

## UNITED STATES PATENT OFFICE

2,108,448

## PURIFICATION OF NAPHTHENIC ACIDS

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No Drawing. Application July 3, 1933,  
Serial No. 678,996

3 Claims. (Cl. 260—108)

This invention relates to the preparation of naphthenic acids from petroleum oils and to the purification of the same for use in the arts and industries. In particular, it refers to the preparation of naphthenic acids which do not contain appreciable quantities of unsaponifiable matter of molecular weight or boiling point range similar to those of the separated and purified acids, which are practically colorless, and which possess none of the strong sour odors commonly associated with naphthenic acids as heretofore prepared.

As used herein, the term "naphthenic acids" is intended to apply to the naturally occurring carboxylic acids of petroleum oils, ordinarily removable from crude petroleum oils or their distillates by treating with a dilute aqueous alkaline solution; it is not intended that the term shall apply to the so-called petroleum sulfonic acids which are formed when petroleum oils or their distillates are treated with a strong sulfuric acid or with sulfuric anhydride.

Ordinarily, naphthenic acids are obtained by washing a petroleum oil or its distillate with a dilute caustic alkali solution; the alkali metal salts of the acids are formed and are removed in solution in the aqueous layer. Alternatively, the petroleum oils or their distillates are neutralized with an alkali and the neutralized oil subjected to distillation; the alkali metal naphthenates remain as a residue in the still bottoms from such a distillation. In either of these two processes the naphthenic acids, as recovered by any ordinary means (generally by acidification of the alkali metal salts or soaps with a dilute mineral acid), are highly contaminated with neutral hydrocarbon oils, color bodies and malodorous substances which require removal prior to the use of the acids or their salts for any of the purposes of the arts and industries. For example, the presence of neutral unsaponifiable oil is objectionable in a naphthenate siccative because it adds to the paint or varnish a heavy, tacky, non-drying oil. Again, I have found that copper naphthenate prepared for use as a preservative for fish nets and the like is not satisfactory unless free from these impurities, as unsaponifiable matter of the character accompanying crude naphthenic acids has a deteriorating effect upon fabrics. Obviously, the presence of neutral oils, color bodies and malodorous substances is objectionable in naphthenic acid esters when used as nitrocellulose plasticizers and the like.

The technical difficulty of removing from naphthenic acids or their salts the unsaponifiable matter, color bodies and malodorous substances

which ordinarily accompany them, is due to the fact that the water soluble soaps of the acids have the property of taking large quantities of oil into clear solution in an aqueous medium. Thus, in treating a petroleum distillate with an aqueous alkaline solution, a considerable amount of neutral hydrocarbon oil will dissolve in the aqueous solution of the alkali metal naphthenate. The amount of neutral oil so dissolved I have found to be dependent upon the concentration of soaps in the aqueous solution and upon the amount of excess caustic alkali present, high concentrations of either increasing the solubility of the neutral oil in the aqueous medium. Even with very dilute naphthenic soap solutions and in the absence of any excess alkali, I have found that an amount of neutral hydrocarbon oil equal to as much as 30% by weight of the naphthenic acids themselves, may be dissolved.

Ordinarily, a simple test for percent unsaponifiable matter would be sufficient to ascertain the purity of a substance of this character. Since alkali metal naphthenates have the property of taking neutral oils into solution, however, such a test is not satisfactory as a criterion of purity as regards naphthenic acids. The purity or freedom of naphthenic acids from neutral oils of the same general molecular weight or boiling point range may be taken as in direct proportion to acid number. For example, purified naphthenic acids from California petroleum lamp oil distillates have an average acid number of about 250. The crude naphthenic acids prepared by the ordinary extraction of such a distillate with a dilute aqueous alkaline solution have an acid number of about 190. From this it appears that the amount of neutral oil in the crude naphthenic acids is about 31.5% by weight—calculated as follows:

$$(250-190)/190=315 \times 100=31.5\%$$

For convenience, acid numbers are referred to herein as a criterion of purity of naphthenic acids.

It is an object of my invention to prepare naphthenic acids from petroleum oils which are free from neutral hydrocarbons, are extremely light colored or colorless, and possess relatively mild and unobjectionable odor.

It is a further object of my invention to disclose and provide naphthenic acids suitable for the preparation of naphthenic acid salts which may be used in the arts and industries for such purposes as preclude the presence of the un-

saponifiable matter, color bodies and malodorous substances which ordinarily accompany them.

