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PROCESS FOR PURIFYING NAPHTHENIC ACIDS

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The present invention relates to naphthenic acids, and more particularly to a new process for treating these acids with some of the well known inorganic acids.

5 Naphthenic acids, such as might be obtained from the alkali wastes arising during the refining of petroleum or shale oil fractions, constitute a complex mixture of acidic compounds containing primarily carbon, hydrogen and oxygen. They
10 range from comparatively low boiling liquids to materials which are semi-solid and even solid at ordinary temperatures. Their viscosities are well as the boiling points of these substances are directly proportional to the viscosities and boiling
15 points of the hydrocarbon fractions in which they were originally present.

The crude naphthenic acids which are derived by acidifying alkali wastes formed during the treatment of various hydrocarbon fractions contain varying amounts of carbonaceous materials.
20 One of the essential steps in the refining of crude naphthenic acids comprises the removal of phenolic materials. This is carried out by a careful acidification and distillation of the substance as described in greater detail further below. This
25 procedure however increases the quantity of the carbonaceous materials present in the crude naphthenic acids, and the thus dephenolized naphthenic acids have been found to contain as much
30 as 3 to 5% and even more of these carbonaceous materials. The major portion of the carbonaceous material exists in a finely suspended or colloidal state and cannot be removed either by settling or centrifuging. The naphthenic acids
35 containing such materials have a dark and turbid color, thereby rendering them practically useless as a commercial product.

The term "alkali wastes" occurring in the present specifications is meant to include the
40 products obtained by treating with a caustic solution an extract resulting from a treatment of hydrocarbon fractions with liquid sulfur dioxide, as well as any other alkaline products or wastes arising from the refining of petroleum
45 fractions.

To produce a commercial product, it has been customary to distil the naphthenic acids to remove the admixed carbonaceous material, and then to treat the overhead product to remove
50 therefrom the dark color and foul odor. However, this distillation was usually accompanied by a plugging of the still due to the presence of the undesirable materials, and the overhead product obtained during such distillation was not
55 materially improved in color.

It is therefore the main object of the present invention to provide a simple and thoroughly satisfactory process for the removal from crude or semi-refined naphthenic acids of the carbonaceous materials admixed therein. It is a
5 further object of the present invention to provide a process of treating crude or semi-refined naphthenic acids to remove therefrom the dark color and foul odor.

It was previously known that the carbonaceous
10 materials and color-producing bodies may be removed from the crude naphthenic acids without any distillation by treating the naphthenic acids, either in the crude or dephenolized state, with inorganic acids. However, it has been found that
15 it was necessary to use diluted concentrations of such acids since the stronger concentrations did not produce any removal of the carbonaceous materials and/or color producing bodies. It was therefore previously necessary to use the inorganic
20 acids, such as sulfuric acid, having a concentration strength of between 50 and 85%, since the use of acids substantially in excess of 85% tends to cause the acid to become miscible with
25 the naphthenic acids, so that while some slight separation does occur during treatment with such concentrations of inorganic acids, the treating loss becomes so great that the process is uneconomical. The treatment of crude or semi-refined
30 naphthenic acids with acids having a comparatively low concentration is uneconomical in that quite large quantities of this treating product are necessary to effect the deposition of the carbonaceous materials and color bodies in the form of a sludge. This process of using acids of weak
35 concentration also necessitated the use of diluents, such as a low boiling hydrocarbon solvent, these diluents aiding in a more rapid and efficient purification of the naphthenic acids.

It has now been discovered that the crude or
40 dephenolized acids (which latter are herein designated as semi-refined acids) may be purified by treating them with sulfuric acid having a strength or concentration above 100% of H_2SO_4 . It has been further discovered that such treatment
45 necessitates the use of a comparatively small percentage of the fuming sulfuric acid. Thus, while amounts of this reagent in the neighborhood of 10 to 15% do not give any appreciable sludge separation or color improvement, apparently due
50 to the solvent effect of the naphthenic acids on excess reagent, the treatment of the crude or semi-refined naphthenic acids with amounts of the fuming sulfuric acid in the neighborhood of one-half to five percent cause the precipitation
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of a quick breaking sludge and produce a naphthenic acid which, after further treatment as described hereinbelow, is of a color superior to that of the acids refined with large amounts of low strength inorganic acid. It has been still further found that it is necessary to employ the sulfuric acid of a concentration in excess of 100% and in the amounts of about one-half to five percent since greater amounts of the reagent when used for the treatment of the naphthenic acids tend to be miscible with said naphthenic acids or else react with them, while concentrations of less than 100% tend to emulsify the naphthenic acid. In other words, the quantity of sulfuric acid having a concentration of over 100% to be used in treating crude or semi-refined naphthenic acid must be such that the inorganic acid does not remain in solution in the naphthenic acid but reacts only with the carbonaceous and other foreign bodies in said naphthenic acid to form an immiscible sludge. Such a reaction causes the precipitation of these undesirable materials in the form of a sludge, leaving naphthenic acid which, after a treatment with an adsorbent material, has no foul odor and a very good color.

