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COMPOSITIONS FROM COAL TAR AND HIGHER FATTY ACID CHLORIDES AND PROCESS OF MAKING THE SAME

Anderson W. Ralston, Carl W. Christensen, and Stewart T. Bauer, Chicago, Ill., assignors to Armour and Company, Chicago, Ill., a corporation of Illinois

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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 products of reacting coal tar fractions with higher fatty acid chlorides in the presence of aluminum chloride by a Friedel-Crafts synthesis, these compositions being oily, viscous liquids, or wax-like solids, of unknown chemical constitution; 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 a higher fatty acid chloride in the presence of aluminum chloride by a Friedel-Crafts synthesis.

The higher fatty acids having six or more atoms of carbon are cheap and abundant materials. They are the normal constituents in animal and vegetable fats and they can be obtained from such fats at relatively little expense. These higher fatty acids have been used almost exclusively in the soap industry for making candles, etc., and in relatively few instances have they been used as reagents in chemical reactions in what might be termed the "fine" organic chemical field.

We have now discovered that valuable compounds can be made from these higher fatty acids when in the form of their acid chlorides. We have discovered that higher fatty acid chlorides will react with coal tar distillates or fractions in the presence of aluminum chloride to give products which are useful in many relations. The products which we obtain vary from rather viscous oils to solid wax-like materials. We find that these products are extremely useful as addition agents to be added to lubricating oils, and this discovery has been separately described and claimed in an application in the names of Ralston, Christensen and Selby filed of even date herewith.

In broad aspects our invention comprises reacting a higher fatty acid chloride with a coal tar distillate, or with acid or basic fractions of such a distillate, in the presence of aluminum chloride by the Friedel-Crafts reaction. In the practice of our invention we can use as starting materials any acid chloride of a higher fatty acid. These higher fatty acid chlorides all have the generic formula RCOCl. Of the class of acid chlorides, acetyl chloride is one of the lowest members, but our invention relates only to the use of acid chlorides derived from higher fatty acids containing at least six carbon atoms beginning with caproic. Hence, in our invention we can use caproyl chloride, capryl chloride, lauryl chloride, myristyl chloride, palmityl chloride, stearyl chloride and also the acid chlorides corresponding to arachidic, behenic, carnaubic, cerotic, and melissic acids. We can also use higher fatty acid chlorides derived from unsaturated fatty acids such as oleic and linoleic. In most instances we use mixtures of various fatty acids. One common mixture occurring in nature is a mixture of stearic and palmitic acid. Such a mixture can be obtained by saponifying fats and treating the soaps thus formed with hydrochloric acid to liberate the free fatty acids. This mixture of free fatty acids can then be converted to a mixture of higher fatty acid chlorides by means of phosphorous pentachloride.

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 boiling from 200° C. upward. 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. The red wax is a fraction boiling between about 432° C. and 500° C.

Ordinarily we do not use coal tar fractions or distillates boiling below about 200° C. except in the case of coal tar bases to be described; and we do not, in the present invention, react pure constituents of coal tar such as pure naphthalene or anthracene wth higher fatty acid chlorides. Many of the coal tar distillates which we use in our invention contain quantities of naphthalene and anthracene admixed with other hydrocarbons, phenols, creosols, and the like, and our invention deals particularly with the treatment of these mixtures and not with pure constituents thereof. Many of the desirable characteristics in the products which we obtain are due to the fact that these products are mixtures of substances and not pure chemical compounds and it is accordingly advantageous that we react higher fatty acid chlorides with coal tar fractions, distillates or extracts containing a plurality of compounds, rather than with pure chemical individuals.

We shall now describe our invention with specific reference to preparing products from many different coal tar fractions. In order to keep our disclosure within reasonable bounds we shall re-

strict our specific examples to the use of stearyl chloride. This acid chloride can be made from stearic acid readily and it is a chloride which we ordinarily use in the practice of our invention. It is to be understood, however, that all of the higher fatty acid chlorides enumerated above can be used instead of stearyl chloride.