It has been found that the neutral oil originally accompanying the naphthenic acids upon their extraction from petroleum oils by treatment with a dilute aqueous alkali solution, may be replaced by a substantially equivalent amount of a neutral oil of a widely different boiling point range, and that subsequent to such replacement, preferably by a neutral hydrocarbon oil of much higher volatility than that originally accompanying the crude naphthenic acids, substantially complete separation of all unsaponifiable matter from the naphthenic acids may be effected by ordinary distillation processes. In the process, a petroleum gas oil or similar petroleum distillate containing naphthenic acids is treated with a caustic alkali solution, preferably one about 4° Bé. gravity. The naphthenic acids are removed in the aqueous layer as sodium soaps. As noted above, the aqueous layer, upon separation from the oil, contains considerable quantities of neutral hydrocarbon oils in clear solution. This aqueous layer is extracted with a light oil solvent, for example, a treated gasoline of relatively high volatility and low end boiling point. By this extraction, a part of the heavy neutral oil contained in solution in the aqueous layer is replaced by the light solvent, an amount of the heavier neutral oil equivalent thereto passing to the supernatant layer.

In the process of my present invention, I make use of this principle of replacing the heavy neutral oil originally accompanying the naphthenic acids with a lighter refined neutral oil later capable of separation by ordinary distillation means, and I combine this principle with a treatment of the acids with a relatively strong sulfuric acid, thereby obtaining also the benefit of a chemical refining action.

The various steps requisite to the refining and purifying process of my present invention may be carried out as follows:

A petroleum gas oil or similar petroleum distillate containing naphthenic acids is treated with a caustic alkali solution, ordinarily one of about 4° Bé. strength. The naphthenic acids are removed in the aqueous layer as alkali metal soaps. As described above, the aqueous layer, after its separation from the petroleum oil, contains considerable quantities of neutral hydrocarbon oils in clear solution, as well as color bodies and malodorous substances. This aqueous naphthenate solution, after settling clear of entrained oil, is acidified with a dilute mineral acid and the crude naphthenic acids, accompanied by their impurities, are skimmed off. These crude acids are very dark colored, contain large quantities of neutral unsaponifiable matter, and possess the strong sour odor characteristic of the naphthenic acids of commerce.

To the crude naphthenic acids is now added a light solvent, water-immiscible, and preferably of a boiling point range considerably lower than that of the heavy neutral oil, such, for example, as a refined light gasoline of relatively low end boiling point. The solution of crude naphthenic acids in the light solvent is then treated with a small quantity of relatively strong sulfuric acid, sufficient to react with the heavy neutral oil originally accompanying the crude acids upon their extraction from the petroleum oil, and sufficient to react upon or combine with the color bodies and malodorous compounds present as impurities. I prefer to treat the naphthenic acids

with sulfuric acid in the presence of the solvent because of the viscosity of the naphthenic acids themselves; thus, when undiluted with solvent or a diluent, it is practically impossible to secure adequate contact of the acids with the treating agent; moreover, the viscosity of the acids, when undiluted, prevents separation of the sulfuric acid sludge after the treatment. When diluted, preferably with a light, acid-treated gasoline, treatment is readily effected by ordinary mechanical means, and separation of the sludge after the treatment is rapid and complete.

After treatment with sulfuric acid and the separation of sludge, as described, I wash the diluted treated naphthenic acids for the removal of mineral acidity, and then neutralize the diluted naphthenic acids with a dilute aqueous caustic alkali solution. The treated naphthenic acids pass into solution in the aqueous caustic as alkali metal soaps, the light gasoline remaining as an immiscible layer above. As noted hereinabove, the alkali metal salts of these acids have the power of carrying a considerable amount of neutral oil into clear solution in an aqueous medium; it will be apparent that here, where the aqueous solution is in contact with a light solvent of different boiling point range from that of the neutral hydrocarbons originally accompanying the acids, the specific amount of neutral oils which are carried into aqueous solution is made up of light, treated solvent, of characteristics such that it may later be removed by simple and ordinary distillation means.

After separation of the clear aqueous alkaline naphthenate layer from the immiscible solvent layer, the purified naphthenic acids are recovered or freed by acidification with a dilute mineral acid. Such amounts of neutral oil as accompany the acids, after acidification and separation of the acid and aqueous layers, may be removed by ordinary volatilization, preferably at reduced pressure in order to avoid decomposition of the acids.

