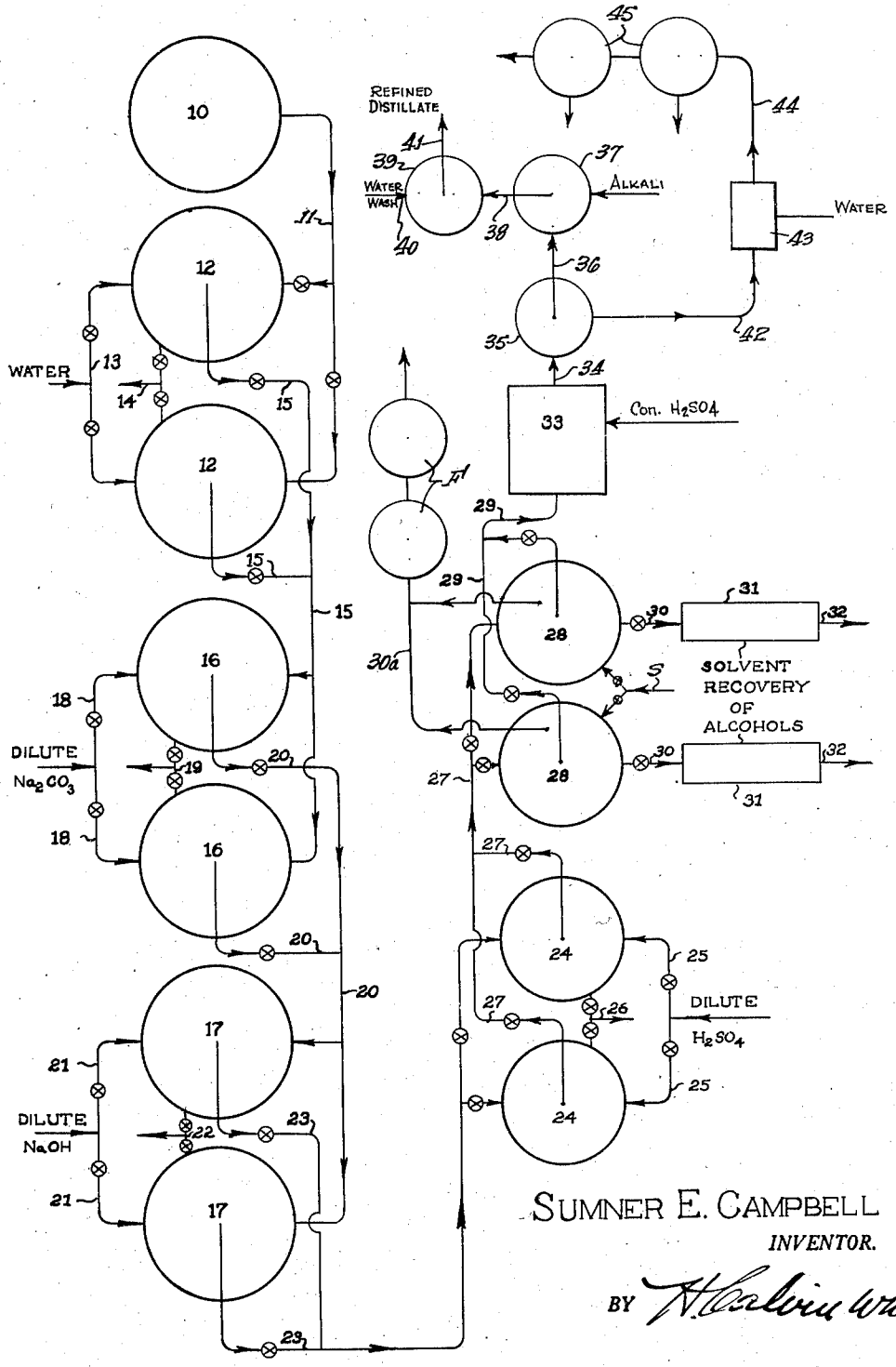
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PROCESS FOR PRODUCING ALCOHOLS BY ACID TREATING OLEFINIC MINERAL OILS

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PROCESS FOR PRODUCING ALCOHOLS BY ACID TREATING OLEFINIC MINERAL OILS

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This invention has to do with the refining of pressure distillates derived from the cracking of hydrocarbon crude oils or fractions thereof whose composition is such as to permit the formation of valuable by-products from constituents requiring removal for proper refining of the distillate, and whose composition otherwise necessitates the removal in particular order, of various impurities in order that the by-product formation and recovery may be accomplished efficiently and profitably. Typical of cracked distillates for the refining of which the present process is especially adaptable, are those derived from California San Joaquin Valley crudes, characterized by the presence in the raw cracked distillates of water-soluble impurities including some of the aliphatic acids and nitrogenous compounds, particularly nitrogenous bases; sulfur compounds, organic acids and phenolic compounds not removable by water washing of the distillate but by its treatment with dilute alkali metal carbonate and alkali metal hydroxide solutions; the olefins and diolefins which are sulfatable by treatment with dilute sulfuric acid and hydrolyzable to form alcohols; and those olefins which cannot readily be sulfated by dilute acid treatment but which are sulfatable by concentrated or fuming sulfuric acid to form among other reaction products on hydrolysis correspondingly high molecular weight alcohols. Hereinafter the invention will be described typically with reference to the treatment of unrefined distillates having e. g. a boiling range of about 100° F. to 450° F., and having the aliphatic acid, sulfur, nitrogenous and phenolic compound content, together with sulfatable olefins and diolefins, characteristic of pressure distillates derived from San Joaquin Valley, California, crude oils.

