Patented Apr. 13, 1937 2,077,068

UNITED STATES PATENT OFFICE

2,077,068

COMPOSITIONS FROM COAL TAR AND HIGHER FATTY ACIDS AND PROCESSES OF MAKING THE SAME

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No Drawing. Application November 21, 1935, Serial No. 50,985

15 Claims. (Cl. 260—131)

This invention relates to useful products derived from coal tar distillates and higher fatty acids, and processes of preparing the same; and it comprises compositions which are the product of reacting coal tar fractions with higher fatty acids in the presence of aluminum chloride, zinc chloride, iron chloride, and other catalytic materials forming intermediate complex compounds with the reactants, these compositions being oily, viscous liquids, or wax-like solids, of unknown chemical composition; and it further comprises processes wherein a coal tar fraction composed of a mixture of substances derived from coal tar by distillation or extraction is reacted with the higher fatty acid in the presence of the above named catalysts, advantageously in the presence of a solvent such as kerosene or carbon disulphide, whereby intermediate complex compounds are formed, the intermediate complex hydrolyzed, and the final reaction product recovered.

The higher fatty acids are the normal constituents of animal and vegetable fats, and they can be obtained from such fats at relatively little expense. Those having six or more carbon atoms are relatively cheap and abundant. Heretofore these higher fatty acids have been used almost exclusively in the soap industry, for making candles, etc., and very rarely have they been used as reagents in the chemical reactions for the production of high grade chemicals.

We have now discovered that valuable compounds can be made from these fatty acids. We have discovered that higher fatty acids will react with coal tar distillates or fractions in the presence of aluminum chloride, zinc chloride, iron chloride, and other catalytic materials forming intermediate complex compounds with the reactants, to give products which are useful. The products which we obtain vary from rather viscous oils to wax-like solid materials. We find, for instance, that these products, when added to a lubricating oil, markedly improve the quality of the oil, which discovery has been separately described and claimed in an application in the names of Ralston, Christensen and Selby and filed of even date herewith.

Broadly speaking, our invention comprises reacting a higher fatty acid with a coal tar distillate or with acid or basic fractions of such a distillate in the presence of a catalyst of the type noted above. In the practice of our invention we can use as starting materials any higher fatty acids and by that we mean fatty acids containing at least six or more carbon atoms. In our invention we can use caproic acid, capric acid, lauric acid, myristic, palmitic or stearic acid, or even higher acids, such as behenic. We also find that we can use unsaturated fatty acids such as oleic acid or linolic acid. In addition we find that we can use synthetic fatty acids, such synthetic fatty acids being made by the oxidation of paraffin wax. Actually in the practice of our invention we usually do not use a pure fatty acid but we use mixtures of fatty acids commonly associated in nature, such as a mixture of the fatty acids obtained by splitting lard or cottonseed oil or garbage grease. These mixtures are cheap and readily available.

In the practice of our invention we can use both liquid and solid fractions of coal tar and we generally begin with those fractions or distillates the major portion of which boil from 200° C. up. The fractions, distillates or extracts which we use are generally mixtures of various aromatic and heterocyclic hydrocarbons, phenols, creosols and other substances of complex structure. One of the most desirable coal tar fractions for use in our process is that known as "red wax". Red wax is a solid waxy material obtained from distilling coal tar pitch. Red wax is a fraction having a boiling range of about 432° C. and 500° C.

Ordinarily we do not use coal tar distillates or fractions boiling below 200° C. except in the case of coal tar bases to be described. We can, however, use either the crude distillation products of coal tar or pure compounds obtained therefrom, such as naphthalene, anthracene, carbazole, phenanthrene, etc. The crude distillates which we use in our invention will contain quantities of naphthalene and anthracene mixed with other hydrocarbons but this invention deals with the treatment of these mixtures or with the treatment of any of the pure constituents thereof. In a number of cases it is desirable to start with a mixture rather than any one of the pure compounds because we find that oils and soft waxes are thereby obtained and that these mixtures have properties different from those observed when pure compounds are used.

