

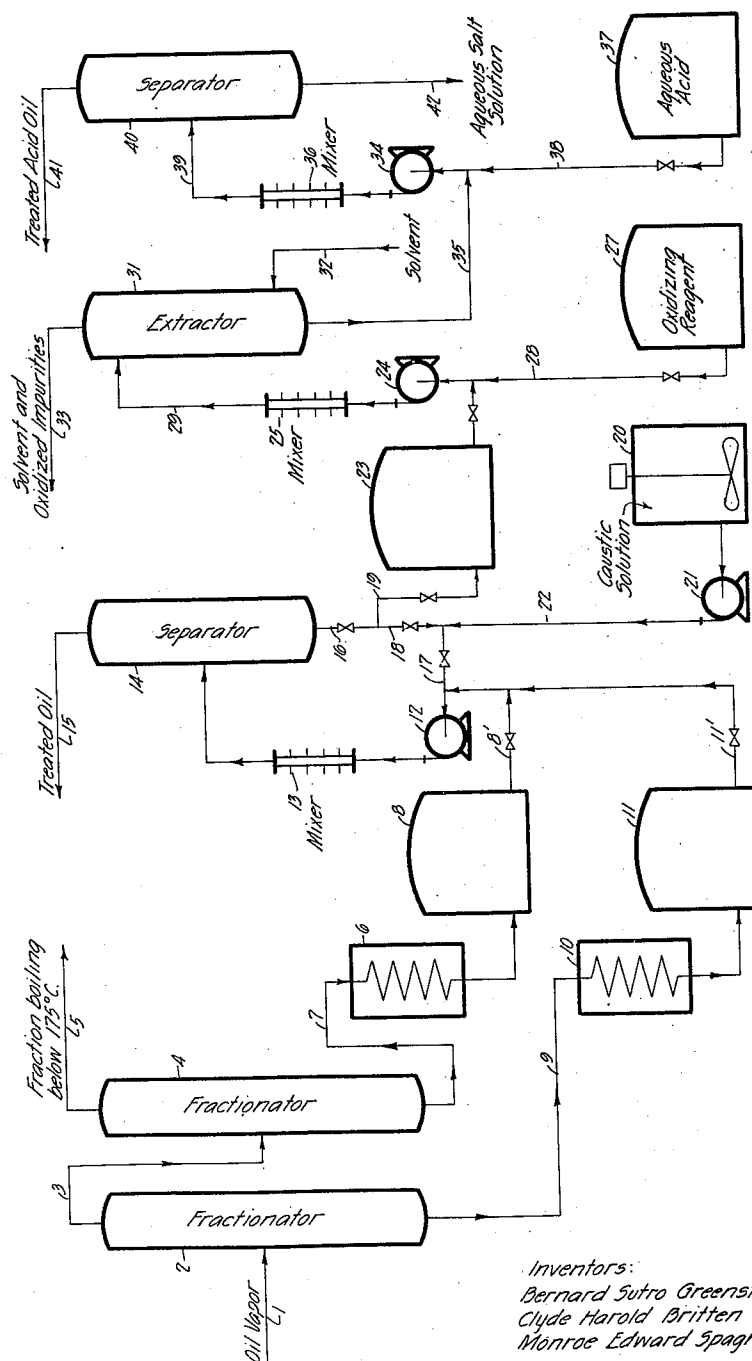
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PROCESS FOR PRODUCING ACID OILS

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PROCESS FOR PRODUCING ACID OILS

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This invention relates to the production of acid oils, and is directed particularly to the extraction of hydroxyaromatic compounds from cracked gasoline distillates.

The term "acid oils", as herein used, refers to oxyorganic acidic substances, consisting predominantly of hydroxy aromatic compounds and occurring principally in cracked hydrocarbon oils, and does not include organic acids produced by the interaction of mineral acids and organic compounds. Such acid oils are useful as selective solvents, gum inhibitors, and for the manufacture of extreme pressure dopes, dye intermediates, etc.

It is a purpose of this invention to provide an improved economical method for the substantial removal and recovery of acid oils from hydrocarbon distillates. It is another purpose to provide a method for refining crude acid oils obtained by the extraction of mineral oils. Incidental to the complete extraction of acid oils, partially refined distillates are produced, which are easily sweetened, cause little contamination and permit low consumption of treating agents subsequently used to refine these distillates.