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 known as "middle" oil and it boils from 200° to 250° C. The next highest cut, called "heavy" oil, boils from 250° to 300° C. The so-called anthracene oil fraction, which consists largely of crude anthracene and some naphthalene, boils from 300° 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 boiling from about 360° to about 432° C. and "red wax" a waxy solid, boiling from 432° to 500° C. What is left in the still is now 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° to 500° C. We can also use products obtained from these fractions by extracting them with acids or bases as will presently be described.

We shall now first refer to products obtained by reacting so-called "crude tower bottoms" with stearyl chloride. 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 the 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 35 parts by weight of the tower bottoms, 73 parts by weight of stearyl chloride, and 258 parts by weight of carbon disulphide. To this mixture we add, at room temperature, 67 parts by weight of aluminum chloride over a period of three hours. The mixture is then refluxed for about two hours at 46° C. and then poured upon a mixture of ice and hydrochloric acid. The mixture is then steam distilled, this resulting in the hydrolysis of a complex aluminum compound probably analogous to the usual type of compounds obtained in the Friedel-Crafts synthesis. When the hydrolysis is complete the product obtained will appear as a reddish-brown, free-flowing oil floating on the surface of the aqueous mixture of aluminum chloride. Hydrolysis should be continued until this oily reaction product is substantially free of aluminum. Should it be difficult to remove all traces of aluminum, we find it advantageous to treat the oily reaction product with a mixture of acetone and hydrochloric acid under a reflux until the oily liquid becomes aluminum free. In most instances it is unnecessary to use an acetone-hydrochloric acid mixture since steam distillation ordinarily effects complete hydrolysis.

The chemical composition of this reaction product is not clearly understood. It probably contains ketonic compounds derived from anthracene and stearyl chloride. But, since phenols and creosols are also present in the initial coal tar fraction, it is apparent that the final reaction products are probably quite complex.

The reddish-brown, free-flowing oil is useful in a number of relations. It has a rather high dielectric constant and can be used in transformer oils. When added to lubricating oils it imparts oiliness to the oil and also lowers the pour point. As noted above this discovery forms the subject matter of a copending application. We can vary the ratios of tower bottoms to stearyl chloride over a wide range. For example, we can use 70 parts of tower bottoms and 73 parts of stearyl chloride, following the same general procedure indicated above, and as a result we get an oil which is dark brown and somewhat more viscous than that obtained in the first example described above.

In each instance we conduct the process steps of our invention in the manner described above for crude tower bottoms. Accordingly we will not specifically describe all of these steps in connection with each of the fractions of coal tar which we can treat and shall now describe.

Instead of beginning with the crude tower bottoms we can start with fractions thereof. In the following table we summarize examples using various fractions of the crude tower bottoms.

Fractions from crude tower bottoms

Cut °C.	*Character of product*
215–245	Dark brown viscous oil
245–320	Reddish-brown viscous oil
300–315	Reddish-brown viscous oil
315–330	Viscous dark brown oil
330–345	Dark brown grease
345–365	Reddish-brown oil
Residue	Tarry mass

In each of these examples tabulated above 35 parts by weight of the cut, or the tower bottom residue, were mixed with 73 parts by weight of stearyl chloride. In most cases the amount of carbon disulphide was about 400 parts by weight, this not being critical, and it acting only as solvent or diluent. In each instance 67 parts by weight of aluminum chloride were used.

We shall now describe a further modification of our invention wherein we use as starting materials the acidic or basic constituents of crude tar bottoms and also the residue left after washing the crude tower bottoms with an alkali, an acid, or both.

