

UNITED STATES PATENT OFFICE

2,011,633

METHOD FOR IMPROVING THE ODOR AND
COLOR OF TAR ACIDSCarl E. Hartwig, Bayonne, N. J., assignor to The
Barrett Company, New York, N. Y., a corpora-
tion of New JerseyNo Drawing. Application August 31, 1932,
Serial No. 631,275

12 Claims. (Cl. 260—154)

This invention relates to the purification of tar acids and more particularly to a process for removing objectionable odors from and improving the color stability of tar acids.

By "tar acids" as used in this specification, I mean the organic cyclic hydroxy compounds (for example phenol, the cresols, the xylenols) resulting from the destructive distillation of organic matter such as bituminous coal, which form salts with caustic soda and are capable of being extracted from solution in organic solvents by means of aqueous caustic soda or other aqueous alkaline solutions. By "carbolate" or "carbolate solution" I mean the solution of reaction products obtained by treating free-tar acids or free-tar-acid-bearing material with aqueous alkaline solutions, especially caustic soda solution. Carbolate solutions contain as solute chiefly sodium (or other metal, e. g., potassium) salts of tar acids. The term "tar acids" is used in the claims in a comprehensive sense and is intended to include tar acids whether free or in combination as metal salts.

It is customary to recover tar acids for tar-acid-containing oils by treating such oils with an aqueous alkaline solution; these oils may be condensates obtained from the distillation of coal tar or of other tar-acid-producing material. Such oils, commonly called "carbolic oils", vary widely in tar acid content, depending on their source. Carbolic oils resulting from by-product coke-oven operation ordinarily contain from 7 to 35 per cent by volume of tar acids, but wide variations from this range may occur. Caustic soda is ordinarily employed for the extraction, although other alkaline materials such as caustic potash or their aqueous solutions may be employed. The solution of the sodium salts of tar acids (i. e., the carbolate solution) is separated from the oil, preferably diluted with water and distilled with steam to remove neutral hydrocarbon material which dissolves in the caustic solution in appreciable amounts. The tar-acid content of such carbolate solutions will vary with completeness of extraction of the oil, strength of caustic solution used, and other factors. Commercial carbolates, before distillation with steam, may contain tar acid salts equivalent to about 15 to 80 per cent by volume of tar acids. The carbolate solution, freed of neutral oil by steam distillation or evaporation, is treated with an acid such as sulfuric acid or with carbon dioxide, or with an acid salt such as sodium acid sulfate, sodium bicarbonate or the like, to liberate the tar acids, which float as an oily layer on the

aqueous salt solution resulting from the acid treatment. The acid layer is separated by decantation for rectification or storage as desired.

The acids produced in the ordinary way as above described readily darken on exposure to light and have an offensive odor, even when refined by rectification. These objectionable characteristics of tar acids may be due to sulfur compounds and greatly lessen the value of the acids or make them worthless for many purposes.

It has been proposed to purify tar-acid-bearing oils (but not carbolates) by distilling such oils in the presence of non-acidic ferric compounds, such as ferric soaps, and collecting the distillate which constitutes the desired purified tar-acid-bearing oil. The explanation advanced for the alleged effectiveness of this process to remove color-producing bodies is that the distillation of the oils in the presence of the ferric compounds results in the oxidation of dihydric tar-acid impurities (the color-forming bodies) contained in the tar acid oils into black water-insoluble non-volatile compounds, permitting the recovery by distillation of a distillate substantially free of such color-forming bodies.

It is an object of my invention to provide a process for treating tar acids which results in substantially complete removal of such objectionable odor-forming bodies and also results in the production of tar acids of improved color stability. The process of this invention may be carried out without seriously interfering with the ordinary routine of tar acid production and requires comparatively simple and inexpensive equipment for its practice.

In carrying out my invention I treat the carbolate solution, preferably after dilution and removal of the neutral oil by steam distillation as described above, with a small amount of a colloidal or gelatinous hydroxide of a heavy metal.

I prefer to use iron hydroxide, either ferric or ferrous hydroxide or a combination of these because these hydroxides are cheap and effective, but other alkali insoluble hydroxides of heavy metals may be used such as the hydroxides of nickel, cobalt, chromium, copper or manganese. It will be noted that the specific gravities of each of the metals mentioned in the preceding sentence exceeds 4. In the claims the reference to a gelatinous hydroxide of a heavy metal is intended to refer to a hydroxide of a metal such as those enumerated which have a specific gravity of at least 4. The amount of hydroxide employed may vary from about 1 to 25 per cent by

weight of the tar acids treated. In the case of iron hydroxide, at least 1½ per cent, but preferably about 2 per cent by weight iron hydroxide, based on the tar acid content of the carbolate, may be used to obtain effective purification, and I may use up to about 25 per cent. It is desirable to heat the carbolate to a temperature of, say, 50 to 90° C. before adding the gelatinous material.

The process may conveniently be carried out by adding the required amount of a metal hydroxide previously prepared (as by the precipitation of a solution of metallic salt with an alkali) to the carbolate solution, agitating the mixture for, say, 15 minutes to one-half hour, allowing the hydroxide to settle, separating the carbolate from the hydroxide and liberating the tar acids by acidification. Instead of the above, the hydroxide may be precipitated in the carbolate by adding thereto a solution containing soluble metal salt such as ferric sulphate, advantage being taken of the alkaline nature of the carbolate to effect precipitation of the metal hydroxide from the solution of the soluble metal salt. The latter procedure is preferred since the metallic hydroxide when precipitated in situ appears to be in a more active form. The mixture of metal salt solution and carbolate may be agitated for 15 minutes to ½ hour, the hydroxide permitted to settle and the carbolate then separated from the hydroxide by filtering and washing. The carbolate may be acidified to convert the tar acid salts to acids and rectified by distillation in vacuo.