Although not often necessary, these purified acids may again be diluted with a light solvent and retreated with sulfuric acid, as before. Ordinarily this need not be done, for the acids provided by a single treatment with sulfuric acid, as described above, are very light in color, contain little or no neutral unsaponifiable matter, have very high acid numbers, and contain little or no malodorous impurities.

As an example of the purification obtained in the process of my present invention:

A 32° A. P. I. gravity California crude distillate was treated with 4° Bé. caustic soda solution. The crude naphthenic acids obtained by acidifying the sodium naphthenate solution were dark brown in color, had a foul sour smell, and had an acid number of 190. These crude acids were diluted with four volumes of a refined gasoline which had an end boiling point of 325° F., and the diluted acids were treated with 1.0 pound of 66° Bé. sulfuric acid per gallon of crude naphthenic acids. After settling and removing the strong sulfuric acid sludge, the naphthenic acids in solution in the light gasoline were saponified with 8° Bé. caustic soda solution. The clear sodium naphthenate solution was removed from the supernatant solvent layer and the purified acids were liberated by acidification with diluted sulfuric acid. These purified acids were skimmed off and such light solvent as accompanied them was removed by volatilization under reduced pressure. The naphthenic acids had a color of

4 N. P. A., and acid number of 250, and a mild unobjectionable odor.

5 Metal naphthenates and naphthenic esters prepared from these acids were free from neutral oils, were light colored and odorless, satisfactory for use under the most exacting requirements for siccatives, nitrocellulose plasticizers, and the like.

10 The amount of the sulfuric acid used to purify the naphthenic acids, as well as the strength of the acid, may be varied considerably. For example, as small a quantity of 66° Bé. acid as 0.5 pound per gallon of crude acids will effect marked improvement in their acid number, color and  
15 odor. Again, I have used as much as 2.0 pounds per gallon of crude naphthenic acids, and in such a case I obtain a purified product which is almost colorless, and of a bland, practically odorless nature even when heated. Some loss in yield of  
20 naphthenic acids is suffered upon treatment with large quantities of sulfuric acid, and I am guided therefore in the severity of my treatment by the use to which the product is to be put, and by the requirements to be met in such use.—In general,  
25 sulfuric acid of below about 80–85%  $H_2SO_4$  is of but little benefit in my process of purification. I have found that 90–98%  $H_2SO_4$  most satisfactorily accomplishes the removal of unsaponifiable matter, color bodies, odorous substances and the  
30 like impurities, and I therefore prefer to use an acid within this range of strengths for the purposes of my invention.

35 While I have described in detail the character of my invention and given illustrative examples of its practice, I have done so by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby.

I claim:

40 1. The process of purifying naphthenic acids which comprises treating crude naphthenic acids

with a strong sulfuric acid in the presence of a water-immiscible diluent more volatile than the naphthenic acids and relatively inert to sulfuric acid and separating the sulfuric acid sludge, saponifying the treated acids with aqueous alkali  
5 in the presence of the diluent, separating the diluent phase, and acidifying the aqueous naphthenate solution with a mineral acid.

2. The process of purifying naphthenic acids which comprises treating crude naphthenic acids  
10 with a strong sulfuric acid in the presence of a water-immiscible diluent more volatile than the naphthenic acids and relatively inert to sulfuric acid treatment, separating the sulfuric acid sludge, saponifying the treated acids with an  
15 aqueous alkali in the presence of the diluent, separating the diluent phase, acidifying the aqueous naphthenate solution with a mineral acid, and removing the volatile diluent accompanying the purified acids by volatilization.  
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3. A process of preparing naphthenic acids from petroleum oils which comprises extracting a petroleum oil with a dilute aqueous alkaline solution, acidifying the aqueous naphthenate solution with a dilute mineral acid, separating  
25 crude naphthenic acids, diluting the acids with about four times their volume of a refined hydrocarbon distillate of end boiling point not over about 325° F., treating the naphthenic acids in the presence of the hydrocarbon distillate with  
30 between 0.5 and 2.0 pounds of strong sulfuric acid per gallon of naphthenic acids, the said strong sulfuric acid having a strength greater than 80%  $H_2SO_4$ , removing sulfuric acid sludge, saponifying the treated acids with an aqueous  
35 alkali in the presence of the hydrocarbon distillate, separating the resulting aqueous naphthenate solution from the supernatant hydrocarbon distillate layer, and acidifying the aqueous naphthenate solution with a dilute mineral acid.  
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