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PROCESS OF REGENERATING CAUSTIC ALKALI SOLUTIONS

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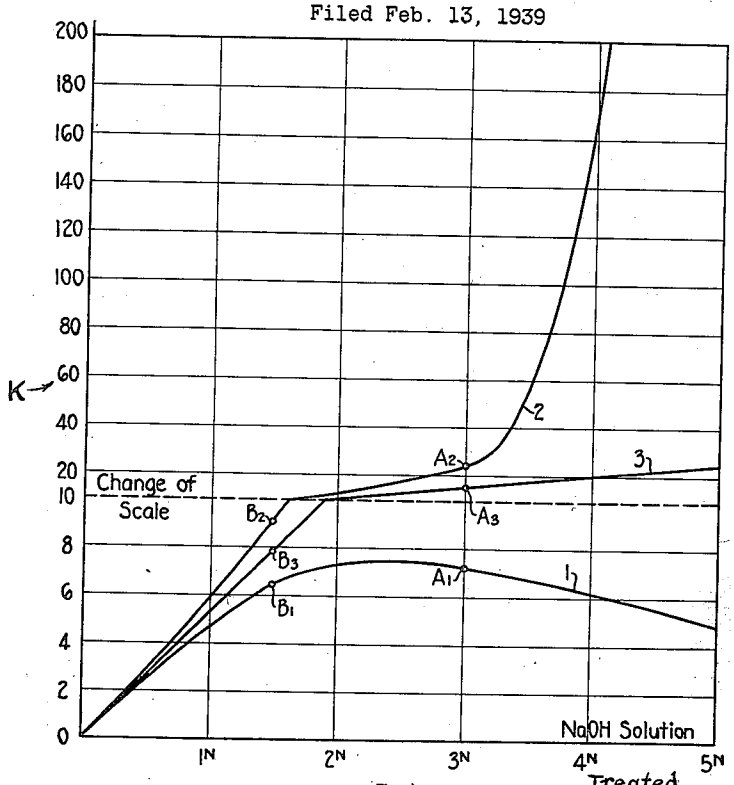


Fig. 1.

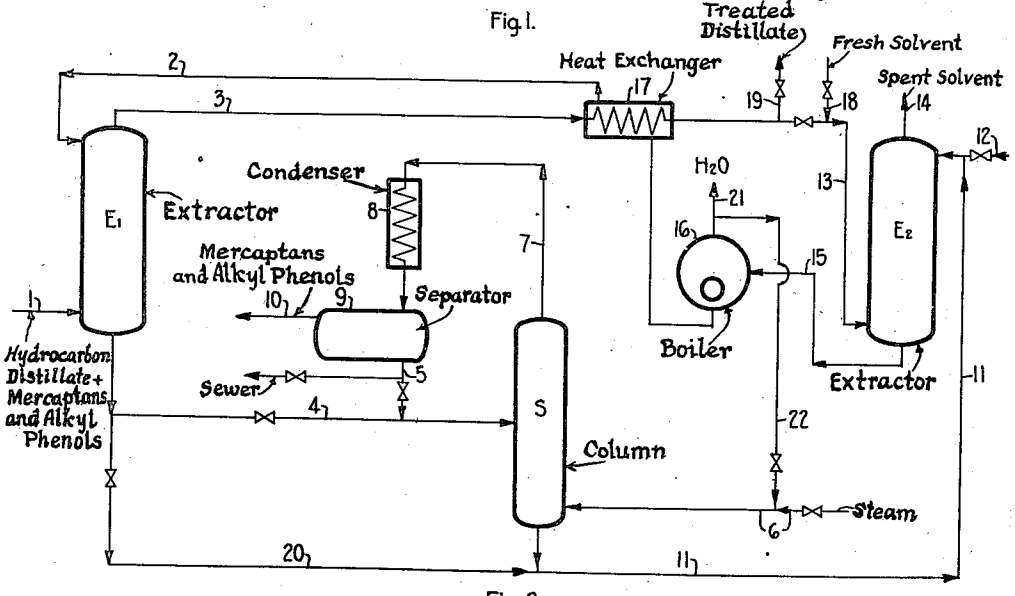


Fig. 2.

