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PROCESS FOR REFINING HYDROCARBONS

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Fig. 1.

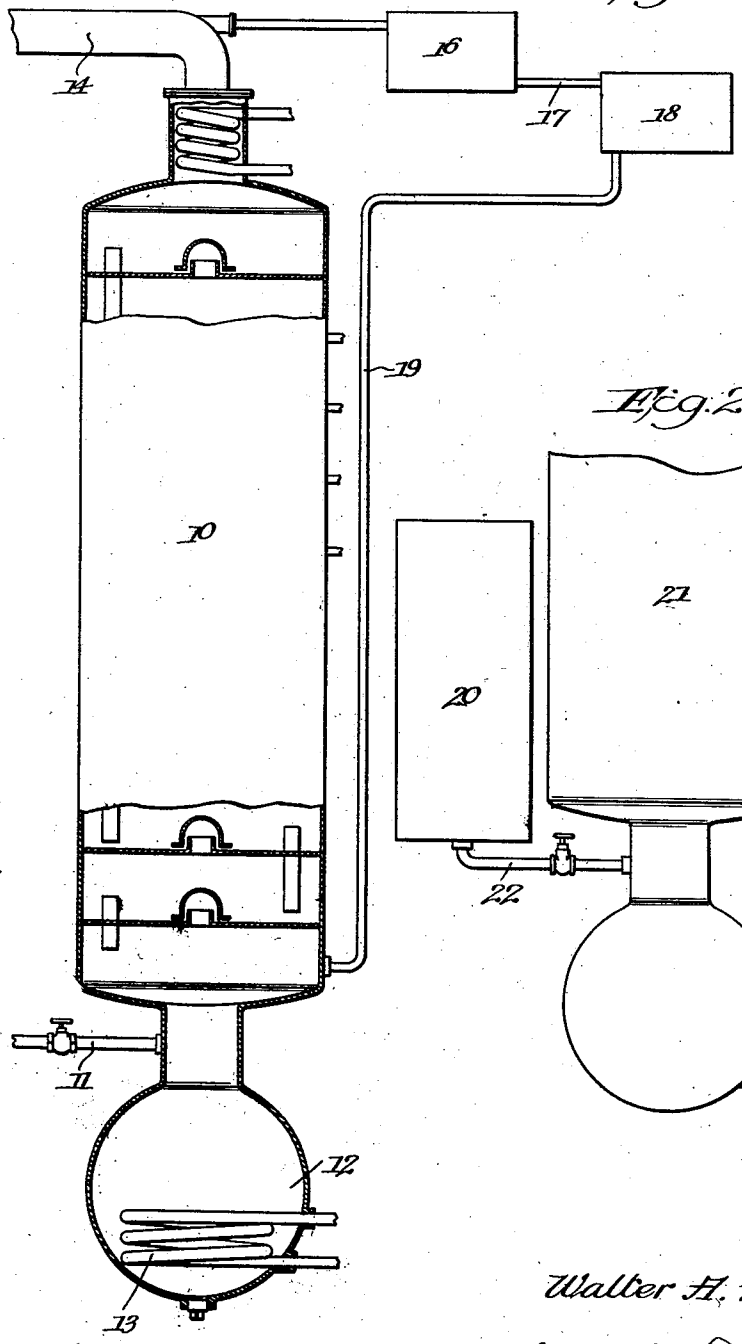

Fig. 2.

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PROCESS FOR REFINING HYDROCARBONS

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4 Claims. (Cl. 196—25)

The present invention is an improved chemical treatment of mineral oils and distillates and the product thereof. In its primary application, the invention relates to the chemical treatment and purification of petroleum hydrocarbons, such as crudes, distillates, products from cracking, as well as oils derived from the processing of shales and coke oven products such as light oils and distillates thereof.

The invention will be described in connection with the treatment of petroleum hydrocarbons but it is to be understood that the process is equally applicable upon shales and coke oven products.

In spite of much effort and study, the method almost universally used to bring about the desired refining of nearly all petroleum products, is that suggested in 1855 by Silliman—treatment with concentrated sulphuric acid followed by washing with sodium hydroxide solution. The objections to the sulphuric acid wash are generally recognized, but no suitable refining substitute has yet been made available (Petroleum and its Products—Gruse—1928, page 121).

The present invention has as an object to provide an improved refining process and a superior product without recourse to the conventional sulphuric acid treatment.