The following is given as an example of the practice of this invention:

Carbolate solution, obtained by extracting coal-tar carbohc oil with caustic soda, was diluted and freed from dissolved hydrocarbons and other volatile non-acid impurities by distilling with steam to produce a carbolate substantially free of neutral oil and containing salts of tar acids equivalent to about 20 per cent by volume of tar acids based on the volume of solution. The residue of this distillation consisted for the most part of a solution of the sodium salts of tar acids, the salts of phenol, the cresols and the xlenols predominating. To 200 cc. of this carbolate solution were added 20 cc. of a 10 per cent aqueous solution of ferric sulphate (the amount of solution added being equivalent to the addition of 2 grams of ferric sulphate). The carbolate was heated to a temperature of about 90° C. prior to the addition of the ferric sulphate and the mixture agitated and warmed for about 15 minutes to ½ hour. The precipitate was allowed to settle for approximately 60 minutes and separated from the solution. The carbolate was then acidified.

In another example, 20 cc. of a 10% aqueous solution of ferrous sulfate (the amount of solution being equivalent to the addition of 2 grams of ferrous sulfate), were added to 200 cc. of the carbolate solution and otherwise the steps of Example 1 were duplicated.

In a further example of the invention, 2 grams of ferric hydroxide were added to 200 cc. of carbolate solution at a temperature of about 90° C. The mixture was agitated for approximately 15 minutes to ½ hour while warming. It was then allowed to settle for approximately 60 minutes and the carbolate separated from the hydroxide by filtering. The carbolate was then acidified.

The tar acids resulting from the process as carried out in the above examples, were on distilla-

tion under vacuum, substantially free of disagreeable odor, of improved color stability, and of enhanced value for many purposes.

While the cause for the improvement in odor and increased purity of tar acids resulting from the practice of the method of the invention is not definitely known, it appears probable that these results are due to the adsorption of objectionable impurities such as dihydroxy compounds, sulfur compounds, and traces of arsenic compounds by the gelatinous materials used in treating the carbolates.

Without departing from the scope of my invention I may treat with the reagents described not only carbolate formed by extracting tar-acid-containing oil, but also carbolate formed by dissolving impure tar acids in caustic soda or other alkaline solutions, or produced in any other way.

The term "iron hydroxide" as used in the specification and claims includes both ferrous and ferric hydroxides.

While I have described a preferred method of carrying out my invention, I do not wish my invention to be considered as limited thereby, but only as limited by the following claims.

I claim:

1. In the process of purifying tar acids which comprises dissolving tar acids in an alkaline solution to form a carbolate solution, the step which comprises treating the carbolate solution with a gelatinous hydroxide of a heavy metal which hydroxide is insoluble in alkali.

2. In the process of purifying tar acids which comprises dissolving tar acids in an alkaline solution to form a carbolate solution, the step which comprises treating the carbolate solution with iron hydroxide.

3. In the process of purifying tar acids which comprises dissolving tar acids in an alkaline solution to form a carbolate solution, the step which comprises treating the carbolate solution with a gelatinous hydroxide of a heavy metal which hydroxide is formed by precipitation in the carbolate solution.

4. In the process of purifying tar acids which comprises dissolving tar acids in an alkaline solution to form a carbolate solution, the step which comprises treating a carbolate solution with iron hydroxide precipitated in the carbohc solution.

5. The process for purifying tar acids which comprises dissolving tar acids in a solution of an alkaline material whereby a carbolate solution is formed, agitating said carbolate solution with a gelatinous hydroxide of a heavy metal, separating the carbolate solution from the metal hydroxide and liberating tar acids from the separated carbolate solution.

6. The process for purifying tar acids which comprises dissolving tar acids in a solution of an alkaline material whereby a carbolate solution is formed, agitating said carbolate solution with iron hydroxide, separating the carbolate solution from the iron hydroxide and liberating tar acids from the separated carbolate solution.

7. In the process of purifying tar acids the step which comprises treating carbolate solution with at least 1½ per cent by weight iron hydroxide, based on the tar acid content of the carbolate solution.

8. In the process of purifying tar acids, the step which comprises forming in situ a gelatinous metal hydroxide precipitate.

9. In the process of recovering tar acids from tar-acid-bearing oils, the combination of steps

which comprise extracting tar-acid-bearing oils with an aqueous alkaline solution whereby a carbolate solution is formed, agitating said carbolate solution with gelatinous iron hydroxide, separating the carbolate solution from the iron hydroxide and liberating tar acids from the separated carbolate solution.

10. In the process of producing tar acids the combination of steps which comprise heating a carbolate solution containing said tar acids as alkali metal salts, adding to the carbolate solution a solution of ferric sulphate equivalent as ferric hydroxide to at least 1½ per cent of the weight of the tar acids present in the carbolate,

whereby gelatinous iron hydroxide is precipitated, agitating the carbolate solution while in contact with said iron hydroxide at an elevated temperature, separating the carbolate solution from the precipitated iron hydroxide and recovering tar acid from the carbolate solution.

11. The method of purifying tar acids, which comprises contacting the tar acids with a gelatinous iron hydroxide.

12. The method of purifying tar acids which comprises contacting the tar acids with a gelatinous metal hydroxide.

CARL E. HARTWIG.