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PHOSPHORIC ESTERS OF TAR ACIDS AND METHOD FOR PRODUCING THE SAME


The present invention relates to methods of producing phosphoric esters of tar acids directly from tar distillates, and it has special utility in connection with the preparation of phosphoric esters of tar acids present in such tar distillates as those obtained in the low temperature distillation of coal under conditions so regulated as to yield as one of the products of such process a primary decomposed, or but partially decomposed, tar.

Among the principal objects of the invention are to provide an improved method for the preparation of phosphoric esters of tar acids; to provide a method of preparing from coal tar distillates the phosphoric esters of tar acids substantially free from impurities such as free tar acids, liquid hydrocarbons, phosphating agents and the like; and to provide for producing a refined product consisting of phosphoric esters of tar acids suitable for use as plasticizers, flotation agents, emulsifying agents, and the like.

The present invention is based on the discovery that tar acids present in coal tar, and especially the tar acids present in low temperature coal tar may be directly esterified in the tar distillate or in any fraction thereof without its first being necessary to separate the tar acids from the hydrocarbon oils, nitrogen bases and the like also present in such tar distillate.

In carrying out the invention the crude coal tar or any distillate or fraction therefrom is treated with phosphating agents such as, for example ortho-phosphoric acid, phosphorus oxychlorid, or other phosphoric acid derivatives, heat being applied to bring the mixture preferably to or near the boiling point thereof and the said heat treatment being continued until the reaction has occurred by which the phosphoric esters of the tar acids are formed.

Where phosphorus oxychlorid is employed as the phosphating agent it is preferably employed in amount less than that chemically equivalent to the tar acids present so that after the reaction has occurred there is an excess of tar acids which remain.

Hydrogen chloride gas is evolved in considerable quantities during the heating of the tar distillate with the phosphorus oxychlorid; and the final product of the treatment with this phosphating agent is a mixture of tri-tar-acid phosphates or neutral aryl phosphates which by virtue of their high boiling points, can be separated from the neutral oil, nitrogen bases and excess tar acids by distillation at temperatures below 245° C. preferably in vacuum, the distillation then being continued after changing receivers, at temperatures of 245° C. or higher, preferably under vacuum whereby the neutral aryl phosphates are distilled off and separately recovered, leaving behind pitch, phosphoric acid, and the like as a still residue.

Hydrogen chloride gas evolved may be recovered in any well known manner, as by absorption in water. The excess tar acids remaining after a phosphorous oxychlorid treatment may be again treated with this phosphating agent, yielding additional tri-tar-acid phosphates. The phosphorus oxychlorid evidently reacts with the tar acids in preference to reacting with the unsaturated hydrocarbons present in the tar distillate.

The tri-tar-acid phosphates obtained by the phosphorous oxychloride treatment are oils varying in color from colorless through various shades of yellow, orange and reddish brown to with or without fluorescence, and they increase in viscosity with increase in the boiling points of the tar acids from which they are prepared. Certain of these phosphates prepared had boiling ranges of between 245° and 340° C. at 10 mm. absolute pressure. They are relatively stable at high temperatures as compared with most oils, and are miscible in all proportions with most organic solvents, and in neutral oil and tar acids; they are, for instance, particularly miscible with petroleum ether; (wholly so in the presence of tar acids); and practically immiscible with water, the latter precipitating them from their alcoholic solution. They are at least partially hydrolyzed by heating with aqueous alkalis or water, forming the acid phosphates, and are completely hydrolyzed by acids such as strong mineral acids. Owing to their resemblance to commercial tri-cresyl phosphates they can be
substituted for the latter as plasticizers for nitrocellulose or bakelite products, as flotation agents, as solvents, or for any purpose where a high boiling stable oil or an oil of definite and uniform viscosity is required, as for example, in tin pots.

When such a phosphating agent as phosphoric acid is employed, the tar acid distillate is boiled with such phosphoric acid in amounts sufficient to react with the tar acids present, the latter preferably being added gradually to the said distillate, whereupon water distills off, provision being made for catching or condensing and returning to the still any oil carried therewith from the water vapor. The reaction occurring takes place slowly and as much as twelve to twenty-four hours may be required for completion of the reaction. The end point is indicated when no more water distils over, but the heating is preferably continued for sometime afterward (for a half hour or more depending on operating conditions) after the evolution of the water vapor has been completed. The crude reaction mixture from the phosphating reaction may comprise in addition to the phosphoric esters of the tar acids, considering amounts of unchanged tar acids, neutral oil, nitrogen bases, excess phosphoric acid, and the like.