We shall now describe our invention with specific reference to preparing products from coal tar fractions. In order to keep our discovery within reasonable bounds we shall restrict our specific examples to the use of stearic acid. It is to be understood, however, that all of the higher fatty acids enumerated above can be used in place of stearic acid.

Before proceeding further it will be helpful if a brief outline of coal tar distillation products

is presented. When coal tar is distilled, the first fraction, or cut, boiling up to about 200° C., is known as "light oil". We do not, in our invention, ordinarily use this fraction although we can prepare useful products from light coal tar bases, about 30 per cent of which boils below 200° C. These will be described presently. The next fraction obtained in the distillation is "middle oil" and it has a boiling point range of about 200° C. to 250° C. The next highest cut, called "heavy oil", boils from 250° C. to 300° C. The so-called "crude anthracene fraction", which consists largely of crude anthracene and some naphthalene, boils from 300° C. to 350° C. If the distillation of the tar be stopped at this point the residue in the still is known as "pitch". The pitch can be further distilled, however, to give another heavy oil with a boiling range of about 360° C. to 432° C. and "red wax", a waxy solid, boiling range about 432° C. to 500° C. What is left in the still now is essentially carbon or coke. In our invention we can use any of the distillates boiling above 200° C. obtained by distilling the coal tar and the pitch. In other words, we use coal tar fractions boiling from 200° C. to 500° C. or any of the pure compounds obtained from these fractions by extracting them with acids or bases, as will presently be described.

We shall now refer to products obtained by reacting so-called "crude tower bottoms" with stearic acid. These crude tower bottoms have a boiling point range of about 230° C. to 375° C. They comprise a part of the heavy oil cut, the anthracene oil cut and a portion of the heavy oil obtained from pitch. The exact composition of these crude tower bottoms is not known. They contain anthracene, naphthalene, phenols, creosols, and probably many other substances.

We first prepare a mixture of about 70 parts by weight of crude tower bottoms, 68 parts by weight of stearic acid, and 125 parts of kerosene as a solvent. To this mixture we add, at 120° C., 100 parts of aluminum chloride over a period of three and one-half hours. The mixture is then refluxed for eighteen hours at 120° C., after which time it is allowed to cool and then poured upon a mixture of ice and hydrochloric acid. The mixture is then steam distilled until hydrolysis is complete. The steam distillation is continued until the product shows no ash of aluminum oxide upon ignition. It is our belief that a complex metallic compound is first formed and that this compound is decomposed by the hydrochloric acid treatment combined with the steam distillation. The final mixture which we obtain is free of any aluminum complex. The product obtained by this treatment is a reddish, rather free flowing oil. The physical properties of this product are entirely different from either of the starting materials. For instance, it is very oily to the touch and its odor and general appearance differ greatly either from the original stearic acid or the crude tower bottoms.

This free-flowing oil has a number of uses. When added to lubricating oils we have found that it imparts oiliness to the oil and also that it lowers the pour point. The product also has a rather high dielectric constant and it can be used as a transformer oil.

Instead of using the crude tower bottoms as such we can fractionate the bottoms into cuts of fairly narrow boiling point range and react these cuts with stearic acid as described above. For example, we can start with a fraction having a boiling point range of 215° C. to 245° C., or one having a range of 245° C. to 315° C. Still other fractions can be first obtained, such as one boiling from 345° C. to 365° C.

As stated, any of these fractions can be used in the reaction and in each case we use about 35 parts by weight of the fraction, 68 parts by weight of stearic acid and 125 parts by weight of kerosene. To this we add 100 parts by weight of aluminum chloride over a period varying from three to four hours, and conduct the process as described above for the crude tower bottoms.

The reaction products we obtain from stearic acid and the above cuts are generally reddish, viscous oils or greasy solids of complex composition.

