxide or other solvent refined extracts. This is accomplished by the use of relatively low sulphuric acid rates normally below ten (10) pounds per barrel and not over 30 pounds per barrel on extracts of high sulphur content. Solvents manufactured in this manner have excellent stability and are particularly adapted for use by the paint, varnish, and lacquer industry where stability against light and weathering is of primary importance and there is no tendency for corrosion due to the elimination of active sulphur compounds.

In order to obtain other products, if it is not desired to use the treated extract as above set forth, or as raw material for solvents, the whole, or part, of the extract may be further treated with up to 100% or more of its volume with concentrated sulphuric acid (varying from 90% acid up to 20% fuming acid) under such conditions of temperature that all the aromatics in the extract are sulphonated and the remainder of the extract will consist of more saturated hydrocarbons (mainly naphthenes and hydroaromatics) which, when neutralized, are especially valuable as special petroleum spirits, thinners, Stoddard solvent, or similar solvents in which extremely low sulphur content, or complete freedom from both active and less active sulphur compounds is required. Due to the naphthenic nature of this remainder it still retains ignition characteristics similar to average motor fuels and therefore can be used either straight or in blends with such fuels.

If the extract has been treated in the first place with but a small amount of concentrated sulphuric acid, for the production of solvents or motor fuel not more than about 10 pounds of acid to the barrel, merely for partial sulphur reduction, the acid sludge therefrom may be discarded, but if it has been treated with acid up to as high as 30 pounds of acid per barrel of extract for further sulphur reduction, the acid sludge may contain a similar concentration of sulphonic acids as is contained in the acid sludge resulting from treatment of the extract with 100% of its volume of concentrated sulphuric acid, and the succeeding steps are applicable thereto.

Depending on the sulphur content of the extract the sulphuric acid treatment may be carried out in one or more steps but preferably in at least two stages for the subsequent recovery of sulphonic acids, naphthenes, and pure aromatics. The initial purification with strong acid is particularly necessary if the sulphur content of the extract is high, and may require up to 30 pounds of sulphuric acid per barrel for desulphurization purposes. The degree of sulphuric acid treatment in one or more stages will depend on the sulphur content of the extract and quality and purification of solvents, motor fuel, sulphonic acids, saturated oils, and other by-products desired. In the acid treatment with two or more stages the initial treatment removes the more easily attacked substances such as non-hydrocarbons, di-olefines, etc. and the subsequent treatments will start to actively sulphonate aromatics.

The acid sludges from the later treats may be contaminated with a small quantity of non-hydrocarbons and sulphonic acid recovery is somewhat more difficult than when these non-hydrocarbons are completely eliminated and only the acid sludges from the concentrated heavy acid treatment of up to 100% by volume or more of sulphuric acid is used.

To definitely illustrate, we can treat a high sulphur extract with 30 pounds per barrel of strong acid in six treats of five pounds per barrel each. The first one or two treats will yield sludges contaminated with the reaction products of non-hydrocarbons which may be discarded in order to avoid contamination of sludges later derived. The remaining treats yield sludges containing substantial quantities of sulphonic acids as the sulphuric acid treatment starts to attack the aromatic hydrocarbons to an appreciable extent. These sludges may be a suitable source of slightly contaminated sulphonic acids, although more purified by-products are obtained particularly pure sulphonic acids from acid sludges formed in later treatment.

With acid sludges containing relatively high percentages of sulphonic acids, as described, novel steps are next used on said sludges for the recovery of sulphonic acids and pure aromatics, and such steps are applicable to any acid sludges containing sulphonated compounds whether derived from the before described treatment or derived from any other sulphuric acid treatment of other hydrocarbons and shows great improvement over the usual and conventional methods of treating acid sludges.