In the past it has been customary to remove acidic components from mineral oils by treatment with caustic solutions of the approximate strength of about 5 to 20° Bé. Most of the acid oils are weak acids, i. e. they have low dissociation constants and, in consequence, aqueous solutions of caustic extract the acid oils incompletely. It has been attempted to overcome this difficulty by treating acid oil-bearing distillates with anhydrous caustic or passing the distillate vapors through molten caustic, or distilling over caustic, etc. These methods, although resulting in a more or less complete extraction of the acid oils, have the disadvantage of being wasteful because of incomplete utilization of the caustic, and moreover, they are quite awkward for mechanical reasons.

Our invention consists essentially of treating the mineral oil distillate containing acid oils with an amount of aqueous caustic solution of 30-50% concentration or aqueous acid oil soap solution containing free caustic and being equivalent to a 30-50% caustic solution, the amount of free caustic used being very slightly in excess of the equivalent to the acid oil content of the distillate. The effect of this treatment is to produce a strong aqueous soap solution containing but a small excess of caustic, which soap solution has a substantial solvent power for acid oils and as a result of the combined actions of the soap and alkali, a more or less complete removal of acid oils from

mineral oils can be achieved with practically no waste of unused caustic. The acid oils which are extracted with this aqueous soap solution are usually highly contaminated with impurities such as sulfur compounds, which render the acid oil malodorous and unstable; to produce a better marketable product we have invented a refining process comprising a strong oxidation of the acid oil while in the caustic solution, followed by a solvent extraction.

We have observed that cracked distillate fractions boiling below about 150° C. are practically free from acid oils; fractions boiling between 150-175° C. contain very small amounts only, while the fractions boiling above 175° C. contain varying amounts of acid oils. For example, a cracked gasoline distillate of an acid oil content of 4% was fractionally distilled. The fraction boiling below 150° C. contained less than .02% acid oil; the fraction boiling from 150-175° C. contained about .12%, and the fraction boiling between 175-225° C. contained 1.5% acid oils, concentration peaks of 1.8% and 2.6% appearing in the fractions boiling from 183-186° C. and 201-207° C. respectively. Fractions boiling substantially above 225° C. such as gas oil fractions boiling above about 300° C. usually are deficient in acid oils.

In accordance with the above mentioned observation we have devised an efficient method for obtaining highly concentrated acid oils from cracked distillates by fractionally distilling such distillate to separate at least one fraction boiling below about 175° C. and subjecting the higher boiling fraction or parts thereof boiling below 300° C. or preferably below 225° C. to the extraction with an aqueous caustic solution of 30-50% concentration or an equivalent acid oil soap solution containing free caustic. The separation of the excessively light and heavy fractions from the fraction boiling within the range of 175° to 300° C. or 225° C. not only reduces the bulk of the oil to be subjected to the chemical treatment and thereby increases the efficiency of its contact with the chemical, but also permits the treatment of the fraction which contains relatively little mercaptans or other sulfur compounds. The net result of this preliminary fractionation is thus more complete recovery of acid oils which are relatively little contaminated with sulfur compounds, reduced losses of distillate, and greater ease of handling.

The caustic extraction is preferably carried out at ordinary temperatures of the order of 10-40° C., although higher or lower tempera-

tures substantially below the boiling temperatures of the reactants may be employed. While any alkali metal hydroxide is suitable for our purposes, in practice, sodium and potassium hydroxides only are the most likely to be used, lithium, cesium, and rubidium being too expensive. The concentration of the caustic solution must be held between the limits of 30-50% for the following reasons: Alkali solutions of concentrations less than 30% do not form soap solutions of sufficient concentration to exert a substantial solvent action on acid oils, the result being incomplete removal of acid oils from distillates; and solutions of concentrations higher than 50% are so viscous that they are difficult to handle, and frequently result in obstinate emulsions. The effect of alkali concentrations on the efficiency of acid oil extraction is illustrated by the data in the table below:

Distribution of acid oils between cracked distillate and sodium hydroxide solutions

Conc. of NaOH solution	Total mols of acid oil in system per mol NaOH used	Vol. percent acid oil in treated distillate
40° Bé (35% NaOH)-----	.85 .98 1.10	.01 .04 .11
25° Bé (19% NaOH)-----	.50 .85 .98 1.10	.15 .20 .30 .55

In the above tabulation it may be seen that an equivalent amount of 40° Bé. sodium hydroxide solution, that is, one in which the total number mols of acid oil in the system per mol of caustic equals one, removes acid oils from the distillate to a greater extent than a 100% excess of a 25° Bé. sodium hydroxide solution. On the other hand, it appears that if more than a molal equivalent of acid oil is treated with a caustic solution of a strength within the optimum range, a substantial amount of acid oil remains in the distillate. For these reasons, we prefer to regulate the ratio of distillate and caustic solution of the requisite strength so as to produce soap solutions containing at least .80 and not more than about .98 mols of acid oil per mol of caustic. Under these conditions the extraction is substantially complete and very little caustic is unused.

