

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 solutions. 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 or ammonium hydroxide. While this latter method of treating the oils has proven 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 oil 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 oil, 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.

The most satisfactory methods heretofore suggested and employed for removing color-producing compounds from tar acid-bearing oils containing them have involved the use of chemical reagents or solvents for washing out the color-producing bodies. Any "washing" method for effecting the removal of impurities is inherently inadventagous in that it involves the introduction of an additional or supplementary step in the regular refining operation, as well as additional equipment in the form of tanks, pumps and piping.

One feature of the present invention contemplates treating tar acid-bearing oils of the class described to remove color-producing compounds therefrom as a part of the regular routine refining treatment to which the oils are commonly subjected, and without the use of additional operating steps or expensive equipment.

With these and other objects and features in view the invention consists in the method of purifying tar acid-containing oils herein-after described and particularly defined in the claims.

Essentially the method of purifying tar acid-bearing oils forming the subject of the present invention, in its preferred form, consists in distilling the oil in the presence of non-acidic ferric compounds such as the hydroxide, basic acetate, borate, phosphate, stearate, oleate and the like, and collecting the distillate freed from the impurities removed by chemical combination with such non-acidic ferric compounds. It has been found that ferric compounds which are non-acidic in character appear to act as oxidizing agents, converting the orthodihydric tar acid impurities into black, water-insoluble compounds which are non-volatile, thus permitting the recovery by distillation of a distillate substantially free of such color-forming bodies. By this method of treatment no additional operation or equipment not commonly employed in treating the tar acid-bearing oils is required, and practically none of the desirable and valuable monohydroxy tar acids of high germicidal value are lost from the purified distillate.

The following procedure has proven satisfactory in treating a tar distillate having a boiling range of from 190-330° C. and containing about 30% valuable tar acid bodies, said tar distillate having been produced by the distillation of a commercial low temperature tar. The tar oil was distilled to a vapor temperature of about 330° C. after adding thereto 5% of the weight of the tar oil of ferric stearate, and a distillate was obtained which, when made up into a disinfectant emulsion, was neither red nor pink in color. The particular tar oil thus treated contained much more of the color-forming impurities than is usually encountered in tar refining practice. Obviously tar acid-bearing oils containing less color-forming matter (orthodihydric tar acids) than the one cited can be purified with correspondingly less of the ferric soap. Experiments have shown that ferric chlorid when added to the tar prior to distillation is not a satisfactory reagent for converting the color-producing bodies into insoluble matter, apparently because of its acid reaction. Ferric soaps, such as stearate and oleate, on the other hand have no acid reaction, and possess the additional characteristic of being readily soluble in the acid-bearing oils under treatment, so that they are particularly well suited for this purpose. As indicated above other non-acid ferric compounds, such as hydroxide, basic acetate, borate and phosphate may be used, and although they are less soluble in the acid-bearing oils than the ferric soaps, their use is often preferred because they are less expensive. In using

non-acidic ferric compounds which are relatively insoluble in the acid-bearing oils it is preferred to employ them as fillings for a reflux column mounted at the head of the distillation still, rather than to add them directly to the tar or tar oil in the still. Thus it has been found that an entirely satisfactory purification can be carried out when the non-acidic ferric treating agent is supported in a reflux column on porous material such as coke, pumice and the like, during the distillation of the tar acid-bearing oils in the underlying still.

It is not intended to limit the scope of the present invention to the treatment of oils containing a definite percentage of color-forming and non-color-forming compounds, nor to the use of definite proportions of purifying agents, nor to the employment of particular temperatures or other particular conditions of distillation. The process is particularly applicable to the preliminary distillation to soft pitch of a tar oil containing tar acid bodies admixed with hydrocarbon oils, but it is not limited to the treatment of such oils and may be applied to the secondary distillation of tar acid-bearing distillates recovered in a preliminary distillation.

By employing the process forming the subject-matter of the present invention for the purification of tar acid-bearing oils, disinfectant emulsions can be prepared from soap base blends of the distillate which will not turn pink, and the purification of the oil can be completed at a relatively small additional expense over that normally incurred in treating similar oils in which the color-producing impurities are not encountered, without materially lowering the value of the disinfectant and germicidal agents prepared therefrom.

The term "tar-acid-bearing oil" is used in the description and claims to define coal tars and all oils derived from such tars, as well as shale oils. The tar acid content of coal tars, particularly those of low temperature origin, may often consist 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 nucleus.

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

1. A method of treating tar acid-bearing oils to remove color-producing bodies therefrom which comprises distilling the oil in contact with a non-acidic ferric compound, and collecting the purified distillate.

2. A method of eliminating color-producing compounds from tar acid-bearing oils

containing them which comprises distilling the oil in contact with an amount of non-acidic ferric compound sufficient to transform all the color-producing bodies into non-volatile compounds which will not pass over with the distillate.

3. A method of removing color-producing compounds from tar acid-bearing oils containing them which comprises distilling the oil, passing the distillation vapors through a reflux column containing a non-acidic ferric compound as a filling, and condensing the purified distillation vapors after they have passed the reflux column.

4. A method of removing color-producing impurities from tar acid-bearing oils containing them which comprises distilling the oil, passing the distillation vapors through a reflux column containing a porous filling impregnated or coated with a non-acidic ferric compound, and condensing and separately collecting the purified distillate.

5. A method of removing color-producing compounds from tar acid-bearing oils containing them which comprises admixing with the oil a non-acidic ferric compound soluble therein, subjecting the mixture to distillation, and condensing and separately collecting the purified distillate.

6. A method of treating tar acid bearing oils to remove color-producing bodies therefrom which comprises the steps of distilling the oil, refluxing the vaporized oil, and condensing the said vaporized oil and, during one of the steps prior to the condensation of the oil, contacting the latter with a non-acidic ferric compound.

In testimony whereof I affix my signature.
SOLOMON CAPLAN.