

UNITED STATES PATENT OFFICE

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METHOD OF INCREASING SOLUBILITY OF
METAL SALTS OF BETA CARBOXY COM-
POUNDS IN MOTOR FUELSWalter S. Guthmann and Herman Kerst, Jr., Chi-
cago, Ill., assignors to Leo Corporation, Chi-
cago, Ill., a corporation of IllinoisNo Drawing. Application September 14, 1936,
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1 Claim. (Cl. 202—42)

This invention relates to a method of increasing the solubility of metal salts of beta-carboxy compounds, such as the beta-diketones and beta-aldehydes, in liquid hydrocarbons, and more particularly in motor fuels and lubricating oils.

It has heretofore been proposed to add metallic salts of beta-diketones to motor fuels and motor lubricating oils for the purpose of increasing the efficiency of combustion of internal combustion engines. When prepared in an aqueous medium, however, the metallic salts of the beta, or 1,3-diketones, such as acetyl-acetone, propionyl-acetone and the like, often contain water of crystallization, or water loosely bound to the compounds.

We have found that the solubility of such hydrous metallic salts of the beta-diketones in gasolines, or other motor fuels, or in lubricating oils, can be considerably improved if the metallic compounds of the beta-diketones are dehydrated, or partially dehydrated. We have further found that such dehydration can best be accomplished by azeotropic distillation. By this means the solubility of the metallic salts of the beta-diketones in benzene and other liquid hydrocarbons is often increased tremendously and the separation of water when the benzene solution of the salt is added to gasoline is greatly minimized.

It is also possible in one step to dehydrate the benzene solution of the metallic salt of the beta-diketones and make them ready for addition to gasoline, or other motor fuel or lubricating oil, thereby avoiding the extra operation of isolating the metallic salts.

It is therefore an important object of this invention to provide a method for increasing the solubility of metallic salts of beta-carboxy compounds such as beta-diketones and beta-aldehydes, in liquid hydrocarbons, motor fuels, lubricating oils and the like by dehydrating or partially dehydrating such salts by means of azeotropic distillation.

It is a further important object of this invention to provide a method of preparing substantially anhydrous solutions of metallic salts of beta-diketones in an organic solvent miscible with gasoline and other motor fuels for direct addition thereto without any intermediate isolation of such metallic salts.

Other and further important objects of this invention will become apparent from the following description and appended claim.

In accordance with this invention, the anhydrous metallic salt of a beta-carboxy compound, such as a beta-diketone, or beta-aldehyde, which it is desired to dehydrate, is first added to a sol-

vent that is immiscible with water but miscible with liquid hydrocarbons, such as gasoline and the like, and lubricating oils. Suitable solvents for use in the dehydration of the metallic salts of the beta-carboxy compounds are aromatic hydrocarbons, such as benzene, toluene, or xylene; halogenated solvents such as carbon tetrachloride, ethylene dichloride; aliphatic hydrocarbons such as hexane and the like or other liquids soluble in gasoline but immiscible with water. Gasoline itself, or a hydrocarbon oil, may be used in place of a solvent.

After the mixture of the metallic salt of the beta-carboxy compound and a suitable solvent has been prepared, it is then subjected to azeotropic distillation, which may be carried out in any suitable apparatus, the most simple being a distillation in which the volume of the liquid in the distilling vessel is maintained constant by the addition either of fresh solvent or by the return of the solvent from a reflux condenser attached to the distilling vessel but so arranged that the water carried off by the distillate may be separated therefrom.

In using carbon tetrachloride, which is heavier than water, the water carried off with the distillate will appear on the surface of the carbon tetrachloride distillate. Where the solvent is lighter than water, the water will form the lower layer in the collected condensate.

The distillation is carried out, preferably, until no more water separates from the distillate in the condensate. The solution remaining in the distilling vessel may then be filtered and concentrated to isolate the metallic salt; or when the solution is to be added to a motor fuel or lubricating oil, an aliquot thereof may be analyzed for the content of metallic compound and the solution then made up to the calculated volume to give the percentage of metallic compound desired and the resultant solution added directly to the motor fuel or lubricating oil.

By way of specific example, whereas the hydrated salt of cobaltous propionyl acetate is soluble in benzene to the extent of about 10% by weight, after azeotropic distillation in benzene, the solubility is raised to well over 20% by weight. Likewise, the solubility of nickel propionyl acetate may be raised in the same way from 10 to 15% by weight.

In the case of chromic acetyl acetate, this metal salt as produced in an aqueous medium contains such a large amount of water of crystallization that the benzene solution, upon addition to gasoline, becomes cloudy. This can be partial-

ly corrected by azeotropic distillation of the chromic acetyl acetate. Likewise, a precipitate of ferric acetyl acetate from water can be taken wet from a filter and dehydrated by azeotropic distillation without the necessity of air drying the precipitate.

The following will serve to illustrate a preferred method of carrying out our invention.

Example

10 100 g. of cobaltous propionyl acetate is added to 1 liter of benzene and the resulting mixture subjected to azeotropic distillation. During the course of the distillation from about 15 to 20 cc. of water are carried off in the distillate and will collect in the condensate. When no more water appears in the distillate, the distillation is stopped, or it may be carried out without refluxing until the desired concentration of the salts in the benzene has been obtained.

If the cobaltous propionyl acetate is then isolated, it will be found to contain an equivalent of approximately 2 mols of water of crystallization. During the distillation the color of the supernatant liquid changes from a red to a purplish or bluish shade, as is characteristic of the change in color from a higher to a lower hydrate of cobaltous compounds.

It will be understood that the degree of dehydration will vary with different salts of the beta-diketones, and that while with some it may be possible to substantially completely remove the water of crystallization, with others some of the water of crystallization will remain. Also, in some instances, it is advisable to use reduced pres-

ures for carrying out the distillation to avoid decomposition.

Although the method of this invention has been specifically disclosed in connection with a dehydration of metallic salts of beta-diketones, it is equally applicable to the dehydration of metallic salts of other hydrated beta-carboxy derivatives, including metallic salts of the beta-aldehydes, such as acetyl acetaldehyde and its homologues. Also, the dehydration of these compounds may be carried out in the manner described for other purposes than to increase their solubility in motor fuels and lubricating oils.

We are aware that numerous details of the process may be varied through a wide range without departing from the principles of this invention, and we, therefore, do not purpose limiting the patent granted hereon otherwise than necessitated by the prior art.

We claim as our invention:

The method of increasing the solubility in hydrocarbon oils and gasoline of a metal compound of a beta-carboxy hydrate which comprises adding a water-immiscible gasoline-soluble organic solvent to said metal beta-carboxy hydrate, heating the mass below the decomposing temperature of the metal compound to vaporize a distillate therefrom, separating water from the distillate, returning the solvent portion of the distillate to the mass and continuing the heating and solvent distillate return until the distillate is substantially dry to produce the hydrocarbon oil and gasoline soluble dehydrated metal-beta-carboxy product in solution in the solvent.

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