The minimum concentration of soap in the aqueous alkali hydroxide necessary to exert a markedly improved solvent action varies considerably with the type of acid oil in the soap as well as in the distillate. It was observed that upon addition of relatively small amounts of acid oils to aqueous caustic of 30 to 50%, soap separates out until, upon further addition of acid oil to the caustic, a critical solubility point is reached where the concentration of the soap becomes such that a single homogeneous aqueous solution of caustic in the soap is formed. We have found that the distribution of acid oils between the oil and aqueous phases becomes particularly favorable to the latter when the concentration of soap in this phase about equals or exceeds that which is necessary for the complete dissolution of the aqueous caustic in the soap.

While as hereinbefore shown, our process of acid oil removal from hydrocarbon distillates is especially advantageous from the point of view of efficiency and economy, it also makes possible

the removal of certain types of acid oils which cannot be removed from the mineral oils by aqueous caustic alone, possibly because of their low solubility in aqueous caustic, except in the presence of a substantial amount of soap. For instance, a cracked gasoline was pretreated with 20° Bé. caustic solution, and the pretreated gasoline was then divided into two portions, one of which was treated with an excess of 40° Bé. fresh caustic solution and the other with an equal amount of partially spent caustic solution containing about .80 mol of acid oil which originally had a strength of 40° Bé. The fresh solution extracted .19% acid oil from the distillate, whereas the partially spent one extracted 40%.

During the treatment with caustic containing soaps, impurities of the type of mercaptans are extracted from distillates jointly with acid oils. Acid oils liberated from the soaps by acidification are, therefore, malodorous and unstable and it is very desirable to subject the acid oils to a refining treatment. We usually proceed by separating the spent caustic from the distillate and subjecting the spent caustic comprising essentially an alkaline reacting solution of soap to an oxidizing treatment in order to convert mercaptides to disulfides, and then extracting the disulfides with a preferential solvent for organic disulfides, such as naphtha, pentanes, hexanes, benzol, carbon-tetrachloride, dichlorethane, etc. The oxidation reaction is preferably carried out with a moderately strong oxidizing agent, for instance, hydrogen peroxide, sodium peroxide, barium peroxide, ozone, chlorine or hypochlorite. Oxidizing with air effects some improvement at elevated temperatures, but generally is not sufficient. Oxidation with more powerful oxidizing reagents than those recited, to wit, potassium permanganate, chromic acid, etc., are apt to destroy the acid oils, and, therefore, should not be used. The temperature of our oxidizing treatment is usually substantially atmospheric of the order of 10° C. to 40° C. although somewhat elevated temperatures may be used to accelerate the reaction.

The oxidized soap solution is now ready for acidification to liberate acid oils. Acidification is preferably carried out with inorganic acids, which must be more strongly acidic than the acid oils themselves. Strong acids such as hydrochloric acid, sulfuric acid, or weaker acids such as phosphoric acid, sulfur dioxide, carbon dioxide, hydrogen sulfide, etc. may be used.

In a particular instance, a soap solution obtained by extracting a distillate, boiling from 160° to 225° C. with a 40° Bé. caustic solution, and containing .98 mol. of acid oil per mol. of caustic was treated with 4% hydrogen peroxide by weight of the acid oil. Heat evolved during the reaction and the mixture darkened. The oxidized mixture was subsequently washed with benzol and acidified with dilute sulfuric acid. Acid oil was liberated and allowed to separate. This acid oil had a light color, phenolic odor, and a sulfur content of .05%. In contrast, raw acid oil separated from the soap prior to the oxidation treatment, was dark brown, malodorous, and had a sulfur content of .61%, while an acid oil obtained after oxidation with air at an elevated temperature contained .31% sulfur.

Our process of acid oil production may be carried out by the batch method or in a continuous manner. In the batch method the distillate containing acid oil is agitated with a quantity of aqueous caustic solution or an acid oil soap solu-

tion containing free alkali of the proper strength, which contains an amount of caustic only slightly greater than the equivalent of the acid oil in the distillate. The mixture of distillate and the resulting soap solution are allowed to separate, the soap solution containing a small amount of free caustic settling as the lower layer, whence it is withdrawn and transferred to a separate vessel for oxidation, extraction and subsequent acidification.