Thus, for example, we wash or extract the crude tower bottoms with a 20 percent solution of sodium hydroxide, using several portions of the caustic soda until the extracted material appears to be acid free. The alkali-washed tower bottoms are then dried and used as starting material. When 35 parts by weight of the alkali-washed tower bottoms (that is, the tower bottoms freed of alkali-soluble constituents) are reacted with 73 parts by weight of stearyl chloride in accordance with the above, the product is a greenish-brown, viscous oil which markedly lowers the pour point of a lubricating oil. In a similar way we can neutralize the aqueous alkaline extracts with an acid, thus liberating the alkali-soluble products extracted from the tower bottoms, and react them with stearyl chloride. With a ratio of 35 parts of the alkali-soluble constituents to 73 parts of stearyl chloride we obtain a reddish,

free-flowing oil which will lower the pour point of a lubricating oil markedly.

In a similar way we extract the crude tower bottoms with 40 percent sulphuric acid solution at room temperature. The dried, acid-washed tower bottoms give, when reacted with stearyl chloride in the proportions noted immediately above, a light reddish-brown grease. The acid-soluble portions of the tower bottoms can be used provided the acid extraction liquor containing them is first neutralized to liberate its content of acid-soluble constituents and these are washed and dried. When 35 parts of the acid-soluble constituents are reacted with 73 parts of stearyl chloride we obtain a brown, waxy solid useful in waxing compositions and in lubricating oils.

We can also extract the tower bottoms first with 20 percent sodium hydroxide solution to remove alkali-soluble constituents and then with 40 percent sulphuric acid solution to remove acid-soluble constituents. The extracted residue gives a dark red, waxy, free-flowing oil when reacted with stearyl chloride as described above.

We shall now describe a further modification of our invention in which we start with a coal tar distillate known as "red wax". This material is a distillate having a boiling point range of approximately 432° to 500° C. It represents approximately 7 percent of the coal tar and is the highest boiling distillate obtainable. As it occurs in commerce it is a mixture of highly condensed aromatic compounds of complex, unknown structure.

Red wax is especially advantageous in our invention since it gives us products having many desirable characteristics.

When using red wax as a starting material we mix from 5 parts by weight to 140 parts by weight of red wax with about 73 parts by weight of stearyl chloride, and from 129 parts by weight to 1,032 parts by weight of carbon disulphide. The higher quantities of red wax require more solvent for reaction purposes. In each instance we use about 67 parts by weight of alminum chloride and the Friedel-Crafts reaction is conducted in the same manner as that described for crude tower bottoms.

This procedure gives us products varying from a yellowish-red, free-flowing oil to a hard, dark red, waxy solid. We find that the best proportions of red wax to stearyl chloride are 1 to 1 or 2 to 1. A ratio of 1 to 1 gives us a soft red wax having an exceedingly desirable pour point lowering characteristic when added to a lubricating oil. A ratio of 2 to 1 gives us a reddish-brown, sluggish-flowing oil also particularly useful as an addition agent for lubricating oils.

We can also extract alkali and acid soluble constituents from the red wax in the manner described above for the extraction of such substances from crude tar bottoms. For example we extract red wax with a 40 percent sulphuric acid solution to remove acid-soluble compounds. This acid-washed red wax residue, now free of acid-soluble compounds, will give a rubber-like solid material when reacted with stearyl chloride in the proportions of 9 to 18 parts by weight of extracted red wax and 73 parts by weight of stearyl chloride. When the quantity of acid washed red wax is increased to 35 parts by weight the product is a dark red wax which, when added to a lubricating oil, will reduce its pour point.

The acid washings from the acid extraction of the red wax also contains substances which will react with stearyl chloride. For example we neutralize the acid washings with sodium hydroxide, extract the acid-soluble constituents with ether, evaporate the ether, and react 35 parts of these acid-soluble constituents with 73 parts of stearyl chloride. The product is a dark red, rather hard wax.

We can also use high boiling fractions of red wax. For example we react a fraction boiling from 450° to 500° C. with stearyl chloride and get products varying from a rubbery material to a heavy, dark red oil.

We find that many of these substances when added to lubricating oils tend to darken the oil. This disadvantage, while not serious, can be obviated by subjecting the oily wax-like products to the action of solid decolorizing substances such as "Filtrol" and "Netrol" or other decolorizing agents of the activated carbon or clay type.