An object of the invention is to obtain petroleum products, for example, gasoline, lubricating oils and kerosene, by a method affording a product substantially free from deleterious substances, such as those which are easily oxidizable or otherwise unstable as well as resinous and asphaltic materials and sulphur impurities or compounds. The presence of such substances in the oils or distillates is generally recognized as impairing the quality of the product.

Another object of the invention is to manufacture gasoline of high quality without recourse to blending. That is to say, the naphthas treated in accordance with the present invention do not have their valuable saturated and unsaturated hydrocarbons substantially affected, and the final product has an octane number considerably higher than that obtained by conventional operations.

The invention comprises treating the mineral oils and distillates, oils derived from the processing of shale and coke oven products such as light oils and distillates thereof with a sulphur halide or reagents which react to form a sulphur halide.

Kendall in his Patent No. 413,187, October 22, 1889, suggests the use of sulphur chloride to deodorize certain oils preliminary to the use of the sulphuric acid treatment and the deodorizing effect of sulphur chlorides has, therefore, been recognized. Meigs (Industrial & Engineering Chemistry, July 1917, page 655) discusses the use of sulphur chloride and carbon disulphide solution in large amounts for testing asphaltic materials and gas engine oils for bituminous content. Lorand (Industrial & Engineering Chemistry, June 1927, page 733) discusses the laboratory use of sulphur chloride in large amounts as a testing material for petroleum hydrocarbons without relation to the refining of the same. Jaeger in his Patent No. 1,741,305, December 31, 1929 discusses the chlorination of aliphatics and thiopene compounds contained in coal tar and its derivatives using sulphur chloride as a carrier.

Many halides of metals and metaloids have been suggested as refining reagents of petroleum products notably $AlCl_3$, $ZnCl_2$, and $FeCl_3$, and others such as $AsCl_3$, $SbCl_3$, $SnCl_4$ have also been mentioned. Their use was directed either to cracking or to cause the complete removal of unsaturated aliphatic hydrocarbons. The halides of sulphur are milder polymerizing agents than the metallic chlorides, making it possible to select conditions that will result in only the elimination of objectionable constituents of the oil.

I have discovered that a sulphur halide, preferably sulphur mono-chloride (S_2Cl_2), properly regulated under suitable reaction conditions, constitutes a highly effective refining agent and may be employed as a substitute for the conventional sulphuric acid treatment.

The sulphur halide which I have most successfully employed is the mono-chloride (S_2Cl_2). But the di-chloride and tetrachloride of sulphur are also useful. Obviously, the same result may be obtained by using other reagents which react to form a sulphur halide.

The principle of my method consists in treating the impure hydrocarbons with sulphur chloride so as to produce a reaction between the actual and/or potential gum forming constituents and the sulphur chloride and thus form a gum or tarry product which is not appreciably volatile at distillation temperatures.

The amount of sulphur chloride must be carefully determined before distillation, since all or substantially all of this reagent must enter into the reaction with some constituent of the oil to be refined. I have discovered that the amount of reagent employed is of vital importance. Therefore, in every instance, the point at which

no further amount of the reagent should be used must be determined.

The exact quantity of the reagent can be determined, for example, by adding small percentages of the same to the oil to be refined, refluxing for a short time, and then subjecting the mixture to distillation. The purity and other characteristics of the distillate will enable one to quickly ascertain the requisite amount of the reagent for the oil.

Moreover, all hydrocarbon oils do not show the same velocity of reaction with the reagent. It is, therefore, necessary to determine the length of the treatment with each variety of oil. This reaction velocity is dependent upon temperature, the nature of the oil to be refined, the concentration and composition of the sulphur chloride, and where a catalyst is employed, the nature of the catalyst.

I have found that ordinarily the sulphur chloride should be used in relatively small percentages, usually less than 1%. The reaction between the sulphur halide and the oil may, in some cases, be accelerated by a catalyst, such as finely divided clay or fuller's earth, copper, lead, zinc, and finely divided anhydrous sulfides of copper, lead, tin, arsenic and antimony. The reaction can take place in the cold, but ordinarily heat will reduce the time period.