The material remaining in the still is then further distilled at temperatures up to 250°C under vacuum until all substances volatilizing at or below 250°C have been driven off. This distillation under vacuum removes nearly all of the neutral oil, the unattacked tar acids and the like, so that the residue in the still consists essentially of a mixture of primary, secondary, and tertiary tar acid phosphates.

During the reaction between the tar acids present in the coal tar distillate and the phosphating agent the temperature, while being controlled by the boiling point of the material employed, will gradually rise to as high as 250°C or above, owing to the steady accumulation of high boiling and non-volatile products in the reaction vessel. It is preferable to keep the temperatures to which the phosphoric esters are exposed from very greatly exceeding 250°C since the aryl acid phosphates are usually unstable above 250°C.

In the modification of the process in which phosphoric acid is used as the phosphating agent the phosphoric esters comprise a mixture of mono-, di- and tri-aryl phosphates, the latter two being present in major proportions and being produced in almost equal quantities. On the other hand, the phosphorus oxychloride is employed as the phosphating agent with excess of tar acids, the resultant phosphatic ester is almost exclusively the neutral tri-aryl phosphate. The mixtures of intermediate or aryl acid phosphates which are obtained along with neutral tri-aryl phosphates by the action of phosphoric acid are dark viscous oils or high boiling points, and are relatively unstable at elevated temperatures. Most of them are practically insoluble in water but soluble in most organic solvents and they have a strong acid reaction so that they liberate carbon dioxide from aqueous sodium bicarbonate solution, while they themselves are not liberated by acetic acid from aqueous solutions of their alkali metal salts. The alkali metal salts are readily soluble in water but are easily salted out as a concentrated aqueous solution which is capable of extracting tar acids from tar acid containing oil. In dilute aqueous solution these salts are frothing agents. The free aryl acid phosphates as well as their water-soluble salts can be used as emulsifying agents and flotation agents.

The following specific examples of the application of the invention to the production of phosphoric esters of tar acids direct from tar distillates are given as indicating certain preferred embodiments of the invention but are not to be regarded as in any way limiting the scope of the invention which resides broadly in the method of producing phosphoric esters of tar acids directly from tar distillates:

**Example 1.**—100 parts by weight of a low temperature tar distillate having a distillation range of from 200°–300°C and containing 40% by weight of tar acids are boiled in a still while 10 parts by weight of 85% ortho-phosphoric acid are gradually added thereto, the temperature being so controlled meanwhile that water present in the material and that formed by the reaction distils over freely with the minimum quantity of the tar distillate. The vapor outlet from the still is so connected with a reflux condenser that the vaporized distillate and the water vapors are condensed and flow by gravity to a trap or separator which effects a separation of the condensed water from any oil distilling over with the water vapors, such oil being returned to the still while the water is led away. The reaction temperature is controlled according to the boiling point of the reaction mixture, and gradually rises during the course of the distillation from about 200°C to in the neighborhood of 250°C or above as the high boiling and non-volatile products accumulate in the still. The reaction takes place slowly and may require from twelve to twenty-four hours for its completion, the end point being indicated by the cessation of steam formation in the still. At this stage the apparatus is evacuated by means of a vacuum pump and the distillation is continued under vacuum at about 10 mm. absolute pressure until no more volatile material can be driven off at temperatures of about 250°C and below.
During this distillation nearly all of the unattacked tar acids, neutral oil, nitrogen bases and the like are distilled away, and the residue consists essentially of a mixture of about equal parts of secondary aryl acid phosphates and tertiary (neutral) phosphates of the tar acids, amounting in all to about 30 parts by weight or more. The distillate obtained during the vacuum stage of the treatment is similar to and may be conveniently disposed of as creosote oil. It is important that overheating be avoided since, because the aryl acid phosphates are usually unstable above 250° C., the latter cannot be distilled, nor can the tertiary phosphates which distill around 300° C. in vacuum, be distilled off from them—without decomposition occurring. To the distillation residue is added with stirring a quantity of warm water (some other alkaline solution may be substituted if preferred, but ammonia works nicely and has less salting out effect) somewhat more than sufficient to neutralize the aryl acid phosphates. A thin, more or less homogeneous liquid is thus obtained, owing to the solubility of the neutral aryl phosphates in rather concentrated aqueous solutions of the salts of the aryl acid phosphates. This liquid may be further thinned with more water, if desired. The neutral aryl phosphates are then easily extracted from the mixture by several washings with petrol. The neutral phosphates may then be further purified, while in solution in the petrol, by treatment with caustic alkalies, acids, etc., if desired, and may be finally recovered by distillation, preferably in vacuum.