In a still further modification of our invention we can start with "crude antharcene". This is a material containing approximately 40 percent anthracene, the rest being naphthalene, methyl naphthalene, carbazol, fluorene, phenanthrene and other substances. When we react 35 parts of crude anthracene with 73 parts of stearyl chloride we obtain a red, waxy material containing appreciable amounts of naphthalene and anthracene. Much of these impurities can be removed by distillation and the somewhat "purified" red, waxy material markedly lowers the pour point of a lubricating oil. It is also useful in many other relations, particularly in dielectrics.

In a similar manner we can use crude anthracene which has been subjected to an acid extraction with sulphuric acid to remove basic constituents, and in these cases we get products which are dark red, highly viscous oils or brownish-red, soft, greasy wax-like materials depending on the ratio of acid-washed crude anthracene to stearyl chloride. As the quantity of acid-washed anthracene increases the product tends to be more solid and wax-like.

In a further modification we use various coal tar fractions boiling from 300° to 500° C. but of rather wide boiling point range. For example we react a coal tar distillate (35 parts) boiling range of 300° to 375° C. with 73 parts of stearyl chloride and obtain a free-flowing oil. Another coal tar distillate, boiling range 400° to 500° C., will give a red, highly viscous oil when reacted with stearyl chloride in the ratio of about equal parts. This product is especially advantageous in lubricating oils.

In another modification of our invention we start with coal tar bases. One such product commercially obtainable is known as "light coal tar bases" and is obtained from coal tar by extracting with sulphuric acid. The material we start with has a boiling point range of from 100° to 355° C., 70 per cent of it distilling above 200° C. One part of this by weight and two parts of stearyl chloride yields a dark red greasy solid.

We can also use the so-called "heavy coal tar bases", which have a distillation range of about 100° to 391° C. but with more than 95 percent boiling above 200° C. One part of the heavy bases to two parts of stearyl chloride gives dark red greasy solids which markedly lower the pour point of a lubricating oil. The ratio of bases to stearyl chloride can be varied over a wide range from about one to four parts of bases to one part of higher fatty acid chloride.

In a further modification of our invention we can use creosote oil residues. These residues are

commercial products and consist mostly of creosote and higher homologues of creosote. These residues are all very high boiling, the boiling point range being from about 150° to 250° C. at 10 mm. pressure. They can also be described as an overhead distillate obtained from the alkali-soluble portions of coal tar. But in connection with these materials we do not wish to be limited to coal tar as the only source of them. Similar creosote oil residues are obtained from wood tar or petroleum oil of certain kinds. Accordingly in the appended claims by "creosote oil residues" we mean to include materials of this kind regardless of their source.

Fifty parts by weight of creosote oil residues, when reacted with 73 parts by weight of stearyl chloride, will give a brown, viscous tar-like material markedly lowering the pour point of a lubricating oil when added thereto in small amounts.

Instead of using the creosote oil residues as such we can use various fractions thereof. For example, we divide the creosote oil, by distillation, into four fractions, the first of which boils up to 150° C. at 10 mm., the second from 150° to 200° C., the third from 200° to 230° C., all at 10 mm., and the fourth being the residue after the distillation. All of these fractions will react with higher fatty acid chlorides in the presence of aluminum chloride to yield products varying from reddish-brown oils to reddish-brown, wax-like mixtures.

In the foregoing disclosure of our invention we have described many different fractions, distillates, and extracts of coal tar which we can use. In order to keep the description within reasonable limits we have omitted operating details in many instances. In every case, however, the coal tar distillate, or extract, and the higher fatty acid chloride is dissolved in carbon disulphide or other organic solvent customarily used in the Friedel-Crafts reaction. The mixture is then cooled or kept at about room temperature during the addition of aluminum chloride, which of course functions in the well-known way. In general the amount of aluminum chloride is practically the same as the amount of stearyl or other higher fatty acid chloride. After the reaction is completed the complex aluminum compound is hydrolized with a mineral acid, the excess solvent steam distilled from the reaction mixture, and the product recovered, usually as an oily material or a wax-like solid. We are not, of course, to be limited to the proportions stated since these can be varied materially.