It is immaterial whether the aqueous caustic solution used in the treatment contains originally acid oil soaps or not, as long as the soap solution resulting from the treatment contains acid oil soap at least to the extent of the critical solubility point and some free alkali hydroxide.

In the continuous process a circulating stream of acid oil soap solution is maintained. Aqueous caustic is continuously introduced at one point of the circuit, and the resulting solution of soap and caustic is contacted with the necessary volume of distillate to convert substantially all of the newly added hydroxide to soap. After separation of the distillate an amount of the soap solution equivalent to the added caustic solution is withdrawn and the remainder is circulated as described.

Referring now to the drawing, which represents a flow diagram of a continuous form of our process: Distillate vapors containing acid oil are introduced from a source not shown, through line 1 into fractionating tower 2, where they are separated into an overhead fraction boiling within gasoline boiling range and a heavier bottom fraction. The overhead fraction, after it passes through transfer line 3 is refractionated in fractionator 4 into overhead vapors boiling below about 175° C. which leave through vapor line 5, and a bottom fraction containing acid oil, which passes through cooler 6 in line 7 to tank 8.

The bottom fraction from fractionator 2, which normally also contains acid oils, is cooled in cooler 10, situated in line 9, and proceeds to tank 11. From tanks 8 and 11 acid oil containing distillates may be fed at separate times through lines 8' and 11', respectively, to the caustic treating system which is as follows: Pump 12 picks up the oil from tanks 8 or 11, and forces it, together with aqueous caustic solution from line 17, through mixer 13 into separator 14. In separator 14 treated oil and aqueous soap solution are separated, treated oil going to storage through top line 15 and soap solution being returned through bottom line 16 and lines 18 and 17 to pump 12, to be mixed with further quantities of oil from tanks 8 or 11. A portion of the soap solution is continuously withdrawn from the cycle, through line 19 into tank 23 and an equivalent amount of fresh caustic is introduced into line 17 from caustic tank 20, conveyed by pump 21 in line 22. Care must be taken that the ratio of freshly added caustic and acid oil containing distillate which jointly pass through the mixer 13 together with a circulating soap solution is such that the soap solution after separation of the distillate in separator 14 contains some free alkali and acid oil at least to the extent of the critical solubility point and preferably between .8 and .98 mol. of acid per mol. of caustic.

The spent caustic comprising a soap solution in tank 23 is now forced by pump 24 together with an oxidizing reagent such as hydrogen peroxide, hypochlorite, etc., from tank 27 and line 28, through mixer 25 into extractor 31, in which the oxidized caustic mixture is extracted with a suitable solvent for disulfides, such as naphtha.

The solvent, introduced through line 32, flows in an upward direction through extractor 31 and is withdrawn through top line 33, while the caustic mixture entering through line 28 flows downward and is transferred by pump 34 in line 35 through mixer 36 to separator 40, together with a sufficient amount of acid from tank 37 and line 38 to produce a slightly acidic mixture, whereby acid oils are liberated. The acidic mixture enters through line 39 into separator 40, where the liberated acid oils are separated from the acidic aqueous solution, treated acid oil being removed from top line 41 and aqueous solution through bottom line 42.

We claim as our invention:

1. In the process of extracting acid oil from a mineral oil distillate containing same with an aqueous alkali metal hydroxide, whereby acid oils are caused to react with the hydroxide to produce a soap solution, the improvement comprising treating said liquid distillate with an amount of a liquid mixture consisting essentially of water, acid oil soap and free alkali metal hydroxide and being equivalent to an original aqueous alkali metal hydroxide solution of 30 to 50% concentration to neutralize a portion only of said free alkali metal hydroxide and to raise the acid oil soap content of the mixture at least to the critical solubility point of the soap above which the mixture forms a single phase, and separating the treated distillate from the resulting aqueous soap solution.

2. In the process of extracting acid oil from a mineral oil distillate containing same with an aqueous alkali metal hydroxide, whereby acid oils are caused to react with the hydroxide to produce a soap solution, the improvement comprising treating said liquid distillate with an amount of a liquid mixture consisting essentially of water, acid oil soap and free alkali metal hydroxide and being equivalent to an original aqueous alkali metal hydroxide solution of 30 to 50% concentration to neutralize a portion only of the free alkali metal hydroxide and to produce a solution in which the mol ratio of acid oil to alkali metal is between the limits of .80 to .98, and separating the treated distillate from the resulting aqueous soap solution.

