SYNTHESIS OF SULFUR-, PHOSPHORUS-, AND NITROGEN-CONTAINING ASHLESS ADDITIVES FOR LUBRICATING OILS
(PATENT REVIEW)

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Within the widely used class of dithiophosphate additives, preference is now beginning to be given to ashless dithiophosphates containing nitrogen. Here we are presenting a review of the principal patents for the period 1950-1972 covering the synthesis of ashless additives that consist of nitrogen-containing triesters of dithiophosphoric acids.

Compounds containing sulfur, phosphorus, and nitrogen are ashless polyfunctional additives: the esters of phosphorus acids serve as antiwear agents that simultaneously improve the antiscoring properties of the oils; the amines and other nitrogen-containing compounds are antioxidants. The amine salts of dithiophosphoric acids are neutral; they have antifriction, antiwear, anticorrosion, and antioxidant properties.

Ashless additives consisting of the completely esterified dithiophosphoric acids, containing nitrogen, are obtained by the interaction of dithiophosphoric acids with various nitrogen-containing organic compounds. The most important of these reactions are the following:

1. Neutralization of dithiophosphoric acids by amines, polyamines, polymeric compounds containing nitrogen, or ethanolamines;
2. Condensation of dithiophosphoric acids with formaldehyde and amines by the Mannich reaction;
3. Interaction of dithiophosphoric acids with formaldehyde or alkene oxides, with subsequent treatment of the reaction products with amines;
4. Interaction of dithiophosphoric acids with amides of unsaturated carboxylic or thiocarboxylic acids;
5. Reaction of dithiophosphoric acids or their sodium or potassium salts with various halogen-containing compounds (haloalkyl amines, amides of halocarboxylic or halodithiocarboxylic acids);
6. Interaction of dithiophosphoric acids with succinimides.

One of the widely used types of ashless additives consists of N-alkyl-substituted quaternary ammonium salts of dithiophosphoric acids.

A wide variety of additives having antiwear, antioxidant, detergent, anticorrosion, and antiscoring properties has been obtained by the interaction of dithiophosphoric acids of various structures with amines or amine derivatives [1-40].

For the synthesis of dithiophosphoric acids, recommendations include the use of alcohols and alkylphenols [34], diols and triols [33], carboxylic acids [1], dihydroxydiphenyl sulfide and dihydroxydiphenylamine [3, 22], bifunctional phenols [23], hydroxylalkylated alcohols and alkylphenols [24, 25, 30, 31], high-molecular-weight esters of aliphatic alcohols with fatty acids, or glycerides [10], products from the reaction of high-molecular-weight carboxylic acids with aminohydroxy compounds [32].

In a series of patents [4, 26-29], as sulfur- and phosphorus-containing reactants, products recommended for use are obtained by the interaction of phosphorus pentasulfide with polyolefins or terpenes [38-40], and also boron-containing dithiophosphates [11].

Of the amine-series compounds, recommendations have been made for aliphatic and aromatic monoamines [10, 11, 21, 24, 32, 33], aliphatic and aromatic polyamines [8, 9, 13, 14, 17, 22, 23, 26-29, 32], thiolamine [2], piperazine derivatives [32], and chlorinated alkyleneamines [34]. Of the other nitrogen-containing compounds for neutralizing dithiophosphoric acids, it has been proposed that the following should be used: diisocyanates [35], carbodiimides [36], products from the reaction of polyhalopolyhydroxydicarboxylic acids with alkanolamines [37], a diamino diphenyl ether [16, 20], nitriles [4], nitrogen-containing polymeric compounds obtained by the interaction of esters of unsaturated carboxylic acids with unsaturated compounds containing nitrogen such as aminoalkyl and aminocycloalkyl esters of acrylic acid, unsaturated amines, or amides of unsaturated carboxylic acids. The additives obtained on the basis of nitrogen-containing polymers are not only good antioxidant and antiwear additives, but they may also have pour-depressant, VI-improving, and antiwear properties.

Now that the ammonium salts of dithiophosphoric acids are coming into widespread use as lubricating oil additives, vulcanization accelerators, and flotation reagents, it has been noted that some of them are unstable, decomposing readily in storage to liberate hydrogen sulfide. In order to improve the stability of these salts, it has been proposed [6] that there should be added certain salts of dithiophosphoric acids with polyamines (hexamethylenetetramine, etc.).

There are patents [5, 7, 12, 34] on the use of quaternary ammonium salts of dithiophosphoric acids as additives having antiwear and antiscoring properties.

Recent patent communications have appeared [18, 19] on the use of ammonium salts of dithiophosphoric acids as the starting material in synthesizing anticorrosion additives, as well as additives with antiwear and antiscoring action.

The ammonium salts of dithiophosphoric acids may be used in additive packages with other sulfur- and phosphorus-containing compounds, thus producing ashless antioxidant and antiwear additive packages [41].

Another class of sulfur-, phosphorus-, and nitrogen-containing additives for lubricating oils consists of the condensation products of diesters of dithiophosphoric acids with aldehydes and amines [42-44]. These compounds, being good antioxidant and anticorrosion additives, have substantial advantages over other types of completely esterified dithiophosphoric acids; they are very stable at elevated temperatures.

The starting material in synthesizing this type of additive may be aliphatic, aromatic, or heterocyclic compounds. Instead of amines, amides or hydroxymethylamides may be used [44]. The resulting products were tested as antioxidant additives in oils. In these tests, a silver-cadmium alloy strip was placed in the oil, together with iron naphthenate, and the oil was heated to 160°C for 10 h with free circulation of air through the oil. The additive efficiency was rated according to the amount of corrosion of the strip. With 0.5-1.0% additive by weight, the corrosion amounted to 3-15 mg, in comparison with 1047 mg for the oil without additive.

Ashless additives having anticorrosion and antiwear properties are also obtained by the interaction of dithiophosphoric acids with alkene oxides and amines [45]. For the purpose of increasing the phosphorus content, a scheme sometimes used is the action of phosphorus pentasulfide (or P_2O_5, H_3PO_4, PCL_3) on hydroxyalkyl esters of dithiophosphoric acids (obtained by the reaction of dithiophosphoric acid with an alkene oxide), the reaction product being subsequently neutralized with an amine [46-50]. Conditions for the condensation of dithiophosphoric acids with alkene oxides have been described in patents [42-44].

Efficient oxidation and corrosion inhibitors are obtained by the reaction of dithiophosphoric acids with amidines of unsaturated carboxylic acids such as acrylic, crotonic, or methacrylic [51-53]. This reaction is exothermic; it is carried out at moderate temperatures, with equimolar quantities of reactants. The end products are viscous, light-yellow, neutral substances which, when added to oil in amounts of 0.1-3.0%, give considerable improvements in the antiwear, antiscoring, and antioxidant properties of the oil.

In a number of patents, methods have been described for obtaining ashless additives by the interaction of dithiophosphoric acids with chlorine-containing compounds in the presence of ammonia [54], potassium or sodium salts of dithiophosphoric acids with N-substituted chloramides of thioacetic acid [55], or halogen-substituted amines [56]. The resulting compounds are corrosion inhibitors for copper-lead and cadmium-silver bearings.

In a series of patents [57-73], applications as multifunctional ashless additives have been described for the reaction products of sulfur- and phosphorus-containing compounds with succinimides.