In the usual method, the acid sludge consisting of sulphonic acids and sulphuric acid is neutralized with calcium hydroxide which converts all the acids present into calcium salts, such as calcium sulphate and calcium sulphonates, which mixture is washed with water to leach out the water soluble sulphonates and leave the water insoluble calcium sulphate, and the sulphonates are then concentrated. This procedure is very tedious and costly as the sulphuric acid is converted into calcium sulphate, a product of low value. The neutralization costs are greater and the sulphuric acid cannot be recovered for future use. The calcium sulphonates must also be acidified to obtain free sulphonic acids.

On the other hand, the acid sludges derived from the above described treatments may be mixed with a volume of water amounting to about one-third (⅓) of the sulphuric acid used on the extract which, after agitation and settling, provides two layers of liquids due to the salting out effect of the free mineral acid on the free sulphonic acids. As a result, the mineral acid content of the upper layer is greatly reduced and the lower layer retains a minimum of organic compounds.

In consequence the upper layer consists mainly of sulphonic acids and the lower layer consists mainly of sulphuric acid of a relatively low degree of concentration.

The lower layer may then be drawn off and distilled under such conditions of temperature and pressure that any traces of sulphonic acids contained therein will be split by heat to free the aromatic hydrocarbons which can be carried off as an overhead vapor and condensed to yield pure aromatics. The liquid remaining in the still consists of dilute sulphuric acid which may be concentrated and recovered in any well known manner for use and is especially adapted for such recovery because of its purity and freedom from nitrogen bases earlier removed from the distillate.

While small amounts of aromatics may be further recovered from the dilute sulphuric acid dur-

ing concentration, the sulphur compounds and other impurities contained in the acid sludge are apparently destroyed during distillation and concentration because the aromatics recovered during these steps are free of such impurities.

The upper sulphonic layer can be isolated for further purification, or treated by a hydrolizing steam distillation to drive off the aromatics as overhead which are condensed and may be mixed with the aromatics derived from the lower layer while the remainder of the upper layer consists of dilute sulphuric acid which can be concentrated for use as described for the remainder of the lower layer.

In the event that the upper, or sulphonic, layer is permitted to stand for some time without distillation, it has been noted that there is a tendency for the formation of crystals of pseudocumene sulphonic acid and such crystals may be readily separated from said sulphonic layer by a centrifuge prior to subjecting the remainder of the sulphonic layer to the hydrolizing steam distillation before described.

The aromatic hydrocarbons thus derived by the aforesaid treatments of the upper and lower layers are exceptionally pure and require only the usual neutralizing and washing treatments prior to use and such purity is due to the prior treatment of the distillate for the removal of organic acids which otherwise would contaminate the sulphonic layer and cause secondary reactions. It may readily be perceived, for instance, that if phenols were not thus removed they would be sulphonated along with the aromatics and then later reappear as contaminating substances in the resultant products.

At the same time it must be noted that while the described removal of organic acids and nitrogenous bases in the original raw distillate is preferably accomplished as an initial step of the process, such removal may be effected at any time prior to, or as far as the nitrogen bases are concerned, during the initial step of subsequent treatment with strong sulphuric acid.

The SO_2 extract may therefore be treated with caustic solution for the removal of organic acids at any time prior to treatment with concentrated sulphuric acid.

Likewise if the SO_2 extract is first treated with caustic soda solution and then treated with concentrated sulphuric acid in relatively small volume, as described, so as only to effect sulphur removal with low sulphonation of aromatics, the extract will then be free of nitrogenous bases because they will be removed by the concentrated acid and also be free of organic acids and thus will be in a condition suitable for use, or for sulphonation to yield pure aromatics.

It is apparent that by suitable variations of the treatments with concentrated sulphuric acid with regard to time of contact, temperature of contact, method of contact, quantity of acids, concentration of acid, the extract can be modified to yield products suitable for the uses enumerated and that such products may yield various types of aromatics.

For instance, if the extract is treated with acid in a plurality of steps including a first step with a small quantity of acid, the aromatics most readily attacked by acid can be extracted first and successive variations of treatment can be used to provide pure aromatics of desired characteristics. Such treatment by selective reactivity of sulphuric acid accomplishes partial separation without distillation.