The aryl acid phosphates may be recovered by acidification of the ammoniacal solution after distilling off the excess of ammonia, if desired, or by decomposing the ammonium salt by further heating, preferably in vacuum. A relatively small but appreciable quantity of the more soluble acid-aryl phosphates will remain in the acidified solution from which they may be extracted by a suitable solvent, such as ether or benzol.

Example 2.—A low temperature tar distillate boiling between 200°-300° C. and containing 50% tar acids is heated with phosphorus oxychlorid, (POCl₃) in the proportions of six parts by weight of the former to one part by weight of the latter, in a still provided with a reflux condenser, the heat being applied gently until the reaction begins, as indicated by evolution of hydrogen chloride gas. The heating is thereafter regulated to maintain the reaction until it is completed which usually requires several hours to complete. The temperature is finally elevated to the boiling point of the mixture and the distilled vapors refluxed. Since the reaction is very slow toward the end thereof owing to the low concentration of the reacting materials, it is desirable to continue the heating for a half hour or more after the evolution of hydrogen chloride gas has apparently ceased. The hydrogen chloride gas given off during the reaction is led off through the reflux condenser, and is recovered by absorption in water. The mixture remaining in the still after the completion of the reaction is then completely distilled under a vacuum of about 10 mm. absolute pressure and the fraction distilling above 245° C. consisting essentially of the tri-aryl phosphates is collected separately, being thus separated from the material not reacted upon. It is desirable that the boiling point range of the starting material should not approach too closely that of the lowest boiling aryl phosphates, namely 225° C. at 10 mm. pressure.

Other methods of separating the phosphoric esters of the tar acids from the crude reaction mixtures may be used. For example, the mixture resulting from the action of phosphoric acid on a tar distillate, as already described, before distilling off the neutral oil, tar acids, etc., or after distilling them off and diluting with a suitable solvent such as neutral oil or with a mixture of benzol and a light petroleum distillate, is just neutralized by gradual addition of an alkali carbonate or bicarbonate solution with agitation. After the mixture thus treated has been permitted to come to rest it separates into two strata, an oily upper stratum, and a lower aqueous stratum. The former is then distilled in vacuum to recover therefrom its content of neutral tri-aryl phosphates in the form of a distillation residue. The aqueous layer after separation from the oily layer is carefully distilled to dryness in vacuum and yields as a final product or residue the sodium salts of the aryl acid phosphates. These salts are leached out of this distillation residue with water, and they may be then treated with a mineral acid such as sulfuric acid to liberate the free acids therefrom. The primary phosphoric esters are extracted from the aqueous acid layer by ether or the like.

If desired, any free phosphoric acid left in the crude reaction mixture, before further treatment may be removed by shaking with water. The amount of free acid, however, is usually not enough to be worth recovering. The water will also remove some of the more soluble aryl acid phosphates, principally mono-aryl phosphates, which may be recovered separately from phosphoric acid, by extracting the water with a suitable solvent, as, for example, ether. It will be obvious that the various aryl phosphoric esters formed in the practice of this invention may be separated from the impurities mixed therewith such as excess tar acids, hydrocarbon oils and the like by either or all of the steps for such separation which are here disclosed or by equivalent process steps.

The term "petrol" is used in the specifica-
tion to designate a petroleum distillate boiling below 100° C.