We find that a particularly advantageous starting material for our invention is a fraction obtained from coal tar known as red wax. Red wax represents approximately 7 per cent of the coal tar and is the highest boiling distillate obtainable. In appearance red wax is a sticky wax with a rather mahogany red color and possessing some tendency towards crystallization. It is probably a mixture of highly condensed aromatic compounds and is quite complex in structure.

The ratio of red wax to stearic acid or other higher fatty acid can be varied over rather wide limits. For instance, when 35 parts by weight of the crude red wax are reacted with 68 parts by weight of stearic acid and 100 parts by weight of aluminum chloride in the presence of the solvent as described above, the product upon hydrolysis is a soft brown wax. When 70 parts by weight of red wax to 68 of stearic acid are used the product is a brown wax, markedly harder than that obtained when 35 parts are used; and when 140 parts by weight of red wax are used the product is a greenish-brown oil. The amount of solvent necessary varies with the amount of red wax. When using 140 parts of red wax we use approximately twice the quantity of solvent required for 70 parts.

We further find that the acid soluble and alkali soluble portions of coal tar, as well as acid or alkali extracted coal tar, are advantageous starting materials. Thus we can extract the coal tar, or fractions thereof, such as the crude tower bottoms, with a 20 per cent solution of caustic soda until no further alkali-soluble constituents are removed. The alkali-soluble materials thus extracted can be recovered from the alkaline liquors by neutralization thereof with a mineral acid and extraction with ether in the usual way. Similarly the coal tar can be extracted with an acid such as 40 per cent sulphuric at room temperature and the acid-soluble constituents recovered from the acid liquors. Crude tower bottoms are advantageous materials from which to extract acid and alkali soluble substances.

All of these extracted materials, as well as the coal tar residues from such extractions can be reacted with higher fatty acids.

Thus 35 parts by weight of crude tower bottoms from which alkali soluble portions have been extracted, and 68 parts by weight of stearic acid, reacted as described above in the presence of 100 parts of aluminum chloride give, on hydrolysis of the aluminum complex, a brown grease. Similar quantities of acid and catalyst reacted with 35 parts of the ether extracted alkali soluble portions give a reddish brown oil as a final reaction product.

The acid extracted tower bottoms give reddish brown oils and the acid soluble constituents of the tower bottoms (i. e. the constituents recovered from the acid washings) give greenish, viscous oils when using 35 parts of tower bottoms, or material extracted therefrom, 68 parts of stearic acid, and 100 parts of aluminum chloride catalyst.

Soft, brown, low melting waxes can be obtained by reacting crude tower bottoms which have been extracted with both acid and alkali, in other words, bottoms from which acid and alkali soluble constituents have been removed.

In another example we wash red wax with a 40 per cent sulfuric acid solution at 100° C. for several hours. The red wax is then separated from the acid solution and carefully dried. We then react 35 parts by weight of the acid-washed red wax with 68 parts by weight of stearic acid and 100 parts by weight of aluminum chloride together with 200 parts by weight of kerosene. After hydrolysis of the aluminum complex the reaction product appears as reddish brown oil.

In a similar manner we can start with "crude anthracene", a material containing approximately 50 per cent anthracene, the rest being naphthalene, methyl naphthalene, carbazole, fluorene, phenanthrene, and other substances. The condensation reaction product using the above mentioned proportions was a greenish viscous oil.

We can wash this crude anthracene with a 40 per cent sulfuric acid solution for several hours and, after drying, use the acid extracted material as a starting material in our process. The product in this case is also a greenish oil, resembling very closely the one obtained when the unwashed crude anthracene is employed.