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PROCESS FOR REGENERATING CAUSTIC ALKALI SOLUTIONS

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6 Claims. (Cl. 260—609)

This invention relates to the removal of weakly acidic organic compounds from aqueous caustic alkali solutions containing same and substantial amounts of solubility promoters for said compounds, and more particularly relates to a process for the regeneration of spent aqueous caustic alkali solutions of this type by a solvent scrubbing method which, if desired, may be used in conjunction with steam stripping.

It is a purpose of the present invention to remove weakly acidic organic compounds, such as those having dissociation constants below about 10^{-5} and which occur naturally in hydrocarbon oils or may be produced by cracking, e. g. mercaptans, phenols, thiophenols, alkyl phenols, etc. from aqueous caustic alkali solutions, particularly those caustic alkali solutions which have been used for the extraction of the acidic compounds from hydrocarbon oils and which contain substantial amounts of solubility promoters for said acidic compounds.

As described in our U. S. Patents Nos. 2,152,720; 2,152,166; 2,149,379; 2,160,632; 2,164,851; 2,152,722, we have found that certain substances, when added to aqueous caustic alkali treating solutions in substantial amounts, greatly enhance the solubility of organic acidic substances therein.

It has been shown that solubility promoters to be suitable must combine the following properties: high specific solubility promoting power, i. e., ability to raise the solvent power of the aqueous caustic alkali for the free organic acids by a relatively large amount for a unit weight addition of the promoter to the aqueous caustic alkali; high solubility of the promoter in the aqueous caustic alkali; and very low solubility of the promoter in the hydrocarbon or other organic water-insoluble liquid containing the organic acids. Moreover, the promoter must be chemically and physically inert to the action of caustic alkalis even at the elevated temperatures of steam stripping.

Among the many substances which combine the above properties in varying degrees, the following were found most suitable: mono-, di- and tri-amino or hydroxy alkyl amines in which the alkyl groups contain 2 or 3 carbon atoms; diamino propanol; polyhydric alcohols or derivatives thereof having at least 1 carbon atom in excess of polar radicals, a ratio of carbon atoms to hydroxyl radicals of at least 1½ and a ratio of carbon atoms to polar radicals not in excess of 2½, examples being propylene glycol, butylene glycols, alkyl glycerines in which the alkyl radical has from 2 to 4 carbon atoms, mono alkyl glycerine ethers in which the alkyl radical has 1 or 2 carbon atoms, di- and tri-ethylene glycol, beta amino beta' hydroxy diethyl ether, di- and tri-ethylene glycol mono alkyl ethers in which the alkyl radical has from 1 to 3 carbon atoms; diamino alcohols of 3 to 5 carbon atoms, etc. Very effective are also the alkali metal salts of alkyl phenols and of certain carboxylic acids, such as fatty acids having 2 to 6 carbon atoms, notably potassium isobutyrate, or of amino or hydroxy fatty acids having 3 to 7 carbon atoms, especially potassium alpha hydroxy n-butyrate; or of phenyl acetic acids, etc.

The amounts of solubility promoters normally employed in solution of the aqueous caustic alkali vary between the approximate limits of 15% to 85%, and preferably 25% to 75% in the case of neutral and basic compounds. In the case of salts, the aqueous caustic alkali is preferably substantially saturated therewith, or at least nearly so.

Various caustic alkalis may be used. While alkali metal hydroxides are preferred, ammonia, quaternary ammonia bases, alkali metal carbonates, etc., may also be suitable.

The efficiency of the extraction of the organic acids from their solutions in organic water-insoluble soluble solvents by means of aqueous caustic alkalis has been expressed by the factor K. in which

$$K = \frac{\text{concentration of salts of the organic acid in aqueous phase}}{\text{concentration of free organic acids in organic liquid phase}}$$

We have found that K may be increased in two ways, (1) by the addition of solubility promoters to the caustic alkali solution, or (2) under limited circumstances by increasing the concentration of the caustic alkali in the aqueous solution. It may, therefore, be seen that when it is desired to do the opposite, i. e., to remove weak organic acids from their caustic alkali aqueous solutions by scrubbing with an organic solvent for the acids, the most efficient removal may occur when the caustic alkali solution is diluted, i. e., when the value of K is low.

