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PATENT SPECIFICATION

(11) 1 474 282

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- (72) Inventors LAJOS AVER,
 KURT HOFER and
 MARTIN PREISWERK



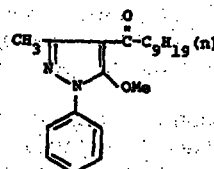
(54) PYRAZOLE DERIVATIVES AND THEIR USE AS STABILIZERS FOR ORGANIC MATERIALS

(71) We, SANDOZ LTD., of 35 Lichtstrasse, 4002 Basle, Switzerland, a Swiss Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention described and claimed in copending application No. 9969 (Serial No. 1474281), filed March 6, 1974 relates to pyrazole compounds useful as stabilizers of organic material against the degradative effect of heat, oxidation and ultraviolet light.

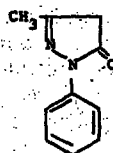
The present invention relates to a narrow group of pyrazole compounds, particularly useful as stabilizers of organic material against the degradative effect of heat, oxidation and ultraviolet light.

Accordingly, the present invention provides compounds of formula I,

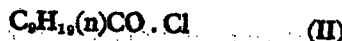


wherein Me is hydrogen or an equivalent of a bivalent metal ion, e.g. nickel, zinc, manganese, copper, chromium, calcium, barium or cobalt, Me preferably being an equivalent of bivalent nickel.

The compounds of the formula are, in accordance with a further aspect of the present invention produced by condensing the compound of formula III,



with the compound of formula II,



preferably in an equimolar ratio, and when Me is an equivalent of a bivalent metal cation, converting the resulting product into the corresponding Me salt.

The reaction is preferably effected in an inert organic solvent and the starting materials being dissolved or suspended therein. The solution is preferably heated to between 20° and 110°C with the cleavage of hydrochloric acid which may be allowed to escape from the reaction vessel at an elevated temperature. Generally, it is, however, more convenient to effect the reaction in the presence of an acid binding agent,

e.g. CaO, an alkali metal carbonate or bicarbonate, pyridine, a trialkyl amine or a dialkyl aniline. The reaction is preferably carried out in the absence of moisture. Appropriate solvents are, for example, benzene, xylene, cymol, diphenyl ether, tetrahydrofuran and dioxane. When Me signifies a bivalent metal ion, the compound of formula I, wherein Me signifies hydrogen, may be converted first into the alkali metal salt, e.g. by dissolving the compound of formula I in alcohol and adding an alkali hydroxide such as NaOH or KOH. A Me— salt, e.g. the chloride, is subsequently added to the reaction mixture and the desired product is then obtained.

Alternatively and preferably, a metal salt may be produced directly from the compound of formula I, wherein Me signifies hydrogen, by heating the compound of formula I wherein Me is hydrogen with an Me— acetate, e.g. the acetate of nickel, zinc, manganese, cobalt, copper, calcium or barium. This reaction is preferably effected in an alcohol such as methanol, ethanol and propanol, at a temperature between room temperature and the reflux temperature of the solvent. On cooling the product generally precipitates.

If the product does not precipitate sufficiently, the precipitation may be accelerated by the addition of water.

The compounds of formula I are useful for stabilizing organic material susceptible to degradation under the effect of heat, oxidation or U.V. light by a method comprising treating the organic material with a compound of formula I. By the term "treating" is meant either surface coating or incorporation into the body of the organic material, in manner known *per se*.

The above method also forms part of the present invention.

The method of the invention comprises treating the organic material, either by way of coating the compound of formula I as a film on the surface of the organic material, or by way of mixing the compound of formula I with the organic material, preferably the latter so as to uniformly distribute the compound of formula I throughout the body of the organic material. Thus, according to a first embodiment the method may be effected by intimately mixing the stabilizer with a particulate form of, for example, a plastics material such as polypropylene, e.g. polypropylene granules, in a kneader or other suitable device, to obtain uniform distribution of the stabilizer throughout the plastics material. The plastics material may thereafter be formed into final shape, e.g. by extrusion or injection moulding. By such method, homogeneous distribution of the stabilizer throughout the plastics material is achieved which is important for good protection.

According to a second embodiment, organic material in final form, for example, a textile filament, is passed through a dispersion of the stabilizer, e.g. in aqueous medium, to provide a protective coating of the stabilizer as a surface film on the organic material. Textile filaments or fabrics of polyethylene terephthalate or cellulose acetate are suited to this mode of application.

According to a third embodiment of the method of the present invention, particularly suited to stabilization of polymers or copolymers, e.g. polypropylene, the stabilizer is mixed with the monomer or prepolymer before polymerisation or, as the case may be, copolymerisation, is effected, to yield the polymer or copolymer having the stabilizer uniformly distributed therethrough. The polymer or copolymer may thereafter be extruded, moulded or otherwise formed into final shape.

Examples of organic materials susceptible to degradation and embraced by the method of the present invention are cellulose derivatives, e.g. cellulose acetate, cellulose acetobutyrate, ethyl cellulose, cellulose nitrate and cellulose propionate, polyalkylenes, notably polyethylene and polypropylene, polyvinyl derivatives, e.g. polyvinyl chloride, polyvinyl chloride acetate and polyvinyl alcohol, polyamides, polyesters, polyacrylonitrile, polystyrene, silicon rubber, melamineformaldehyde resins, urea-formaldehyde resins, alkyl casting resins, polymethylmethacrylate, polypropylene oxide, polyphenylene oxide polyurethanes, copolymers such as acrylonitrile-butadiene-styrene copolymers and natural products such as natural rubber, cellulose, wool and silk.