Although we have more specifically referred to the use of our products in lubricting oils to impart oiliness thereto, and to modify the pour point of the oil, it is to be understood that our products have many other uses. Many of them are good dielectric materials. Others can be used in waxing and polishing compositions, as water-proofing materials, and in other relations.

In the appended claims we are obliged to define our products by reference to the process of making them since we do not know the exact chemical constitution of them. We do know that they are all mixtures of substances, possibly ketonic, possibly condensed higher hydrocarbons, and various heterocyclic compounds especially in the case of products made from coal tar bases. And, in the appended claims, the term "fraction" is intended to cover distillates and extracts broadly.

Having thus described our invention, what we claim is:

1. The process which includes reacting by a Friedel-Crafts synthesis a coal tar fraction, the major portion of which boils above about 200° C., with a fatty acid chloride having at least six carbon atoms in the presence of aluminum chloride.

2. The process as in claim 1 wherein the acid chloride is stearyl chloride.

3. The process which includes reacting by a Friedel-Crafts synthesis a coal tar distillate, the major portion of which boils above 200° C., with a fatty acid chloride having at least six carbon atoms in the presence of aluminum chloride.

4. The process as in claim 3 wherein the acid chloride is stearyl chloride.

5. The process which includes reacting by a Friedel-Crafts synthesis a coal tar fraction chosen from the group consisting of alkali-soluble and acid-soluble portions of coal tar with a fatty acid chloride having at least six carbon atoms in the presence of aluminum chloride.

6. The process as in claim 5 wherein the acid chloride is stearyl chloride.

7. The process which includes reacting by a Friedel-Crafts synthesis a coal tar fraction boiling within the range 200° C.–500° C. with a fatty acid chloride having at least six carbon atoms in the presence of aluminum chloride.

8. The process as in claim 7 wherein the acid chloride is stearyl chloride.

9. The process which includes reacting by a Friedel-Crafts synthesis the coal tar fraction having a boiling point range of about 432° C. to 500° C. with a fatty acid chloride having at least six carbon atoms in the presence of aluminum chloride.

10. The process as in claim 9 wherein the acid chloride is stearyl chloride.

11. The process which includes reacting by a Friedel-Crafts synthesis heavy coal tar bases with a fatty acid chloride having at least six carbon atoms in the presence of aluminum chloride.

12. The process which includes reacting by a Friedel-Crafts synthesis crude anthracene with a fatty acid chloride having at least six carbon atoms in the presence of aluminum chloride.

13. The Friedel-Crafts reaction product from a fatty acid chloride having at least six carbon atoms and a coal tar fraction, the major portion of which boils above about 200° C.

14. The Friedel-Crafts reaction product from a fatty acid chloride having at least six carbon atoms and a coal tar distillate, the major portion of which boils above about 200° C.

15. The Friedel-Crafts reaction product from a fatty acid chloride having at least six carbon atoms and a coal tar fraction chosen from the group consisting of alkali-soluble and acid-soluble portions of coal tar.

16. The Friedel-Crafts reaction product from a fatty acid chloride having at least six carbon atoms and the coal tar fraction having a boiling point range of about 432° C. to 500° C.

17. The Friedel-Crafts reaction product from a fatty acid chloride having at least six carbon atoms and heavy coal tar bases.

18. The Friedel-Crafts reaction product from a fatty acid chloride having at least six carbon atoms and crude anthracene.

19. The Friedel-Crafts reaction product from stearyl chloride and the coal tar fraction having a boiling point range of about 432° to 500° C.

ANDERSON W. RALSTON.
CARL W. CHRISTENSEN.
STEWART T. BAUER.