Our invention thus comprises removing weak organic acids, particularly those having dissociation constants below about 10^{-5}, from aqueous solutions of caustic alkali containing said acids and substantial amounts of solubility promoter, by first diluting the solutions with water and

thereafter scrubbing the resulting diluted solutions with a solvent for organic acids.

Solvents to be suitable should be substantially immiscible with the aqueous caustic alkali solutions, and should be chemically inert to the action of the caustic alkali under the conditions of the extraction.

Suitable solvents are, for example, hydrocarbon distillates such as gasoline, kerosene; substantially pure liquid hydrocarbons as pentane, hexane, benzene, toluene, xylene; chlorinated hydrocarbons as ethylene dichloride, chlorpropane; higher alcohols as octyl alcohols; ethers as diisopropyl ether, dibutyl ethers, etc. While many polar solvents such as diisopropyl ether, etc., may be better solvents for the organic acids than hydrocarbons and may even dissolve some salts of the organic acids, we often prefer to use the latter because of certain advantages which are disclosed later.

The above-mentioned effect of dilution on the K value is more fully explained in connection with Fig. 1 of the drawing. In Fig. 1 a coordinate system is shown in which K is plotted on the ordinate against the normalities of caustic soda solutions of various degrees of dilution, when extracting normal butyl mercaptan therewith from a gasoline. Three cases may be distinguished as indicated by curves 1, 2 and 3, respectively.

Curve 1 shows the change of K for the normal butyl mercaptan with concentration of the caustic soda solution in the absence of a solubility promoter. It begins at about zero value for K, rises approximately as a straight line over a short distance and then drops off with increasing normality of the caustic soda solution. This drop in the value of K in spite of increasing alkalinity of the aqueous solution beyond a certain point is due to the salting out of the free mercaptan by the dissolved caustic soda in the aqueous solution, the free mercaptan being in equilibrium with the dissolved mercaptide.

Curve 2 represents the change of K with changing concentration or dilution of a caustic soda solution containing two parts by weight of sodium isobutyrate for each part of caustic soda. Obviously, the ratio of caustic soda to isobutyrate remains the same over the entire range of concentrations up to the point of saturation of one of the dissolved components. This curve begins like curve 1 at about zero value for K, but instead of dropping back, turns strongly upward. In other words, the presence of the isobutyrate completely overcomes the salting out effect, and with increasing alkalinity of the solution and a proportionate increase in the isobutyrate concentration, K increases at a greater rate than is proportional to the increase of the normality of the caustic soda solution.

Curve 3 represents the boundary case in which the caustic soda solution contains the minimum amount of solubility promoter necessary to overcome the salting out effect and is therefore essentially a straight line.

Now when attempting to improve the removal or scrubbing of weak organic acids from their solution in caustic alkali by the expedient of dilution, another factor besides the value of K must be taken into consideration, namely, the increased volume of the aqueous solution. In order to gain anything by dilution, it is necessary that the drop in the K value be larger than the proportionate increase in the volume. Thus, if the volume of the aqueous solution is doubled by diluting it with an equal volume of water, no increased removal efficiency of the organic acids will result unless the K value of these acids is reduced to less than half of its former value.

Referring again to curve 1, it will be seen that in the low normality range below about 1N, dilution has the effect of increasing the volume and lowering the K value in approximate inverse proportion. In the range of higher normality, however, the change in K is less than inversely proportional to the increase in volume, the latter resulting, within a certain range, in an increase in K. For example, K for a 3N caustic soda solution in the absence of a solubility promoter is 7.2, as indicated by point A_1. If now this caustic solution is diluted with an equal volume of water, the volume of the solution is doubled, but the K is reduced only from 7.2 to 6.5, the latter point being indicated by B_1. This means that the scrubbing efficiency on the basis of equal volumes of caustic soda solution is improved by the factor

$$\frac{7.2}{6.5}=1.1$$

but on the basis of actual volumes the net efficiency is lowered by the factor 0.55.

