

UNITED STATES PATENT OFFICE

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PURIFICATION OF TAR ACID-BEARING OILS

No Drawing.

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The present invention relates to the purification of tar acid-bearing oils, and more particularly to a process for eliminating color-producing compounds from tar acid-bearing oils containing them.

Some tar acid-bearing oils (such as low temperature tars, blast furnace tars, vertical retort tars, shale oils and other liquid condensates resulting from the distillation of bituminous material under carbonizing conditions mild enough to preserve the liquid by-products in a substantially primary and undecomposed form) contain certain impurities which render them unsatisfactory or make them undesirable for certain uses. One form in which these impurities manifest themselves is in the production of colored compounds when such oils are used for the manufacture of disinfectants, animal dips, saponified cresol or tar acid solutions and related products. After exhaustive and thorough investigation of the chemical compositions and properties of these colored compounds their origin has been traced to certain strongly reducing ortho-dihydric tar acids, similar to but not including catechol. Thus one of these bodies has been isolated and identified as a new homologue of catechol comprising 3, 4- or 3, 6-dimethyl catechol.

The primary object of the present invention is to provide a process for removing color producing compounds of the type referred to from tar acid-bearing oils containing them.

Heretofore in preparing and refining tar acid-bearing oils of the class described for use in the manufacture of disinfectants, animal dips and similar products, the oils have been subjected to washing treatments with aqueous sodium carbonate solution. This treatment, however, fails to give even approximately complete removal of the color forming matter except with oils which contain unusually small amounts of such color-producing bodies. In treating other tar acid-bearing oils, washing with dilute caustic soda solution has been employed, but this treatment involves a very considerable loss of the desirable tar acids of high germicidal value, which are extracted together with the color-forming materials by the caustic soda

treatment. Another method has been recently proposed for removing these color producing compounds from coal tar distillates and the like, which comprises washing the oils with aqueous solutions of weakly alkaline "buffer" agents such as calcium hydroxide and ammonium hydroxide. While this latter method of treating the oils has proved to be much more satisfactory than methods now in use in the trade, it has been found that the action of the alkaline buffer agents is often incomplete in the case of tar acid-bearing oils containing appreciably large quantities of color-producing matter. Fractionation of the oils with rejection of the portion boiling above 230° C. has also been advocated, but since this excludes the larger portion of the oil, including most of the high boiling tar acids which are the most valuable germicides present in the oils, the method is not commercially feasible.

Another object of the present invention is to provide a process by which the color-producing bodies present in such tar acid-bearing oils can be cheaply and completely extracted without also removing valuable tar acids.

With these and other objects and features in view the invention consists in the process for purifying tar acid-containing oils hereinafter described and particularly defined in the claims.

Essentially the process for purifying tar acid-bearing oils forming the subject of the present invention, in its preferred form, consists in precipitating the color-producing bodies from the oil by means of a water-soluble non-acidic salt of a heavy metal, particularly antimony salts or lead acetate. It has been found that the salts of various heavy metals, and particularly antimony salts and lead acetate readily precipitate the ortho-dihydric tar acids from aqueous solutions. This precipitation does not occur if the solution be distinctly acid, so that lead nitrate, for instance, is not a satisfactory precipitating agent, whereas normal lead acetate gives complete precipitation. The addition of sodium acetate to a lead nitrate solution provides a treating agent which will satisfactorily precipitate the ortho-dihydric

tar acids from a tar acid-bearing oil. No favorable catalysis of secondary reactions with the color-producing compounds appears to take place, and practically none of the desirable and valuable monohydroxy tar acids of high germicidal value are precipitated from the oil.

The following procedure is set forth as an example of a satisfactory method of treating tar acid-bearing oils having a relatively large percentage of color-producing impurities contained therein. One volume of a 30% tar acid-bearing oil obtained by the distillation of a commercial low temperature tar was agitated for thirty minutes at 60° C. with an equal volume of a 10% aqueous solution of normal lead acetate. After suspending agitation and allowing the oil to separate, the aqueous layer was drawn off and subsequently employed for washing another batch of oil. The treated oil, which was turbid owing to the presence of gelatinous lead salts of color-producing impurities originally present in the oil, was mixed with 1% of its weight of a filter-aid (for example bone black, fuller's earth, activated carbon or the like) and filtered with suction. The resulting oil filtrate was clear, and a disinfectant prepared from it by means of rosin soap gave an emulsion with water which was practically free of red color. The oil may be distilled either before or after treatment if desired, although such distillation is not necessary for the removal of the color-producing bodies. Without the use of some filter aid such as bone black, fuller's earth or the like, experiments have shown that it is extremely difficult to get a complete separation of the insoluble lead salts of the color-producing bodies from the oil in which they are suspended. Filtration or centrifuging of the oil has been tried, but in many cases the oil obtained by either of these treatments is not entirely freed of the insoluble salts of the color-producing bodies. It has been found desirable to heat the oil during the period of agitation with the treating agent, for the reason that since the reaction leading to the formation of insoluble metal salts takes place in the aqueous phase, the heat increases the solubility of the color-forming material in the aqueous phase and thereby hastens the completion of the reaction and insures the completeness of interaction between the reagent and the color-producing impurities. Once formed, the insoluble metal salts leave the aqueous phase and pass into the oil, where they remain in suspension. If an excess of the precipitating agent is present in the aqueous solution, the latter may be drawn off and used again for treating another batch of oil, and this process repeated as long as sufficient precipitating agent remains in the aqueous solution.