The principal objects of the invention are directed both to improved processes for refining of the pressure distillate for its conversion to high quality motor fuel, and to conversion and recovery of constituents ordinarily discarded. In this connection I refer particularly to the recovery of alcohols of both lower and higher molecular weight, resulting from a hydrolysis of sulfated olefins and diolefins. In certain of its aspects, the invention is predicated upon the discovery that recovery of these alcohols in profitable yields and the required purities, necessitates the removal of various impurities from the distillate in antecedent treating steps, and that the nature and order of these preliminary treatments is of essential importance to the alcohol by-product production as well as the quality of the final treated pressure distillate. Specifically, in order that the pressure distillate may first be most effectively conditioned for sulfation of the olefins and diolefins to yield upon hydrolysis alcohols in such quantities and purity as to render commercially profitable their separation and recovery as by-products, it is essential that compounds such as the aliphatic acids, at least the more readily separable sulfur compounds, nitrogen bases and phenolic compounds, be removed in advance so that the sulfation and hydrolysis reactions, as well as their products, will not be interfered with or contaminated by the presence of these impurities. Also it is found that for most complete

and efficient removal of all such impurities in the treating stages ahead of sulfation, it is of importance that the impurities be selectively removed in an order involving first the extraction of the water-soluble impurities, followed by the removal of others in a subsequent stage involving treatment with either or both alkali metal carbonate and alkali metal hydroxide solutions.

All the various objects and details of the invention will be understood most readily and to better advantage without necessity for a preliminary discussion, by reference to the accompanying drawing illustrative of the treating sequence in flow sheet form.

The pressure distillate, taken for example from storage **10**, is pumped through line **11** alternately, as for treatment batchwise, into tanks or columns **12** which may be of any suitable type wherein the distillate may be brought into intimate contact and thorough admixture with a treating liquid, which in this first stage consists of water delivered through line **13**. As illustrative of equipment in the form of columns, suitable for effecting intimate contact between the distillate and water at this stage, or with reagent solutions in the later described stages, I may use treating columns of the type disclosed in my issued Patents Nos. 2,158,690 and 2,179,008. Water washing of the distillate at atmospheric temperature, and using volumes of water that may be as high as the volume of distillate, I extract from the distillate those water-soluble compounds such as aliphatic acids, some sulfur compounds, nitrogen compounds, e. g. bases and any water soluble phenols. The wash water may be separated by gravity and sent to disposal through line **14**.

Leaving columns **12**, the water washed distillate is passed through lines **15** to what may be regarded generally as a second treating stage conducted in columns or tanks **16** and **17**, which may include provision for the treatment of the distillate with either or both dilute alkali metal carbonate and alkali metal hydroxide solutions. Preferably the distillate passes first into columns **16** wherein it is contacted with a dilute, e. g. about 5% to 10%, sodium carbonate solution introduced through line **18**. The quantity of the carbonate solution (as in the case also of the later used sodium hydroxide solution) may vary depending upon the quantities of impurities to be removed from the distillate. The effect of the sodium carbonate solution treatment is to remove some sulfur compounds and organic acids. The spent sodium carbonate solution is sent to disposal through line **19**, and the treated distillate is passed through lines **20** to be contacted in columns **17** with a dilute (e. g. 5% to 10%) sodium hydroxide solution introduced through line **21**. At this stage other sulfur compounds and phenolic bodies not soluble in the water and sodium carbonate solutions previously used, are extracted and sent to disposal through the spent caustic solution line **22**.

The distillate then is taken through lines **23** to tanks or columns **24** wherein the distillate is contacted with relatively dilute sulfuric acid solution introduced through line **25**. The acid concentration preferably is kept low within the range of about 1% to 10% acid, although depending upon the character and reactivity of the olefinic content of the distillate, the acid concentration may run as high as 50%. In this stage those olefins and diolefins present in the distillate and which are reactive with the dilute acid solution, are sulfated at about atmospheric temperature, using at least a stoichiometric quantity of the acid as required for sulfation of these olefins and diolefins which it is desired to sulfate, or which are capable of sulfation at an acid concentration under 50%. The sulfated olefins and diolefins immediately are hydrolyzed by the water to form alcohols, substantial quantities of which are soluble in the distillate. The spent acid is removed from columns **24** through line **26**.