If we now consider points A_2 and B_2 on curve 2, it will be seen that K is lowered from 25 to 9.2 upon diluting the caustic soda solution with an equal volume of water. This will result in a net improvement of the scrubbing efficiency based on actual volumes of

$$\frac{25}{9.2\times 2}=1.36$$

times the original scrubbing efficiency.

The above comparison clearly shows that dilution for the purpose of removing weakly acidic organic substances from alkaline solutions of their salts by scrubbing with an organic solvent for the acids is beneficial for all solutions which contain amounts of solubility promoters at least sufficient to compensate for the salting out of the free acids from their aqueous solutions by the caustic alkali.

A further increase in removal efficiency may be obtained by raising the temperature at which the acidic substances are extracted from the caustic aqueous alkali solution. The temperature of the removal, therefore, is preferably as high as practical, and is limited only by the boiling temperature of the solutions and/or solvents used in this treatment. Superatmospheric pressure may be employed so that the extraction may be carried out at a temperature higher than the normal boiling temperatures of any of the solutions. Preferably the temperature is over 60° C.

To give a specific example of the way in which the present invention can be utilized, reference is had to our copending patent application Serial No. 174,512, filed November 15, 1937. In that application it was shown that in extracting mercaptans from hydrocarbon distillates with caustic alkali solutions containing solubility promoters for mercaptans, the spent caustic alkali solution may be regenerated by steam stripping most effectively if the solution is diluted with water before being steamed. However, in that process it is frequently desirable to extract hydrocarbon solutions, which contain alkyl phenols as well as mercaptans. Since alkyl phenols are set free only to a small degree by steaming, it has been found that alkyl phenols remain in the caustic alkali treating solution, and build up upon recirculation to an undesirable degree, an ex-

cess of alkyl phenols causing the treating solution to become excessively viscous. However, by combining the two inventions, it has been found that hydrocarbons containing alkyl phenols can be treated with caustic alkali solutions, which can be regenerated with steam followed by a solvent extraction process, so that alkyl phenols do not unduly build up in the treating solutions.

The above example is illustrated in Fig. 2, representing a flow diagram of a regenerative extraction process for weak organic acids from hydrocarbon distillates, which diagram includes our invention of scrubbing the spent caustic alkali solution with a solvent for the acids, preceded by dilution with water.

A hydrocarbon distillate, which may contain both mercaptans and alkyl phenols, is introduced near the bottom of extractor E_1 through line 1, E_1 being of conventional design adapted to the contacting of two substantially immiscible liquids and preferably containing packing or other means of effecting intimate contact between the two liquids. A caustic alkali solution containing sufficient solubility promoter at least to compensate for the salting out of mercaptans and alkyl phenols by the dissolved caustic alkali is introduced near the top of extractor E_1 through line 2. Treated hydrocarbon distillate being at least partially freed of mercaptans and alkyl phenols, is removed from the top of E_1 through line 3. The foul caustic alkali solution, which now contains salts of mercaptans and alkyl phenols, is removed from E_1 through line 4. Water of dilution may be added through line 5, and the resulting diluted solution is introduced into a column S, preferably under superatmospheric pressure. Steam is admitted into the column S through line 6, either from an outside source not shown or from within the process as will be explained later, and the mercaptans, along with the steam and a small amount of the alkyl phenols are taken overhead through line 7, are condensed by condenser 8 and introduced into separator 9. In this separator, two layers are formed, an upper oily layer containing the mercaptans and those alkyl phenols which were taken overhead, and a lower aqueous layer. The upper layer is withdrawn through line 10 and the lower layer may be reintroduced as water of dilution into the foul caustic alkali solution through line 5, or may be discarded. The caustic alkali solution, which is now substantially free of mercaptans but which may be diluted by the condensed steam used for steaming off the mercaptans is removed from F through line 11. If it is undiluted or insufficiently diluted, water of dilution is added through line 12 and the diluted solution is introduced into scrubber-extractor E_2 near its top, E_2 being similar in design to E_1. A solvent for alkyl phenols, which may or may not be the same distillate which was treated in extractor E_1, is introduced through line 13 near the bottom of the scrubber-extractor E_2 to scrub out as much as possible the alkyl phenols and other remaining weak acids from the caustic soda solution. Spent solvent which contains a substantial portion of the alkyl phenols is removed from the top of the extractor E_2 through line 14. The scrubbed dilute caustic alkali solution, now having substantially reduced contents of both the mercaptans and alkyl phenols, is withdrawn through line 15, and is reconcentrated in boiler 16 to its original strength, to be recirculated through line 2 into extractor E_1. Steam produced in the boiler may be withdrawn through line 21 or may be returned through lines 22 and 6 to the stripping column S to be used in the stripping of the mercaptans. Since the regenerated caustic alkali solution is hot as it leaves boiler 16, it can advantageously be placed in heat exchanging relationship with the distillate entering extractor E_2 by means of heat exchanger 17, since, as pointed out above, increasing the temperature in the scrubbing step lowers the value of K which governs the efficiency of this step. Alkyl phenols being valuable as gum inhibitors for the distillate, the distillate originally containing the alkyl phenols may be used advantageously for scrubbing the dilute caustic alkali solution. However, if desired, a different solvent may be used, provision being made for its introduction through line 18 and for the withdrawal of the distillate treated in E_2 through line 19. As an alternative of the above process, if it is not desired to include a steam stripping operation, the spent caustic alkali solution from extractor E_1 may be by-passed through lines 20 and 11 directly to the top of the scrubber-extractor E_2.

