United States Patent Office 2,925,419 Patented Feb. 16, 1960

2,925,419

PROCESS FOR STABILISING ESTERS OF ACIDS OF PHOSPHORUS AND STABLE COMPOSITIONS OF ESTERS OF ACIDS OF PHOSPHORUS

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No Drawing. Application November 18, 1957
Serial No. 696,921

Claims priority, application Switzerland
November 30, 1956

6 Claims. (Cl. 260—251)

The present invention concerns a process for the stabilising of phosphoric acid esters which can be used, for example, in the production of pesticides.

Surprisingly it has now been found that phosphoric acid esters can be stabilised by adding compounds which contain an epoxide group to such esters or preparations thereof. In this connection, protection from hydrolysis as well as from any other type of decomposition is meant by stabilisation. Compounds having an epoxide group which are suitable stabilising agents are, in particular, epichlorohydrin, cyclohexene oxide, propylene oxide and styrol oxide. Depending on the molecular weight of the additive used and stability of the compounds to be stabilised, about 2–30% (calculated on the weight of the phosphoric acid ester) of a compound containing an epoxide group is added to the compounds to be stabilised.

In this invention, esters of all acids of pentavalent and also trivalent phosphorus are meant by phosphoric acid esters, thus, for example, apart from the esters of orthophosphoric acid also those of pyro-, tri- and tetra-phosphoric acid, thiophosphoric acid, dithiophosphoric acid, those of phosphorous acid and of phosphonic and phosphinic acids are to be understood. The invention is particularly concerned, however, with the stabilising of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester and phosphoric acid-[3-methyl-pyrazolyl-(5)]-diethyl ester.

In particular, active ingredients for pesticides of all types as pure substances, as technical crude substances, as ready-for-use preparations or as solid, semi-solid or liquid concentrates for the production of the latter are meant by phosphoric acid esters to be stabilised. In addition they can also be, for example, additives to lubricants and fuels, antistatic agents and flame-proofing agents.

The invention is also concerned with new stable compositions which comprise essentially a phosphoric acid ester, an emulsifying agent such as an alkyl phenol-ethylene oxide condensation product, an organic solvent such as xylene, benzene, diesel oil, kerosene, spindle oil or a petrolatum product, and 2–30% (calculated on the weight of said ester) of one of the above mentioned stabilising agents.

The stabilising effect of additives to phosphoric acid esters and compositions according to the present invention is illustrated in the following examples. Parts are always given as parts by weight and the temperatures are in degrees centigrade.

Example 1

An emulsifiable solution for the preparation of insecticidal emulsions consisting of

20 parts of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester
35 parts of an alkylphenol-ethylene oxide condensation product (condensation product of 1 mol of nonyl-, octyl- or iso-octyl-phenol with 5–10 mols of ethylene oxide), and
45 parts of xylene

is stored for 240 days at 50°. As the end of this time, the content of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester has sunk to 10 parts.

Under the same storing conditions, an analogous composition in which 1 part of xylene has been replaced by 1 part of epichlorohydrin, remains stable, i.e. there is no loss of content of the thiophosphoric acid ester named.

Example 2

An emulsifiable solution having a high concentration of insecticidal active ingredient, consisting of

60 parts of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester
33 parts of an alkyl phenol-ethylene oxide condensation product (condensation product of 1 mol of nonyl-, octyl- or iso-octyl-phenol with 5–10 mols of ethylene oxide), and
7 parts of xylene

is stored for 180 days at 50°. At the end of this time, the content of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester has sunk to 20 parts whereas in this case also, the content of the thiophosphoric acid ester named remains unchanged when an analogous composition containing 3 parts of epichlorohydrin instead of 3 parts of the condensation product is stored under the same conditions.

Example 3

An emulsifiable solution for the production of insecticidal emulsions consisting of 20 parts of phosphoric acid-[3-methyl-pyrazolyl-(5)]-diethyl ester, 35 parts of an alkyl phenol-ethylene oxide condensation product (condensation product of 1 mol of nonyl-, octyl- or iso-octyl-phenol with 5–10 mols of ethylene oxide) and 45 parts of xylene is stored for 130 days at 50°. At the end of this time, the content of phosphoric acid-[3-methyl-pyrazolyl-(5)]-diethyl ester has sunk to 10 parts. An analogous composition in which 1 part of xylene has been replaced by 1 part of epichlorohydrin, remains unchanged after storing under the same conditions.