It is not intended by the above description

to limit the scope of the present invention to the treatment of oils containing definite compounds, nor to the use of definite proportions of the precipitating agent, nor to the employment of particular temperatures or particular time limitations of agitation, nor to the use of any particular metal salt as a precipitating agent or particular methods of separating the oil and insoluble material. Any metal salt which gives an insoluble compound on interaction with orthodihydric tar acids of the class referred to may be employed. The process is applicable not only to the treatment of the tars themselves, but also to the treatment of a tar acid fraction alone (unadmixed with hydrocarbon oil). The volume of the precipitating agent used is preferably limited to a slight excess above that required for removing the color-producing impurities.

By employing the process forming the subject matter of the present invention for the purification of tar acid-bearing oil, disinfectant emulsions can be prepared from a soap base blend of the oil which will not turn pink, and the purification of the oil can be completed at relatively small expense without materially lowering the value of the disinfectants and the germicidal agents prepared therefrom.

The term "tar acid-bearing oil" is used in the description and claims to include all tar acid containing oils or liquid condensates obtained in the distillation of coal or oil shale. The tar acid content of most of such oils, and particularly those obtained by the low temperature distillation of coal, often consists almost entirely of compounds, which, while they resemble the phenols or tar acids of coke oven tar in some of their properties, do not come within the generally accepted definition of a phenol, but are rather hydroxyl derivatives of cyclic hydrocarbons which are non-aromatic in character, having hydrogen and alkyl side chains attached to the aromatic nucleus.

The preferred form of the invention having been thus described, what is claimed as new is:

1. The method of removing color-producing compounds from an oil containing monohydric tar acids while conserving the content of the latter, which comprises agitating the oils with an aqueous solution of a non-acidic salt of a heavy metal.

2. The method of removing color-producing compounds from an oil containing monohydric tar acids while conserving the content of the latter, which comprises adding a non-acidic salt of a heavy metal to the oil, and separating the insoluble metal salts of the color-producing bodies thereby precipitated from the residual purified oil.

3. The method of removing color-producing compounds, including orthodihydric

tar acids, from an oil containing the same together with other tar acids without substantial removal of the latter from the oil which comprises agitating a mixture of the oil and a non-acidic salt of a metal which forms insoluble compounds with ortho-dihydric tar acids, and subsequently separating the purified oil and the insoluble compounds thus formed.

4. The method of removing color-producing compounds, including ortho-dihydric tar acids, from an oil containing the same together with other tar acids without substantial removal of the latter from the oil which comprises agitating a mixture of the oil and an aqueous solution of a non-acidic salt of a metal which forms insoluble compounds with ortho-dihydric tar acids, and separating the insoluble compounds thus formed from the residual oil.

5. The method of removing color-producing compounds from an oil containing monohydric tar acids while conserving the content of the latter, which comprises agitating the oil for about thirty minutes at a temperature of about 60° C. with about an equal volume of a 10% aqueous solution of normal lead acetate, separating the aqueous layer from the treated oil, mixing with the latter a small percentage of a filter aid material, and filtering to separate the insoluble metal salt precipitates of the color-producing bodies from the oil filtrate.

6. The method of removing color-producing compounds from an oil containing monohydric tar acids while conserving the content of the latter, which comprises agitating the oils with an aqueous solution of normal lead acetate.

7. The method of removing color-producing compounds from an oil containing monohydric tar acids while conserving the content of the latter, which comprises agitating the oil with an aqueous solution of a non-acidic salt of a heavy metal, separating the aqueous solution of excess treating agent from the treated oil, and employing the solution thus separated in purifying another batch of oils containing tar acid.

8. The method of removing color-producing compounds from an oil containing monohydric tar acids while conserving the content of the latter, which comprises agitating the oils with an aqueous solution of a non-acidic salt of a heavy metal, separating the aqueous layer from the treated oil, mixing with the oil layer a small percentage of a filter aid and filtering to separate the insoluble metal salt precipitates from the oil filtrate.

In testimony whereof I affix my signature.
STEPHEN P. BURKE.