Coal tar distillates of wide boiling range can also be used. For example, we condense a coal tar distillate, boiling between 300° C. and 375° C., with stearic acid in the presence of aluminum chloride and obtain as a product a red viscous oil. When a coal tar distillate boiling between 400° C. and 500° C. is used a waxy solid is obtained. In the latter case the proportions were 70 parts by weight of coal tar distillate, 68 parts by weight of stearic acid and 100 parts by weight of aluminum chloride. In a further modification of our invention we can start with coal tar bases. One of the bases which we employ is known as "light coal tar bases" and is obtained by extracting the original coal tar with sulfuric acid. This material has a boiling point range from 100° C. to 355° C., 70 per cent of it distilling above 200° C. This gives, with stearic acid and aluminum chloride, a reddish-brown oil.

Also we can use what is known as "heavy coal tar bases" a material which has a distillation range of 100° C. to 391° C., and more than 95 per cent boiling above 200° C. In this example we vary the amount of coal tar bases to stearic acid in the following proportions: 35 to 68; 70 to 68; 140 to 68. In all cases the amount of aluminum chloride is 100 parts by weight. The product in the case of the 35 parts by weight is a reddish-brown viscous oil; with the 70 parts by weight, also a reddish-brown viscous oil; and with the 140 parts by weight a reddish-brown waxy solid.

We have further found the product known as creosote oil to be admirably adapted to our process. With 35 parts of a creosote oil boiling between 200° C. to 250° C. at 10 mm. we obtained as a condensation product a free flowing oil. We also used a product known as creosote oil residue and obtained in this case, as a condensation reaction product, a free flowing oil. In both of the above mentioned cases the proportion of creosote oil to stearic acid is 35 parts to 68 parts.

In the preceding examples we have described reaction products made from stearic acid and many different fractions or distillates of coal tar, using aluminum chloride as a catalyst or condensing agent. We find that other metallic salts such as zinc chloride and ferric chloride can be used. Thus, for example, we start with 35 parts by weight of crude tower bottoms, 68 parts by weight of stearic acid and 100 parts by weight of zinc chloride, and 125 parts by weight of kerosene as a solvent. The zinc chloride is added at 120° C. over a period of three hours, after which the product is heated at 120° C. for fifteen hours. It is then cooled and poured onto an ice-hydrochloric acid mixture after which it is steam distilled in the presence of hydrochloric acid until the material gives no ash on ignition. The product is a reddish oil, very closely resembling that obtained when aluminum chloride was used as the condensing agent.

We also find that iron chloride may be substituted for the aluminum chloride or zinc chloride but in this case the reaction is not quite as smooth and necessitates rather prolonged heating.

Although we have referred to the use of these products in lubricating oils to impart oiliness and to lower the pour point, it is believed that they have many other uses. Among the uses which could be mentioned are dielectrics, water-proofing agents, polishes, waxes, etc.

While we are not certain as to the exact chemical composition of these products, we have reason to believe that they are probably ketonic in nature and that they are formed by condensation between the aromatic used and the fatty acid. We believe a complex compound is first formed which is hydrolyzed by the hydrochloric acid and steam to give the desired products. In no case did the products described above contain any residual metallic complexes.

Our reaction, and process steps, in their more specific embodiments, are somewhat similar to the conventional Friedel-Crafts reaction in that we condense an aromatic constituent with an aliphatic constituent in the presence of a catalyst or condensing agent of the type forming complex intermediate, metal-containing compounds which must be hydrolyzed to liberate the metal-free final reaction product. In this respect the process steps, as stated, are somewhat analogous to the usual Friedel-Crafts methods. In common with the Friedel-Crafts synthesis our catalysts or condensing agents (such as aluminum chloride) are used in relatively large, stoichiometric quantities, enough to form the intermediate metal complex.

Although we ordinarily use a solvent such as kerosene or carbon disulphide to facilitate the reaction, we can omit the solvent if desired. When the solvent is omitted, the intermediate metal complex must nevertheless be hydrolyzed as described above.