Example 4

Another emulsifiable solution of a phosphoric acid ester which can be stabilised according to the present invention is obtained by dissolving 20 parts of phosphoric acid-[3-methyl-pyrazolyl-(5)]-diethyl ester, 8 parts of an alkyl phenol-ethylene oxide condensation product (condensation product of 1 mol of nonyl-, octyl- or iso-octyl-phenol with 5–10 mols of ethylene oxide) and 1 part of epichlorohydrin in 71 parts of xylene.

Example 5

Another emulsifiable solution of a stabilised phosphoric acid ester according to the present invention is obtained by mixing 80 parts of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester with 16 parts of an alkyl phenol-ethylene oxide condensation product (condensation product of 1 mol of nonyl-, octyl- or iso-octyl phenol with 5–10 mols of ethylene oxide), and 4 parts of propylene oxide.

Example 6

The solution of Example 5 can also be stabilised if 4 parts of cyclohexene oxide are used instead of 4 parts of propylene oxide.

Example 7

An emulsified stabilised solution according to the

present invention which can be used for the preparation of an insecticidal emulsion is obtained by dissolving 40 parts of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester, 20 parts of an alkyl phenol-ethylene oxide condensation product (condensation product of 1 mol of nonyl-, octyl- or iso-octyl-phenol with 5–10 mols of ethylene oxide) and 12 parts of styrol oxide in 28 parts of xylene.

Example 8

Another emulsifiable stabilised solution according to the present invention is obtained by dissolving 25 parts of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester, 10 parts of an alkyl phenol-ethylene oxide condensation product (condensation product of 1 mol of nonyl-, octyl- or iso-octyl-phenol with 5–10 mols of ethylene oxide) and 0.5 part of cyclohexene oxide in 64.5 parts of benzene.

Example 9

A solution which can be used as an insecticidal spray and which consists of 436 parts of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester and 564 parts of kerosene is stored for 26 days at 75°. At the end of this time the content of the said ester has sunk to 365 parts.

Under the same storing conditions, an analogously composed solution in which 25 parts of kerosene have been replaced by 25 parts of epichlorohydrin, remains stable, i.e. there is no loss of content of the thiophosphoric acid ester named.

What I claim is:

1. The process for the stabilising of a phosphoric acid dialkyl ester selected from the group consisting of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester and phosphoric acid-[3-methyl-pyrazolyl-(5)]-diethyl ester, which comprises adding to said ester from 2% to 30%, calculated on the weight of said ester, of a stabilising agent selected from the group consisting of epichlorohydrin, cyclohexene oxide, propylene oxide and styrol oxide.

2. The process for the stabilising of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester, which comprises adding to said ester from 2% to 30%, calculated on the weight of said ester, of the stabilising agent epichlorohydrin.

3. The process for the stabilising of phosphoric acid-[3-methyl-pyrazolyl-(5)]-diethyl ester, which comprises adding to said ester from 2% to 30%, calculated on the weight of said ester, of the stabilising agent epichlorohydrin.

4. The composition of matter comprising a phosphoric acid dialkyl ester selected from the group consisting of thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester and phosphoric acid-[3-methyl-pyrazolyl-(5)]-diethyl ester, and from 2% to 30% calculated on the weight of said esters, of a stabilising agent selected from the group consisting of epichlorohydrin, cyclohexene oxide, propylene oxide and styrol oxide.

5. The composition of matter comprising thiophosphoric acid-[2-isopropyl-4-methyl-pyrimidyl-(6)]-diethyl ester, and from 2% to 30%, calculated on the weight of said ester, of the stabilising agent epichlorohydrin.

6. The composition of matter comprising phosphoric acid-[3-methyl-pyrazolyl-(5)]-diethyl ester, and from 2% to 30%, calculated on the weight of the said ester, of the stabilising agent epichlorohydrin.

References Cited in the file of this patent

FOREIGN PATENTS

690,585 Great Britain ---------- Apr. 22, 1953

OTHER REFERENCES

Culvenor: Jour. Chem. Soc. (London), 1949, pp. 278–282.

Hazen et al.: Soap and Sanitary Chemicals, vol. 22: 8, pp. 151, 153 and 155 (1946).