This invention relates to new chemical compounds and their preparation, more particularly to dithiophosphoric acid esters of abietyl alcohols, salts of such acid esters and methods of preparing the same.

As is generally known the naturally occurring wood and gum resins consist principally of abietic acid and smaller amounts of isomeric acids such as d-pimeric, sapinic, etc. These acids are tricyclic hydroaromatic acids, possessing an alkylated phenanthrene nucleus, of the general formula C_{15}H_{24}O. These acids and their esters may be reduced by hydrogenation processes in known manner to yield a series of abietyl alcohols and isomers thereof, the principal ones of which are abietyl alcohol, dihydro-abietyl alcohol, tetrahydro-abietyl alcohol anddehydroy-abietyl alcohol, the latter possessing a diaecyclo- monoalicyclic structure.

We have now discovered, and this discovery constitutes an essential feature of the present invention, that these alcohols may be reacted with P_{2}S_{5} to yield dithiophosphoric acid esters of abietyl alcohols and that the salts of these acid esters may be prepared in the manner to be hereinafter described. The present invention is directed therefore principally to the preparation of such acid esters and their salts as new chemical compounds.

The compounds of the present invention have an unexpectedly high solubility in hydrocarbon lubricating oils and when added thereto in small amounts are found to have the unusual characteristics of showing anti-oxidant properties in preventing decomposition of the oil when employed at high temperatures under severe lubricating conditions. These new compounds act as corrosion inhibitors preventing corrosion of certain alloy bearings and other metal parts in internal combustion engines. They have also been found useful as detergents and dispersing agents in lubricating oils in which they prevent formation of sludge and prevent formation on the pistons and other parts of the engine of lacquer-like deposits which cause sticking of the piston rings and sometimes even the piston itself. Being water-insoluble and polar in character they are also valuable in the preparation of slushing oils. Because of their sulfur and phosphorus content they may be advantageously added to hypoid gear lubricants and other high pressure lubricants. Compounds of the present invention are also useful in the flotation of ores and some of their salts, particularly their lead and mercury salts, may be employed in insecticides and fungicides. Being thick, viscous liquids of good heat stability they also are of value as plasticizers, particularly for synthetic rubber.

Our new compounds may be prepared by heating a resin derived alcohol of the group consisting of abietyl alcohol, dihydro-abietyl alcohol, tetrahydro-abietyl alcohol and dehydro-abietyl alcohol with phosphorus pentasulfide (P_{2}S_{5}) at temperatures of the order of 90-110°C; the reaction of 1 mole of P_{2}S_{5} with 4 moles of the abietyl alcohol resulting in the formation of 2 moles of a dithiophosphoric acid ester of the corresponding abietyl alcohol with the elimination of 1 mole of H_{2}S. The reaction may be brought about by merely mixing P_{2}S_{5}, preferably in a finely ground form, with the desired abietyl alcohol with heating and stirring until the evolution of H_{2}S has practically ceased. Should excessive foaming occur due to the evolution of H_{2}S the addition of a small amount of toluene to the reaction mixture will reduce the foaming to a point at which it is no longer troublesome. The crude di(abietyl) dithiophosphoric acid ester is obtained in the form of a viscous liquid which may be decanted from the unreacted P_{2}S_{5}. The desired salt of the di-(abietyl) dithiophosphoric acid ester may then be prepared by simple neutralization of the compound with salt-forming bases or by double decomposition with its sodium salt.

As pointed out above the abietyl alcohols which may be employed by us in the preparation of our new compounds are known products derived by the reduction, usually catalytic hydrogenation, of abietic acid or a primary, secondary or tertiary ester of abietic acid or hydroabietic acid. The product usually contains mixtures of the various abietyl alcohols depending upon the particular conditions employed in the hydrogenation. The product also contains alcohols isomeric with abietyl alcohols in amounts depending principally upon the source and type of resin employed as starting material. Accordingly, while the appended claims may recite esters of particular abietyl alcohols it will be understood that mixtures thereof and esters of isomeric alcohols are also included within the purview of our invention.

As stated above, the di(abietyl) dithiophosphoric acids may be made into salts by simple neutralization with a suitable salt-forming base or by double decomposition. A wide variety of salt-forming radicals including those such as nickel, aluminum, lead, mercury, cadmium, tin, zinc, magnesium, sodium, potassium, ammonium,
copper, strontium, calcium, lithium and barium may be introduced by neutralizing the acid with their oxides, hydroxides, carbonates and in some cases sulfides. The alkaline earth salts of our abietyl alcohol esters of dithiophosphoric acids are preferred as lubricating oil additives, since these salts are neutral, stable, and resist emulsification well.

The preparation of our new compounds will now be described in greater detail by means of the following example to which, however, our invention is not limited since it is given merely for purposes of illustration. Obviously, modifications thereof may be made without departing from the scope of our invention as set forth in the appended claims.

1810 parts by weight of dihydro-abietyl alcohol and 382 parts by weight of finely ground PsSs were heated with stirring at 100–105° C. for 3 hours. At the end of this time most of the PsSs had reacted and the evolution of H2S had practically ceased. The crude di(dihydro-abietyl) dithiophosphoric acid thus obtained was decanted from unreacted PsSs. The product was a viscous liquid with a light blackish-brown color.

The barium salt of di(dihydro-abietyl) dithiophosphoric acid was prepared as follows: 2100 parts by weight of di(dihydro-abietyl) dithiophosphoric acid as obtained above was dissolved in 550 parts by weight of ethyl alcohol (97.5%) and 1200 parts by weight of toluene. 240 parts of finely powdered barium oxide was added gradually with stirring and cooling so that the temperature of the reaction mixture was maintained below 40° C. As soon as the product was neutralized 1200 parts by weight of toluene was added and the solution filtered from traces of barium salts. The solvent was then removed by evaporation under reduced pressure with stirring.

Barium di(dihydro-abietyl) dithiophosphate was obtained as a viscous light yellow liquid.

The barium salt of di(dihydro-abietyl) dithiophosphoric acid may also be prepared by treating the acid ester with barium sulfide. The use of barium sulfide in this preparation is advantageous in that the formation of water during the neutralization is avoided, H2S being formed instead and is evolved from the reaction mixture during the neutralization. The other abietyl alcohols may be reacted with PsSs in the same way as described above using similar proportions of materials. For this reason description of the preparation of these products is not thought necessary. When these esters are to be added to lubricating oils as detergents, sludge dispersants and corrosion inhibitors it is convenient to add a suitable hydrocarbon lubricating oil such as 10–W grade to the preparation before all of the solvent has been evaporated. In this way it is possible to obtain a concentration of the abietyl ester in lubricating oils of as high as 50% which composition may be sold, shipped and stored as such for convenient handling and blending purposes.

These compounds have also been found to exert solubilizing effects on other less oil-soluble alkyl esters of dithiophosphoric acids such as barium diamyl dithiophosphate and the two types of esters may be advantageously blended before being incorporated in a lubricating oil.

What we claim is:

1. Barium di(dihydro-abietyl) dithiophosphate.

2. A method of preparing barium salts of di(dihydro-abietyl) dithiophosphate which comprises heating dihydro-abietyl alcohol with PsSs until the evolution of H2S has substantially ceased and neutralizing the resulting product with barium oxide.

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