Therefore, the present invention may be said to reside in the process of purifying impure naphthenic acids which comprises treating them with relatively small percentages of sulfuric acid having a concentration in excess of 100%, said treatment tending to remove the suspended carbonaceous materials present in the naphthenic acids and to improve the color thereof as well as to render them more susceptible to color improvement upon subsequent treatment.

The invention further resides in a process for purifying crude or semi-refined naphthenic acids which comprises commingling said impure naphthenic acids with quantities of fuming sulfuric acid (i. e. acid having a concentration in excess of 100%) insufficient to result in miscibility of acids and sludge but only sufficient to react with the suspended carbonaceous materials and other foreign bodies in said naphthenic acids, whereby said carbonaceous and foreign materials are caused to precipitate from the acids being purified in the form of a sludge, and whereby the thus purified naphthenic acids, after a subsequent treatment with an adsorbent material, such as clay or fuller's earth, have good color and odor.

The invention may further be stated to reside in a process for purifying crude or semi-refined naphthenic acids which comprises treating them with substantially one-half to five percent of fuming sulfuric acid.

It is, of course, obvious that the treatment of the impure naphthenic acids with the above small quantities of highly concentrated sulfuric acid must be carried out within certain definite temperature limits. It has been still further discovered that the best results may be obtained if the treatment is carried out within the temperature range of 100 to 175° F. and that the best results have been obtained at a temperature of 135° F.

Therefore, the invention still further resides in a process for treating impure naphthenic acids which comprises treating them at a temperature of between 100 and 175° F. with quantities of sulfuric acid, having a concentration in excess of 100%, only sufficient to cause the precipitation of the impurities in the naphthenic acid, and not sufficient to cause miscibility between the two acids and the sludge.

It has been still further discovered that a treatment of impure naphthenic acids with fuming sulfuric acid according to the present process does not require any subsequent vacuum distillation to improve color and odor of the acids being treated. Instead of this distillation step, the desired result is obtainable by following the acid treatment with a treatment using an adsorbent material, such as clay, or by some similar simple filtration step.

In carrying out the process of extracting and refining naphthenic acids, an alkali waste, such as might be obtained by treating crude kerosene or a liquid sulfur dioxide extract thereof with sodium hydroxide, is acidified so that it is slightly acidic toward phenolphthalein. Such a procedure prevents the liberation of the naphthenic acids from the alkaline metal salts, the naphthenates remaining as sodium naphthenates. The resulting mixture of these sodium naphthenates, phenols and admixed hydrocarbons is then steam distilled. If desired, distillation may be carried out in the presence of small quantities of Edeleanu extract or of similar liquid hydrocarbons. The added substance may be the same as the one from which the phenols and naphthenates were obtained by the above described acidification. The function of the added extract, or of its equivalent, is to prevent frothing during distillation of the mixture of sodium naphthenates, phenols and hydrocarbon oils. The distillation, which as stated above, is preferably carried out in the presence of steam, permits the removal of the hydrocarbon oils and phenols, the sodium naphthenates remaining in the still. The sodium naphthenates thus remaining as a residue are then dissolved in water and treated with sulfuric acid to produce naphthenic acids which contain only very small amounts of phenols and admixed hydrocarbons. The naphthenic acids thus produced are of a poor color, contain considerable amounts of insoluble carbonaceous material and possess a foul odor. The major portion of this carbonaceous material and color-producing bodies (which are present in these naphthenic acids in amounts varying from 2 to 5% or higher) exists in a finely suspended or colloidal state so that it is not removable by settling or centrifuging. The presence of these materials constitutes a serious objection in the marketing or further refining of the thus semi-refined or dephenolized naphthenic acids, and it is the refining of these semi-refined naphthenic acids which constitutes one of the objects of the present invention.