The reaction is characterized by (1) chlorination of the valuable aliphatic and aromatic compounds does not take place so that addition or substitution chlorinated products of the valuable hydrocarbons are not formed; (2) the potential gum forming constituents of the oil are reduced or condensed or polymerized to form separable bodies which are insoluble or are but slightly soluble, i. e., of reduced solubility in the oil, and which have a boiling point above that employed for distillation so that the valuable constituents of the oil are removable by distillation; (3) formation of substantially dry hydrochloric acid gas which, in some cases, may be recovered in the gaseous phase, and (4) the sulphur chloride reacts upon the potential gum forming constituents and sulphur compounds of the oil and is in such small percentage that no opportunity is afforded for the formation either of an increase of sulphur impurities, or objectionable chlorinated products, both of which would impair the final product. That is to say, the reaction of the sulphur chloride is controlled so that it acts to reduce the solubility of the deleterious substances in the oil and form separable relatively stable heavy bodies having a boiling point above the normal distillation temperatures.

My improved process has numerous advantages as compared to the conventional sulphuric acid treatment to which there are objections so generally recognized that they need not be discussed. From the standpoint of yield, the recovery of the valuable and useful hydrocarbons is materially increased, as compared to the sulphuric acid treatment. The increased yield is equal to the amount of the valuable unsaturated hydrocarbons which are usually destroyed by sulphuric acid treatment, and in the case of cracked gasolines has amounted to substantially 10%. The sulphur chloride is relatively inexpensive and the simplicity of the process reduces the refining expense, having in mind particularly that only small percentages of sulphur chloride are employed. The amount of the gum or tarry residue obtained is considerably less than the sludge produced by the acid treatment. Further, the handling of large quantities of sulphuric acid with its attendant problems is avoided.

In addition, there is a substantial reduction in the time period of operation.

The gasoline obtained has characteristics which clearly distinguish it from the product of the sulphuric acid treatment and has a number of definite advantages.

It is well known, of course, that aromatic hydrocarbons are desirable in the gasoline; my improved process does not attack the aromatic hydrocarbons but preserves the same. The gasoline produced is substantially water-white and sweet. Repeated tests have shown that it has a high octane number as compared to gasoline obtained from the same crude naphtha by the sulphuric acid treatment. Under comparative test the product has exhibited an octane number substantially greater than the octane number for gasoline produced from the same oil refined by the sulphuric acid treatment. Under the copper-dish test, both the factors of corrosion and gum residue are satisfactory. In other words, the product is not only satisfactory under the copper-dish test, from the standpoint of actual and potential gums, but is also comparatively rich in the valuable anti-knock constituents which are lost in the sulphuric acid method of refining. An examination of the sulphur content of the gasoline prepared in accordance with this invention discloses that it is less than one-tenth of 1%.

The gasoline is highly stable. When allowed to stand for a considerable period after distillation, even in the sunlight, it exhibits no appreciable deterioration, whereas gasoline obtained by the sulphuric acid treatment shows very appreciable deterioration when subjected to the same tests. More particularly, the product of this process when subjected to this stability test shows little or no dropping of octane number or discoloration, and at the end of the period of test responds to the copper-dish test equally as well as before exposure.

The process is applicable to all oils and distillates which normally require chemical refining treatment. I will describe the invention in connection with the manufacture of gasoline.

Ordinary crude naphthas are treated, such as straight run or cracked distillates. The oil is tested by refluxing or in any suitable manner to determine the quantity of potential gum forming constituents and the boiling point. These factors I find determine (1) the quantity of sulphur halide to be added, and (2) the control of the operation.

Where the amount of potential gums is high, a greater percentage of the chemical is employed. In cases where the oil is relatively low boiling or contains appreciable low boiling unsaturated hydrocarbons, the quantity of the chemical is regulated so as to avoid chlorination of the valuable low boiling constituents. I have found that the low boiling hydrocarbons require lesser amounts of the sulphur chloride and that, in fact, the use of an excessive percentage is objectionable.

I have found that for most crude naphthas, the percentage of sulphur halide need not be in excess of 1%, the exact percentage being determined as explained by the boiling point and actual and potential gum content. The amount will vary in the case of raw crudes, or kerosene and lubricating oils.

The oil is treated in a suitable chamber by running therein a determined quantity of liquid sulphur mono-chloride, or the sulphur halide in gaseous phase is bubbled through the oil. The reaction may take place in the cold or room temperature where the hydrocarbons have a low boiling point, but is speeded or accelerated at elevated temperatures. The factors of heat and time required to satisfactorily complete the reaction will vary in accordance with the oil under treatment.

In some cases I find the use of a catalyst or accelerator, such as one of the accelerators above mentioned, will materially decrease the time factor.

