

UNITED STATES PATENT OFFICE

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PREPARATION OF ESTERS OF ACIDS OF PHOSPHORUS

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3 Claims. (Cl. 260-403).

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This invention relates to the preparation of hitherto unknown esters of the acids of phosphorus and more particularly to the preparation of phosphated and phosphited compounds derived from unsaturated acids.

This invention has for its object to provide a process for producing certain new chemical compounds which are esters of the acids of phosphorus. A further object is to provide new phosphated and phosphited compounds which are derived from blown unsaturated carboxylic acids. A still further object is to provide improved phosphated and phosphited compounds having exceptional usefulness as surface-active agents, wetting, washing, and dispersing agents, and as lubricating, anti-static and conditioning agents for textile yarns, particularly those composed of or containing cellulose acetate and related cellulose derivatives. Other objects will appear herein-after.

These objects are accomplished by the following invention, which is based upon the unexpected discovery that if certain unsaturated carboxylic acids containing the group

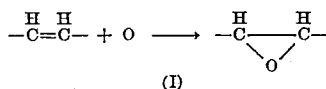


are heated and then blown with air or oxygen until an appreciable increase in specific gravity of the compounds occurs, such compounds will react with acids of phosphorus such as phosphorous, hypophosphorous, phosphoric, thiophosphoric, and the various pyro- and polyphosphorous and phosphoric acids. This is a most unusual phenomenon when it is taken into consideration that compounds containing the group

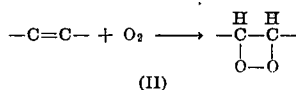


such as oleic acid, butyl oleate, oleyl alcohol, carbitol oleate, ethylene glycol dioleate, and butyl ricinoleate, do not add acids of phosphorus, such as phosphorous and phosphoric acids when mixed and heated therewith.

While we do not confine ourselves to any specific theory or explanation of the mechanism of the reaction involved when the unsaturated compounds are blown as above described, the reaction may be as follows:



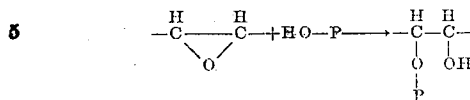
or



The reaction between the phosphorus acid and

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the structure resulting from the blowing operation may be represented conventionally as follows:



It will thus be seen that the phosphato or phosphito group adds to the carbon chain at the position originally occupied, before blowing, by an unsaturated linkage.

In general, the unsaturated compounds selected for blowing, such as oleic acid, erucic acid, ricinoleic acid, acetylated ricinoleic acid, oleic acid ester of ricinoleic acid, undecylenic acid, dehydrogenated (2H) sebacic acid, and the acids from oils such as soyabean, cotton, sardine, menhaden, peanut, and the like, are heated from 50° to 200° C. (125-180° C. preferred) and air or oxygen is passed in until a product having the desired properties is obtained. When the unsaturated compound is blown the iodine value falls, while the specific gravity, refractive index, acetyl value and saponification equivalent rise. One skilled in the art can by following the progress of the above constants, determine when to stop blowing the unsaturated compound so as to obtain a product that will readily react with an acid of phosphorus.

Any of the -ous or -ic acids of phosphorus may be employed for phosphating or phosphiting the blown compounds in accordance with our invention. Typical examples of such acids are phosphoric acid, metaphosphoric acid, monosodium phosphate, pyrophosphoric acid, tetraphosphoric acid, phosphorous acid, hypophosphorous acid and pyrophosphorous acid.

In view of the foregoing explanation the compounds of our invention may then be regarded as esters of acids of phosphorus prepared by reacting an -ous or -ic acid of phosphorus with a blown unsaturated carboxylic acid.

In the following examples and description, we have set forth several of the preferred embodiments of our invention, but they are included merely for purposes of illustration and not as a limitation thereof.

Example 1

100 g. of oleic acid is blown at 150°± until the specific gravity has increased 0.05-units. Then 30 g. phosphoric acid are added and the mixture heated with stirring on a steam bath for 10 hours. The excess acid is removed with cold water or cold aqueous salt solutions. The brownish viscous product is water soluble. For phosphoric acid substitute phosphorous acid, pyrophosphoric

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acid, tetraphosphoric acid or any other poly acid of phosphorous.

Example 2

100 g. of erucic acid are blown as above and reacted with phosphorous acid as in Example 1. The product is soluble in water.

Example 3

100 g. of ricinoleic acid are blown and reacted as in 1 with 60 g. of tetraphosphorous acid. The product is soluble in water.

Example 4

100 g. of acetylated ricinoleic acid are blown as in 1 and phosphated as above with 60 g. of phosphoric acid. The product is water soluble.

Example 5

100 g. of the oleate of ricinoleic acid are blown as in 1 and phosphated as above with 70 g. of phosphoric acid. The product is water soluble.

Example 6

100 g. of the acids from soyabean oil are blown as in 1 and phosphated as above. The product is water soluble.

While we have found it convenient to illustrate our invention by reference to procedures involving the blowing of certain specific unsaturated carboxylic acids, it will be evident that many modifications in such procedures may be made within the scope of our invention. In general, it may be said that, irrespective of the particular acid dealt with, the blowing operation may be carried out in a manner analogous to that which is customarily employed in the blowing of various oils, fats, and waxes.

The blown and phosphated or phosphited compounds of our invention have many valuable applications in industry. For example, they may be employed as surface-active agents, wetting, washing and disbursing agents. We have also found them to have outstanding properties when employed as lubricating anti-static and conditioning agents for textile yarns, particularly those composed of or containing cellulose acetate and related cellulose derivatives.

The preparation of novel esters of an acid of phosphorus is disclosed and claimed in our co-pending applications Serial No. 602,412, filed June

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29, 1945, issued as Patent No. 2,466,393, and Serial No. 602,415, filed June 29, 1945, now abandoned.

What we claim is:

1. The process of producing an ester of an acid of phosphorus which comprises blowing an unsaturated acid having the formula:



wherein R represents an unsaturated hydrocarbon chain containing from 17 to 21 carbon atoms in which the unsaturation is limited to olefinic unsaturation, at from 50° to 200° C., until an appreciable increase in specific gravity occurs, and thereafter treating the blown acid with an acid of phosphorus selected from the group consisting of phosphoric and phosphorous acids.

2. The process of producing an ester of an acid of phosphorus which comprises blowing oleic acid, at from 50° to 200° C., until an appreciable increase in specific gravity occurs, and thereafter treating the blown acid with an acid of phosphorus selected from the group consisting of phosphoric and phosphorous acids.

3. The process of producing an ester of an acid of phosphorus which comprises blowing erucic acid, at from 50° to 200° C., until an appreciable increase in specific gravity occurs, and thereafter treating the blown acid with an acid of phosphorus selected from the group consisting of phosphoric and phosphorous acids.

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