Modifications and alternations of treatment of the raw distillate are provided in addition to those stated.

For instance, while the treatment of a raw gasoline distillate has been described to yield a finished motor fuel of high anti-knock value, if the raw distillate initially is of gasoline boiling range, or of any other overlapping boiling range, the SO_2 or other extract derived therefrom may be distilled to yield a light fraction within the gasoline boiling range and bottoms heavier than such range. Such bottoms can then be recovered as a dark liquid of high fluidity and penetrating power suitable for use for the destruction of plant life, or a so-called weed killer, as a fuel for certain types of Diesel engines, a cutback oil or solvent for asphalt, pitch, coke, heavy residua, or due to its penetrating power and wetting ability, as a flotation oil.

The light fraction may then be treated according to the described steps for the same uses as described.

It is thus clear by the steps enumerated that the treatment of a raw distillate may be so conducted that not only is the distillate recovered in a pure state, but that every step assures the recovery of products of value which heretofore in most cases have been useful in only a minor degree.

It is understood that in referring to the boiling or distillation range of any particular distillate that the limits of such distillation range are those included in the every day, or commercial sense, such for instance as are found in the U. S. Government or A. P. I. specifications.

It will be noted that, while certain of the described steps have been shown as batch operations for the sake of simplicity, many of the same may be carried on in well known continuous operations and therefore such descriptive operations impose no limitations beyond the scope of the appended claims.

Although the above inventions have been directed towards the processing of distillates and the recovery of valuable by-products therefrom, it should be understood that we also include the refinement of those light and heavy crudes containing substantial quantities of non-hydrocarbons heretofore defined. Certain California Crudes such as those originating from the Ventura, Southern California, Kettleman Hills and Belridge fields contain appreciable quantities of non-hydrocarbons and/or unsaturated and aromatic hydrocarbons which are desirable sources of by-products. Depending on the nature of the crude and the particular by-product recovery desired distillation may be first used to greater advantage in the later stages of processing and this mode of operation is also claimed, utilizing the inventions fully described for the preferred treatment of light distillates.

This application is a division of our co-pending application Serial No. 134,020, filed March 31, 1937. Application Serial Number 134,020 in turn is a division of application Serial Number 67,370, filed March 5, 1936.

We claim as our invention:

1. The process of preparing solvents which comprises: removing non-hydrocarbons like organic acids, sulphur compounds and nitrogen bases from a distillate of petroleum oil containing aromatics, treating the thus purified oil with a selective solvent to remove an extract therefrom containing mainly naphthenic, unsaturated and aromatic hydrocarbons, distilling such ex-

tract to recover a desired light fraction therefrom, and treating such light fraction with sulphuric acid of sufficient concentration and in an amount up to 100% by volume of the fraction to remove aromatics, sulphur compounds and unsaturates and leave the remaining oil of high naphthene content after the removal of acid sludge.

2. The process of preparing solvents which comprises: removing non-hydrocarbons like organic acids, sulphur compounds and nitrogen bases from a distillate of petroleum oil containing aromatics, treating the thus purified oil with liquid sulphur dioxide to remove an extract therefrom containing mainly naphthenic, unsaturated and aromatic hydrocarbons, distilling such extract to recover a desired light fraction therefrom, and treating such light fraction with sulphuric acid of sufficient concentration and in an amount up to 100% by volume of the fraction to remove aromatics, sulphur compounds and unsaturates and leave the remaining oil of high naphthene content after the removal of acid sludge.

3. The process of preparing solvents which comprises: removing non-hydrocarbons like organic acids, sulphur compounds and nitrogen bases from a distillate of petroleum oil containing aromatics, treating the thus purified oil with a selective solvent to remove an extract therefrom containing mainly naphthenic, unsaturated and aromatic hydrocarbons, and treating such extract with sulphuric acid of sufficient concentration and in an amount up to 100% by volume of the fraction to remove aromatics, sulphur compounds and unsaturates and leave the remaining oil of high naphthene content after the removal of acid sludge.

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