The reaction which takes place, I believe to be (1) a combining of the sulphur chloride with the gum forming and sulphur compound constituents of the oil with liberation of substantially dry hydrochloric acid gas; (2) the changing or polymerization of these and other deleterious compounds into definite relatively stable bodies which are high boiling, separable, i. e., stable above usual distillation temperatures and less soluble in the oil.

The S_2Cl_2 is used in amount to react with the deleterious substances present, but in insufficient amount to attack the valuable aliphatic and aromatic hydrocarbons under the conditions of reaction. The reaction conditions, such as time period, temperature and pressure, and quantity of sulphur monochloride and/or catalyst are controlled to produce the desired result. Stated again, the desirable hydrocarbons are not affected, but the substances, such as gums, resins, and sulphur compounds are changed or stabilized or formed into polymerized compounds which, upon distillation, are separable as a residue.

The reaction proceeds with formation of hydrochloric acid gas which is liberated and recovered as a dry gas. The oil under treatment turns a dark color and a heavy precipitate forms comprising the gums, resins, and reaction compounds, together with free sulphur. It is noted that the heavy precipitate is much less in quantity than the "sludge" or "tar" formed when a sulphuric acid wash is employed.

The naphtha so treated is now distilled and this is satisfactorily accomplished in any suitable fractionating tower in the usual manner. The temperatures employed will be determined by the oil under treatment, and, if desired, the distillation may be accomplished under reduced pressure and/or condensing means disposed intermediate the tower or at the outlet thereof for returning certain fractions back to the chamber. Likewise, various of the fractions may be condensed and collected from the tower, i. e., separate fractions may be taken off.

The gasoline or distillate upon examination contains a minimum of deleterious substances and is much more efficient from the standpoint of anti-knock characteristics and more stable than gasolines obtained by chemical treatment with sulphuric acid. In fact, the gasoline recovered by the present method is remarkably free of gums and resins, as well as sulphur compounds, such as mercaptans, polysulphides and other sulphur impurities. The characteristics of the product have been described above.

In practicing the process, any suitable apparatus may be employed and various methods of procedure may be adopted as best suited to plant installation.

In the accompanying drawing,

Figure 1 is a diagrammatic view of a typical apparatus.

Figure 2 is a fragmentary diagrammatic view of a modified form of apparatus.

Referring to the drawing, 10 indicates a conventional fractionating column into which the crude naphtha may be introduced through a pipe 11 leading from any suitable source. The lower end of the column forms a residue receiving chamber 12 having a draw-off outlet, and heat may be applied to the oil within the column as by means of a suitable internal heating coil 13. The treating agent, such as sulphur mono-chloride, may be initially introduced through pipe 19 in a percentage predetermined as hereinbefore described, and the reaction permitted to take place preferably in the presence of heat supplied by means of the heating coil. Such pressures may be employed as will prevent any substantial distillation of the product during the reaction period. The reaction conditions, however, will be such that hydrochloric acid gas as liberated may be taken off through the pipe 14 at the upper end of the column and carried either to an absorber and/or to a chamber 16, wherein chlorine may be separated from the hydrochloric acid gas for the purpose of supplying additional reagent to the still in further operations. That is to say, the chlorine liberated in the chamber 16 may be conducted by pipe 17 to a chamber 18, wherein it will be combined with sulphur in a conventional manner to produce sulphur chloride. The sulphur chloride may be conducted as by the pipe 19 to the column, as required. The sulphur obtained from the reaction in the column may be removed from time to time, and treated for use in the chamber 18 to produce the sulphur chloride.

Instead of the apparatus illustrated in Figure 1, it may be desirable, in some instances, to treat the crude naphtha in a chamber independent of the fractionating column and store the same for supply to the fractionating column as required. For example, as illustrated in Figure 2, a storage chamber 20 may be utilized to store the crude naphtha which has been previously treated with the reagent and the same may be supplied to a distillation column 21 or a battery of such columns through a pipe or pipes 22.

In order that the practical application of the process may be more clearly understood and merely by way of example, I will describe typical reaction processes which have heretofore been conducted.