The compounds according to the invention are preferably used for the stabilization of polypropylene, polyethylene, polyester, polyamide, polyurethanes, polyacrylonitrile, copolymers such as acrylonitrile-butadiene-styrene (ABS) terpolymer, acrylic ester-styrene-acrylonitrile terpolymer, styrene-acrylonitrile copolymer or styrene-butadiene copolymer.

Stabilized organic materials according to the invention may exist in solid form, e.g. panels, rods, coatings, sheets, films, tapes, fibres, granules or powders, or in liquor form, e.g. solutions, emulsions or dispersions.

The amount of stabilizer employed in the method of the present invention will

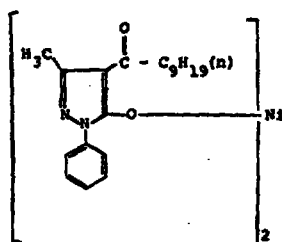
of course vary with the mode of application, the compound employed and the nature of the organic material to be treated. In general, however, satisfactory results are obtained when the amount of stabilizer employed is between 0.01 and 5%, preferably between 0.05 and 1% of the weight of organic material to be treated.

The compounds of formula I may be employed in formulation form for the stabilization of organic materials, in association with an inert carrier or diluent. Such formulations may be in the form of polishes, creams and lotions, e.g. for surface application to the organic material so as to form a barrier or filter coating. Such formulations also form part of the present invention.

In the following Example the parts and percentages are by weight and the temperatures in degrees centigrade. The indicated structures is verified by microanalysis and spectroscopic analysis.

EXAMPLE

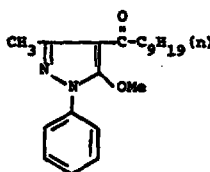
34.8 parts of 1-phenyl-3-methyl-pyrazolone (5) and 13.2 parts of CaO are entered into 40.0 parts of dioxan at room temperature. The mixture is then heated in an oil bath to 80°C. At 75°C, 38.0 parts of capric acid chloride is added dropwise with stirring over a period of 45 minutes. The temperature increases to 95°C to result in a thick brown, well-stirred paste. After the addition of the acid chloride, the mixture is allowed to further react at 80°C for 1 hour. The mixture is then cooled to 50°C, 100 ml of methanol and 23.0 parts of hydrochloric acid are added thereto and the mixture is stirred for 30 minutes. 24.8 parts of nickel acetate are then transferred to the mixture and stirring is effected for 30 minutes at 70°C. The precipitated nickel complex is filtered off at 50°C, washed with 1.5 parts by weight of distilled water, washed twice with 30 part amounts of methanol and dried at 110°C. When the above procedure is followed, a product is obtained having between 0 and 2 mols of water of crystallisation and being in accord with the following formula



Melting point 158—162°C.

WHAT WE CLAIM IS:—

1. A compound of formula I,

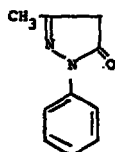


wherein Me is hydrogen or an equivalent of a bivalent metal ion.

2. A compound according to Claim 1, wherein Me is hydrogen or an equivalent of bivalent nickel, zinc, manganese, copper, chromium, calcium, barium or cobalt.

3. A compound according to Claim 1, wherein Me is nickel.

4. A process for the production of a compound of formula I, defined in Claim 1, which comprises condensing the compound of formula III,



with a compound of formula II,

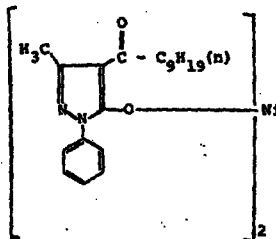
of course vary with the mode of application, the compound employed and the nature of the organic material to be treated. In general, however, satisfactory results are obtained when the amount of stabilizer employed is between 0.01 and 5%, preferably between 0.05 and 1% of the weight of organic material to be treated.

The compounds of formula I may be employed in formulation form for the stabilization of organic materials, in association with an inert carrier or diluent. Such formulations may be in the form of polishes, creams and lotions, e.g. for surface application to the organic material so as to form a barrier or filter coating. Such formulations also form part of the present invention.

In the following Example the parts and percentages are by weight and the temperatures in degrees centigrade. The indicated structures is verified by microanalysis and spectroscopic analysis.

EXAMPLE

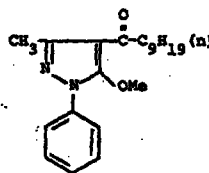
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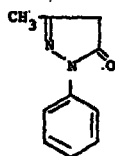


wherein Me is hydrogen or an equivalent of a bivalent metal ion.

2. A compound according to Claim 1, wherein Me is hydrogen or an equivalent of bivalent nickel, zinc, manganese, copper, chromium, calcium, barium or cobalt.

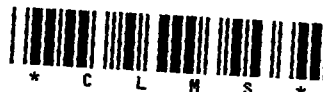
3. A compound according to Claim 1, wherein Me is nickel.

4. A process for the production of a compound of formula I, defined in Claim 1, which comprises condensing the compound of formula III,



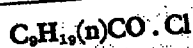
III

with a compound of formula II,





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(II)

and when Me is an equivalent of a bivalent metal cation, converting the resulting product into the corresponding Me salt.

5 5. A process according to Claim 4, substantially as described herein with reference to the Example.

6. A compound of formula I, whenever produced by the process of either Claim 4 or Claim 5.

7. A method of stabilizing organic material against the degradative effect of heat, oxidation or U.V. light which comprises treating the material with a stabilizing amount of a compound according to any one of Claims 1 to 3 and 6.

10 8. A method according to Claim 7, substantially as described herein.

9. Organic material whenever stabilized by a method according to either Claims 7 or Claim 8.

B. A. YORKE & CO.,
Chartered Patent Agents,
98, The Centre,
Feltham,
Middlesex, TW13 4BP,
Agents for the applicants.

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