3. In the process of extracting acid oil from a mineral oil distillate containing same with an aqueous alkali metal hydroxide, whereby acid oils are caused to react with the hydroxide to produce a soap solution, the improvement comprising fractionally distilling said distillate to produce a light fraction boiling substantially below 175° C. and a heavier fraction, treating the heavier fraction with an amount of a liquid mixture consisting essentially of water, acid oil soap and free alkali metal hydroxide and being equivalent to an original aqueous alkali metal hydroxide solution of 30 to 50% concentration to neutralize a portion only of said free alkali metal hydroxide and to raise the acid oil soap content of the mixture at least to the critical solubility point of the soap, above which the mixture forms a single phase, and separating the treated distillate from the resulting aqueous soap solution.

4. In the process of extracting acid oil from a mineral oil distillate containing same with an aqueous alkali metal hydroxide, whereby acid oils are caused to react with the hydroxide to produce a soap solution, the improvement comprising fractionally distilling said distillate to produce a fraction boiling between 175° and 300° C., treating this fraction with an amount of a liquid mixture consisting essentially of water, acid oil soap

and free alkali metal hydroxide and being equivalent to an original aqueous alkali metal hydroxide solution of 30 to 50% concentration to neutralize a portion only of said free alkali metal hydroxide and to raise the acid oil soap content of the mixture at least to the critical solubility point of the soap above which the mixture forms a single phase, and separating the treated distillate from the resulting aqueous soap solution.

5. A continuous process for the substantially complete recovery of acid oil from mineral oil containing acid oil, by extraction with an aqueous solution of alkali metal hydroxide whereby acid oil is caused to react with the alkali metal hydroxide to produce soap and water, comprising continuously circulating an aqueous acid oil soap solution which contains free alkali metal hydroxide and acid oil soap at least to the extent of its critical solubility point, said soap solution being equivalent to a 30 to 50% alkali metal hydroxide solution, continuously admixing a quantity of fresh aqueous alkali metal hydroxide solution of 30 to 50% concentration, continuously treating with the resulting aqueous mixture a volume of said mineral oil containing a quantity of acid oil absorbable in the said mixture which is sufficient to raise the acid oil soap content of the said mixture at least to the critical solubility point of the soap, above which the mixture forms a single phase, thereby converting the mixture to the aforementioned aqueous acid oil soap solution, separating the treated mineral oil from the aqueous acid oil soap solution, and continuously withdrawing an amount of the latter having the same alkali metal content as the said quantity of fresh aqueous alkali metal hydroxide.

6. A continuous process for the substantially complete recovery of acid oil from mineral oil containing acid oil, by extraction with an aqueous solution of alkali metal hydroxide whereby acid oil is caused to react with the alkali metal hydroxide to produce soap and water, comprising continuously circulating an aqueous acid oil soap solution in which the molal ratio of acid oil to alkali metal hydroxide is not less than .80 and not more than .98, said soap solution being

equivalent to a 30 to 50% alkali metal hydroxide solution, continuously admixing a quantity of fresh aqueous alkali metal hydroxide solution of 40 to 50% concentration, continuously treating with the resulting aqueous mixture a volume of said mineral oil containing a quantity of acid oil absorbable in the said mixture which is approximately equivalent to the said quantity of fresh aqueous alkali hydroxide, thereby converting said mixture to the aforementioned aqueous acid oil soap solution, separating the treated mineral oil from the aqueous acid oil soap solution, and continuously withdrawing an amount of the latter having the same alkali metal content as the said quantity of fresh aqueous alkali metal hydroxide.

7. In the process of producing stable acid oil from a mineral distillate containing acid oil and acidic sulfur compounds, the steps comprising treating said distillate with aqueous acid oil soap solution containing free alkali metal hydroxide and being equivalent to an aqueous alkali metal hydroxide solution of 30 to 50% concentration under conditions to react acid oil and acidic sulfur compounds with the alkali metal hydroxide and to form a soap solution containing acid oils and sulfur compounds at least to the extent of the critical solubility point of the soap, separating the treated distillate from the resulting soap solution, subjecting the latter to an oxidizing treatment sufficiently strong to convert alkali metal mercaptides to disulfides but insufficiently strong to oxidize a substantial amount of acid oils, washing the oxidized soap solution with a solvent for disulfides, acidifying the washed soap solution to liberate acid oil and separating the liberated acid oil from the acidified solution.

8. The process of claim 7 in which the oxidizing treatment is effected by means of an oxidizing agent selected from the group consisting of hydrogen peroxide, sodium peroxide, barium peroxide, chlorine, hypochlorite.

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