Commercial crude naphtha resulting from a cracking process is supplied to a column, such as illustrated in Figure 1. Into the naphtha is introduced 0.6 of 1% of sulphur mono-chloride; the mixture is refluxed for twenty (20) minutes and heated to the boiling point of the naphtha. The oil becomes dark and a tarry precipitate and reaction products settle into the bottom of the chamber. Thereafter the oil is distilled to approximately 150° C., or as long as the distillate is clear or colorless. It has been observed that at about 150°, it may be desirable to reduce the pressure in the column, as by evacuation, thereby permitting the distillation to continue without increasing the temperature to a point which will cause the reaction products to vaporize. The distillation process is continued as long as the distillate is clear. It has been observed, in some cases, that it is desirable to keep the distillation temperature below 170° C., in order to avoid vaporizing or cracking the reaction products. However,

it will be understood that this temperature will vary with different oils. The distillate produced by this process has been found to have all the characteristics hereinbefore described.

As an alternative procedure, the crude naphtha introduced into the chamber may be partially distilled before introducing the sulphur chloride. For example, it is distilled sufficiently to take off the lighter hydrocarbons of low boiling point. In some instances, I have distilled to about 120° C., and the cut taken off up to this temperature has been treated in two ways. For example, (1) it has been given a treatment of 0.1 of 1% of sulphur mono-chloride and because of the character of the distillate, this can be done at atmospheric temperature and pressure. Ordinarily, it is found, however, that this distillate need not be treated at all or it may (2) be given instead a very mild sulphuric acid wash. After such treatment, the product is redistilled.

The naphtha remaining in the column then has added thereto 0.4 of 1% of sulphur chloride and is heated for fifteen to twenty minutes, thereby producing the reaction products described. Where a catalyst is used, the time period is shorter. The treated naphtha is then distilled as long as the distillate has the desired characteristics.

In some instances, it has been found helpful to combine the distillate obtained in the first step with the distillate from the second step, and then redistill the mixture to approximately 200° C.

Another method of operation consists in adding the initial or low boiling distillate in either treated or untreated condition, as mentioned above, to the remaining undistilled treated body of oil, and then distilling the mixture. In other words, the low boiling constituents and high boiling constituents are each separately chemically treated and then mixed and distilled. Frequently, it is unnecessary to chemically treat the low boiling distillate, and when this is added to the body of undistilled treated oil, a small percentage of residual sulphur halide which may remain in the treated oil, will be sufficient to react upon any deleterious substances in the untreated initial distillate. Such mixture of untreated low boiling distillate and treated oil will be distilled, as described.

I further proceed by reacting upon the oil to be treated with a very small percentage of the sulphur halide, and distilling off fractions of the oil as long as their recovery indicates they are the valuable ones or the ones desired, and are free of deleterious substances. When this ceases, the fractionation is discontinued, and another small percentage of sulphur halide is added and allowed to react with the remaining body of oil. When the reaction has been completed, distillation and fractionation are resumed. This semi-continuous and partial treatment with relatively small percentages of sulphur halide, followed by distillation, may be carried on until no more desirable fractions are recovered and assures that a relatively high yield, i. e., substantially all of the valuable constituents, will be obtained.

As explained, it may be desirable to employ a catalyst, such as one of those described above preferably in finely divided condition, and these have been used with satisfactory results in each of the processes described.

With reference to the treatment of raw crudes, oils derived from the treatment of shales, and liquid coke-oven products, i. e., light oils and distillates thereof, it will be understood that the sulphur chloride will be added in amounts and conditions maintained to assure efficient reaction with the deleterious substances, as above described. The same considerations will govern the refining of kerosene and lubricating oil products.

I claim:

1. The process of chemically treating petroleum hydrocarbon oils and distillates thereof and light oils and distillates thereof, in liquid phase to obtain products free of potential gum-forming substances and undesirable sulphur compounds, which comprises reacting upon the oil containing the said substances with up to one percent of sulphur chloride, thereby polymerizing the said substances into relatively high boiling and stable compounds of reduced solubility, and separating out such high boiling compounds.

2. The process of chemically treating petroleum hydrocarbon oils and distillates thereof and light oils and distillates thereof, in liquid phase, to obtain products free of potential gum-forming substances and undesirable sulphur compounds, which comprises reacting upon the oil containing the said substances with up to one percent of sulphur mono-chloride, thereby polymerizing the said substances into relatively high boiling and stable compounds of reduced solubility, and separating out said high boiling compounds.

3. A process in accordance with claim 1 in which the reaction of the oil with sulphur chloride takes place in the presence of a catalyst.

4. A process in accordance with claim 1 in which the reaction of the oil with sulphur chloride takes place at elevated temperature.

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