While in the foregoing we have described a preferred form of our process, it shall be understood that many modifications are within the scope of our invention. In particular, it shall be understood that the addition of pumps, coolers, heat exchangers, heaters, by-passes, etc., not shown in the flow diagram, is within the skill of the average designer for such equipment.

The following example further illustrates our invention:

A sample of an aqueous 6N KOH solution containing 135 grams per liter potassium isobutyrate and 135 grams per liter alkyl phenolate was scrubbed with 10 volumes of a gasoline. The amount of alkyl phenols dissolved in the gasoline after the scrubbing treatment was estimated by measuring the oxygen bomb induction period of the resulting gasoline, which period was 4.0 hours.

Another sample of the same aqueous KOH solution was then diluted with an equal amount of water, and the resulting dilute solution was scrubbed with 5 volumes of the same gasoline, which developed an induction period of 13.1 hours. Since the induction period is approximately proportional to the content of inhibitors, it may be said with fair accuracy that after dilution more than 3 times the amount of alkyl phenol was scrubbed out than prior to the dilution.

We claim as our invention:

1. In a regenerative process wherein weakly acidic organic substances having dissociation constants below 10^{-5} are extracted from hydrocarbon oils containing them with an aqueous solution of caustic alkali containing dissolved therein alkali metal salts of fatty acids having 2 to 6 carbon atoms in an amount sufficient at least to compensate for salting out of said weak acids from the aqueous caustic alkali solution, to produce a treated oil and a fat aqueous solution, the latter containing absorbed said weakly acidic organic substances, and wherein said fat solution is regenerated by scrubbing to produce a regenerated aqueous solution containing substantially all of said solubility promoter but having a reduced content of said organic acids, the improvement comprising diluting said fat solution with water and thereafter scrubbing the diluted solution with an organic solvent for said weakly acidic substances, which solvent is insoluble in and inert to said caustic alkali solutions under conditions of scrubbing, thereby removing from the fat solu-

tion weakly acidic substances having dissociation constants below 10^{-5} without removing fatty acids.

2. The process of claim 1 in which the scrubbing is carried out at a temperature above 60° F. but below the boiling temperatures of the solvent and the caustic alkali solution.

3. The process of claim 1 in which the extraction is carried out under superatmospheric pressure at temperatures higher than the normal boiling point of either the solvent or the caustic alkali solution.

4. The process of claim 1 in which the solvent is a normally liquid hydrocarbon distillate.

5. The process of claim 1 in which the solvent is diisopropyl ether.

6. The process of claim 1 in which the fatty acid is isobutyric acid.

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