My invention provides in a commercially practicable manner for the production of organic phosphates containing a cyclic nucleus and having utility in many industrial fields from coal tar distillates and particularly from those obtained from tar formed in low temperature carbonization processes. The invention is capable of modification within the scope of the appended claims.

I claim:
1. The process for producing organic phosphates containing a cyclic nucleus which comprises the steps of heating a mixture of a coal tar distillate and a hydrated phosphating agent to a temperature sufficient to cause a reaction between the said substances and the formation of water vapor and gaseous products of reaction, removing the said water vapor and gaseous products of reaction as rapidly as formed, and subsequently fractionally distilling the remaining materials in undiluted form under high vacuum.

2. The process as defined in claim 1 in which the fraction distilling over at temperatures of 245° C. and above under high vacuum is separately condensed.

3. The process for preparing mixtures of neutral and acidic organic phosphates containing a cyclic nucleus, which comprises heating and reacting a mixture of coal tar acids in hydrocarbon oil with ortho-phosphoric acid while maintaining the reaction mixture at a temperature sufficiently high to drive off the water vapors produced by the reaction, but below that at which the said organic phosphates are substantially decomposed.

4. The process for preparing organic phosphates containing a cyclic nucleus which comprises the steps of heating a liquid mixture containing tar acids with phosphoric acid at temperatures sufficient to produce reaction therebetween and liberate water vapor, removing the water vapor as rapidly as formed until substantially all thereof has been removed, thereafter separating from the residue the primary aryl acid phosphates by means of water, separating the secondary aryl acid phosphates by ammonium hydroxide solution, and fractionally distilling the tri aryl phosphates in vacuum.

5. A new composition of matter consisting of a mixture of aryl acid phosphates obtained from a coal tar distillate containing tar acids by heating the latter with a hydrated phosphating agent, and recovering from the resultant reaction mixture the said aryl acid phosphates.

6. A new composition of matter comprising a mixture of neutral aryl phosphates and aryl acid phosphates essentially as derived from the tar acids of a coal tar distillate, the said composition being practically insoluble in water but soluble in most organic solvents, strongly acid in reaction and capable of forming alkali metal salts that are easily soluble in water.

7. An emulsifying agent comprising a mixture of aryl acid phosphates derived directly from a tar distillate containing tar acids, the said agent being a dark viscous oil of high boiling range, which is unstable at temperatures substantially above 230° C.

8. In the process of preparing an organic phosphate containing a cyclic nucleus, the steps of reacting a coal tar distillate containing tar acids with a phosphating agent, thereafter neutralizing the resultant reaction mixture with an aqueous solution of a weak alkali, forming an oily layer and an aqueous layer, separating the said layers from each other and removing from the aqueous layer by distillation under vacuum, any free tar acids, hydrocarbons and other volatile substances present therein, leaching the salts of the aryl acid phosphates from the distillation residue by means of water, and liberating the free aryl acid phosphates from the resultant aqueous solution.

9. In the process of preparing organic phosphates containing a cyclic nucleus, the steps of reacting a coal tar distillate containing tar acids with a phosphating agent, thereafter neutralizing the resultant reaction mixture in undiluted form with an aqueous solution of a weak alkali, forming an oily layer and an aqueous layer, separating the said layers, distilling the former in vacuum and recovering as a distillation residue a mixture of neutral organic phosphates containing cyclic nuclei.

10. The process of preparing organic phosphates containing a cyclic nucleus which comprises reacting a liquid mixture containing coal tar acids with a hydrated phosphoric acid while removing the water vapors thus produced, and thereafter distilling the reaction mixture in undiluted form under high vacuum at temperatures below those at which substantial decomposition of the resultant organic acid phosphates occurs.

11. The process of preparing an organic phosphate containing a cyclic nucleus which comprises reacting a tar distillate containing tar acids and having a distillation range of from 200° to 800° C. with phosphoric acid while removing the water vapors thus produced, thereafter distilling the reaction mixture under vacuum at temperatures below those at which substantial decomposition of the resultant organic acid phosphates occurs, thereby distilling off the neutral oil, unattacked tar acids and nitrogen base components of the tar distillate, and recovering a mixture of tertiary and secondary phosphates of the tar acids in the form of a still residue.

12. The process for producing organic phosphates containing a cyclic nucleus which...