In carrying out the refining of the thus obtained semi-refined naphthenic acids according to the present process, a charge of naphthenic acids to be purified is commingled and agitated at a temperature of about 100 to 175° F. with a small quantity of sulfuric acid having concentration above 100%. This quantity of the fuming sulfuric acid reagent must be such that the inorganic acid does not result in complete miscibility of acids and sludge but is only sufficient to cause the coagulation of the undesirable carbonaceous and color-producing bodies and the precipitation of the thus produced sludge from the solution. Although the quantity of the reagent necessary depends to a great extent on the amount of the undesirable constituents in the impure naphthenic acids, it has been found that ordinarily one-half to five percent by volume is sufficient to produce the desired result, and that good results have been obtained with

the use of about four percent of fuming sulfuric acid.

After the removal of the sludge from the supernatant naphthenic acids the latter may be water-washed and clay treated. The resulting naphthenic acids have a higher organic acidity as compared with the acid number of the original semi-refined acids. Also, the thus refined naphthenic acids have a six to seven N. P. A. color, being transparent when viewed through a four ounce oil sample bottle, whereas the same acids before refining were black and had no such transparency. The thus refined naphthenic acids also possess a much larger degree of fluidity than the crude product, are free from admixed carbonaceous materials, and have a sweet odor.

The same semi-refined naphthenic acids, when treated with approximately the same quantities of fuming sulfuric acid at temperatures below 100° F. and above 175° F. did not produce satisfactory results in that the carbonaceous materials did not precipitate in the form of a sludge.

As a modification of the above described method of operation, in which special precautions were first taken to remove the phenols from the crude naphthenic acids, the fuming sulfuric acid treatment may be employed in purifying crude naphthenic acids, i. e. those from which the phenols have not been removed. In such a case, the naphthenate soaps containing the phenols are first treated with sulfuric acid of any strength for the purpose of liberating the naphthenic acids. The water produced during this treatment is then removed, and the resultant mixture of naphthenic acids and phenols is then treated, according to the present invention with small quantities of fuming sulfuric acid only sufficient to cause the carbonaceous materials in said mixture to precipitate in the form of a sludge. Obviously, the above method of operation is applicable in cases where the presence of phenolic materials together with the naphthenic acids is not undesirable.

Although the term "fuming sulfuric acid", as used in the petroleum industry, means a sulfuric acid of a concentration of about 103%, within the meaning of the present disclosure it includes sulfuric acids of a concentration above 100%.

This invention is not limited to any specific example herein set forth, nor to naphthenic acids derived from any particular hydrocarbon frac-

tion as all naphthenic acids derived from any source, may be refined thereby. As to the scope of this invention, reference is made to the appended claims.

I claim:

1. In a process for purifying naphthenic acids contaminated with carbonaceous materials, the step of contacting said acids at a temperature substantially between 100° F. and 175° F. with a quantity of sulfuric acid having a concentration above 100%, said quantity of sulfuric acid being only sufficient to cause precipitation of said carbonaceous materials.

2. A process according to claim 1, wherein the acid treatment is followed by a treatment with an adsorbent material.

3. In a process for purifying naphthenic acids contaminated with carbonaceous materials, the step of contacting said acids at a temperature substantially between 100° F. and 175° F. with quantities of fuming sulfuric acid only sufficient to cause precipitation of said carbonaceous materials, but insufficient to cause miscibility between the acid and the precipitated carbonaceous materials.

4. A process according to claim 3, wherein the quantity of fuming sulfuric acid is substantially between one-half of one percent and five percent by volume of the naphthenic acid being treated.

5. A process for deodorizing and decolorizing impure naphthenic acids which comprises treating said acids at a temperature substantially between about 100° F. and 175° F. with fuming sulfuric acid in a quantity sufficient to cause the precipitation of the impurities in the form of a sludge, but insufficient to cause miscibility between the acids and the thus formed sludge, and subsequently treating the naphthenic acids with an adsorbent material.

6. In a process for purifying naphthenic acids contaminated with carbonaceous materials the steps of contacting said acids with a quantity of sulfuric acid having a concentration above 100% only sufficient to cause precipitation of said carbonaceous materials but insufficient to cause miscibility between the acid and the precipitated carbonaceous materials, and operating within such temperature range that said precipitation of carbonaceous materials is effected.

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