In the specific examples given above we have indicated a wide range of ratios of coal tar fraction to higher fatty acid. Similarly we can vary the temperature over a reasonably wide scale but we do, of course, operate at temperatures below the decomposition point of the higher fatty acid used. We do not wish to be limited to any

particular temperature except that the temperature is high enough to cause reaction between the constituents.

In the appended claims we have referred to the use of catalysts. Sometimes these substances are also called condensing agents since they take part in the reaction to form intermediate complex compounds. We use catalysts and condensing agents interchangeably in this respect. And although we have referred particularly to the use of fatty acid starting materials, it is to be understood that the anhydrides of the fatty acids can also be used. The anhydrides and the fatty acid both react in the same way to give substantially the same end products and we regard them as equivalents and cover them in the appended claims.

Having thus described our invention what we claim is:

1. The process which comprises reacting a coal tar fraction having a boiling point range of about 432° C. to about 500° C. with a fatty acid having at least six carbon atoms in the presence of a catalyst which forms a hydrolyzable intermediate metal complex with the reactants, and hydrolyzing the intermediate metal complex to liberate a metal-free reaction product.

2. The process which comprises reacting a coal tar fraction having a boiling point range of about 432° C. to about 500° C. with a fatty acid having at least six carbon atoms in the presence of a metal chloride which forms a hydrolyzable intermediate metal complex with the reactants, and hydrolyzing the intermediate metal complex to liberate a metal-free reaction product.

3. The process which comprises reacting a coal tar fraction having a boiling point range of about 432° C. to about 500° C. with a fatty acid having at least six carbon atoms in the presence of aluminum chloride to form an intermediate aluminum chloride complex and hydrolyzing the complex to liberate an aluminum-free reaction product.

4. The process which comprises reacting a coal tar fraction having a boiling point range of about 432° C. to about 500° C. with a fatty acid having at least six carbon atoms in the presence of aluminum chloride and an inert solvent for the reactants to form an intermediate aluminum chloride complex, and hydrolyzing the complex to liberate an aluminum-free reaction product.

5. The process which comprises reacting a coal tar fraction having a boiling point range of about 432° C. to about 500° C. with a fatty acid having at least six carbon atoms at an elevated temperature in the presence of a metal chloride which forms a hydrolyzable intermediate metal complex with the reactants and an inert solvent for the reactants, and hydrolyzing the complex to liberate a metal-free reaction product.

6. The reaction product obtained by reacting a coal tar fraction with a fatty acid having at least six carbon atoms in the presence of a catalyst which forms a hydrolyzable intermediate metal complex with the reactants and hydrolyzing the complex to liberate said reaction product.

7. The reaction product obtained by reacting a coal tar fraction with a fatty acid having at least six carbon atoms in the presence of a metal chloride which forms a hydrolyzable intermediate metal complex with the reactants and hydrolyzing the complex to liberate said reaction product.

8. The reaction product obtained by reacting a coal tar fraction with a fatty acid having at least six carbon atoms in the presence of aluminum chloride to form an intermediate aluminum chloride complex and hydrolyzing the complex to liberate said reaction product.

9. The reaction product obtained by reacting a coal tar fraction with a fatty acid having at least six carbon atoms in the presence of aluminum chloride and an inert solvent for the reactants to form an intermediate aluminum chloride complex and hydrolyzing the complex to liberate said reaction product.

10. The product as in claim 6 wherein the coal tar fraction used has a boiling point range of about 432° C. to about 500° C.

11. The product as in claim 7 wherein the coal tar fraction used has a boiling point range of about 432° C. to about 500° C.

12. The product as in claim 8 wherein the coal tar fraction used has a boiling point range of about 432° C. to about 500° C.

13. The product as in claim 9 wherein the coal tar fraction used has a boiling point range of about 432° C. to about 500° C.

14. The product as in claim 6 wherein the fatty acid is stearic acid.

15. The product as in claim 6 wherein the fatty acid is stearic acid and the coal tar fraction has a boiling point range of about 432° C. to about 500° C.

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