The acid treated distillate with its alcohol content may be passed directly through lines **27** into chambers or columns **28** containing a granular bed of solid adsorbent, silica gel, bauxite, or fuller's earth, any of which may be activated by, for example, sulfuric acid or its equivalent. Passage of the distillate into chambers **28** may or may not be preceded by a water wash. The adsorptive earth has selective adsorptive affinity for the alcohols, so that in the course of flow of the distillate batchwise through one and then the other of the chambers **28**, the adsorbent removes and retains the alcohols from the distillate stream flowing out through lines **29** to the next treating stage. At such time as the adsorbent in either of the chambers **28** approaches such saturation by the alcohols, the adsorbent is treated, with or without removal through either of lines **30**, for recovery of the alcohols. The alcohol recovery may be by desorption involving washing the adsorbent at stages **31** with an alcohol of sufficiently high molecular weight, usually heavier than ethanol, to dissolve the adsorbed alcohols out of the adsorbent. The adsorbent may be reused and the alcohol solution taken through lines **32** for separation (distillation) of the solvent, and recovery of the product alcohols. Preferably however the alcohols are recovered by steam extraction from the adsorbent, as by introducing steam alternately to the chambers **28** from line S as each adsorbent charge becomes saturated with the alcohols. The latter thus are vaporized out of the adsorbent and conducted through line **30***a* to one or more fractionators F, wherein the alcohols, as by steam distillation are separated into such fractions as may be desired.

The distillate treated up to this point may be sent through line **29** to a known type of low temperature concentrated acid treating plant diagrammatically indicated at **33**, wherein the distillate is treated at a temperature that may range between about 0° F. to 32° F. with strong acid ranging in concentration from 95% sulfuric acid to the fuming acid. This stage in itself corresponds to the widely used treatment known as the cold acid process. At this stage the higher molecular weight olefins, not sulfatable by the previously used dilute sulfuric acid treatment, undergo sulfation for subsequent hydrolysis to form alcohols.

From the low temperature concentrated sulfuric acid treatment in stage **33**, the oil and acid mixture goes through line **34** to a sludge separator **35** from which the treated distillate is taken through line **36** to alkali neutralizer **37**, the distillate thence flowing through line **38** to tank **39** to be washed by water introduced through line **40**, the completely refined distillate thence being taken through line **41** to storage. From separator **35** the cold acid sludge is taken through line **42** to tank **43** wherein the sludge may be mixed with up to about equal parts of water, depending upon the sludge content of compounds hydrolyzable to produce alcohols. The aqueous mixture in tank **43** is maintained at low temperature, preferably within the 0° F. to 32° F. range, in order that the hydrolysis may occur without loss of valuable compounds through polymerization. From tank

43 the alcohols are taken through line **44** for fractionation in one or more fractionating columns **45** to effect such separation of the alcohols as may be desired.

I claim:

1. For the treatment of cracked hydrocarbon distillates containing impurities (1) of the class consisting of water soluble aliphatic acids and nitrogenous compounds, (2) sulfur compounds, organic acids and phenolic compounds, (3) lower molecular weight olefins and diolefins sulfatable by dilute acid and hydrolyzable to form correspondingly lower molecular weight alcohols, and (4) higher molecular weight olefins sulfatable by concentrated acid to form correspondingly high molecular weight alcohols; the process that includes first water washing said distillate to remove therefrom water soluble impurities including said aliphatic acids and nitrogenous compounds, separating the wash water from the distillate, then in a second stage removing sulfur compounds, organic acid and phenolic impurities from the washed distillate, contacting the distillate with a water solution of between 1% to 50% sulfuric acid to sulfate lower molecular weight olefins and diolefins in the distillates and form lower molecular weight alcohols by hydrolysis of the sulfated compounds, contacting the resulting distillate with solid adsorbent to selectively adsorb thereon the alcohols formed, separating the distillate from the adsorbent, recovering the alcohols from the adsorbent, treating the distillate in a final treating stage with concentrated sulfuric acid solution to remove therefrom sulfur compounds and form sulfated olefins, and separating the resulting acid liquor from the distillate.

2. The process as defined in claim 1, in which the distillate is treated in said second stage with a dilute alkali metal hydroxide solution.

3. The process as defined in claim 1, in which the distillate is treated in said second stage successively with dilute alkali metal carbonate and dilute alkali metal hydroxide solutions.

4. The process as defined in claim 1, in which said adsorbent containing the adsorbed alcohols is treated with steam to separate the alcohols therefrom.

5. The process as defined in claim 1, in which said adsorbent containing the adsorbed alcohols is treated with a solvent to separate the alcohols therefrom.

6. The process as defined in claim 1, in which the distillate in said final treating stage is treated at a temperature between about 0° F. to 30° F. with acid ranging in concentration from about 92% to fuming sulfuric acid.

7. The process as defined in claim 6, in which the aqueous acid residue separated from the distillate in the final treating stage is mixed with water to form oil and aqueous alcohol-containing phases, and the alcohols are recovered from the aqueous phase.

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