(54) Title: PYRAZOLE- AND PIPERIDINE-CONTAINING COMPOUNDS AND THEIR METAL COMPLEXES AS LIGHT STABILIZERS

(57) Abstract

Novel pyrazole-containing compounds useful as light stabilizers for polymers, their Ni, Zn, Cu, and Co metal complexes, and methods for the synthesis of such complexes are provided. The compounds include a hindered amine light stabilizer (HALS) such as a substituted piperidine, thereby incorporate the properties of UV absorbers and radical scavengers. The compounds are of formulas (I) and (II), where R₁ is phenyl, R₂ is methyl, X is oxygen or sulphur, Z is oxygen or N-aryl, and R₃ is hydrogen, alkyl, a derivative of carboxyacyloyl or carboxybenzoyl or a derivative of pyrazole. The compounds and their metal complexes are highly compatible with various polymers, thermostable, and retain their photostability under conditions of continuous and intensive irradiation. Methods for the synthesis of metal complexes include the reaction of: (a) a compound with metal acetate; or (b) a metal complex with anhydride or a pyrazole derivative.
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PYRAZOLE- AND PIPERIDINE-CONTAINING COMPOUNDS AND THEIR METAL COMPLEXES AS LIGHT STABILIZERS

FIELD AND BACKGROUND OF THE INVENTION

The present invention relates to novel pyrazole derivatives and their use as light stabilizers for inhibiting the degradation of various polymers and, more particularly, to compounds which incorporate UV absorbers such as pyrazole derivatives and radical scavengers such as hindered amine light stabilizers (HALS), metal complexes of such compounds, and methods for the synthesis of such metal complexes.

Various industrial applications require the use of polymers which are durable and resistant to ultraviolet light. Examples for such applications can be found in the fields of agriculture, building, manufacture of coatings, machine and aircraft constructions and space exploration.

However, many of the polymers used, such as polyester, polyethylene (LD and HD), polypropylene, polystyrene and polycarbonate are susceptible to photodegradation induced by ultraviolet (UV) light, present in sunlight and various kinds of light sources.

The chemical effects of UV irradiation on such polymers are rooted in the presence of carbonyl groups which may have been formed by various uncontrolled reactions during the synthesis or the processing of the polymer. When these carbonyl groups are exposed to UV-light, they are easily excited to singlet and triplet states which could subsequently initiate some of a number of photochemical reactions in which free radicals are a main product.

Thus, the oxidative degradation of polymers is due to a propagation reaction which involves the formation of free radicals such as alkyl (R·) and peroxy (ROO·) radicals, and compounds such as hydroperoxides (ROOH) which easily decompose to free radicals of the type R·, RO·, and ROO·. Such radicals may take part in further attacks of additional polymer molecules. These repeated radical attacks may result in scission and crosslinking of polymer chains, while
scission may turn a solid polymer into a thin liquid and crosslinking may create a brittle polymer network.

Various attempts have been made to develop light stabilizers which inhibit the photodegradation of polymers. These light stabilizers can be classified according to their stabilization mechanisms into several groups, such as: (a) UV absorbers (UVAs), which absorb the harmful UV light and re-emit it as vibrational (thermal) energy without being themselves destroyed, and without sensitizing the oxidation of the polymer; (b) excited state quenchers, which deactivate the excited states (singlet or triplet) of the polymer, by a mechanism of energy transfer which occur between an excited chromophore in the polymer molecule (donor) and the photostabilizer molecule (acceptor); (c) hydroperoxide (ROO•) decomposers which decompose hydroperoxide molecules to non-radical products such as ions; and (d) radical scavengers, which react with free radicals such as R•, RO• and ROO•, to form non-radical products such as olefins and ions, or stable radicals such as nitroxy•.

Further attempts have been made to incorporate two or more components acting according to the above stabilization mechanisms, such as a UV absorber and an excited state quencher, a UV absorber and a hydroperoxide decomposer, and a UV absorber and a radical scavenger, since such compounds show a synergistic behavior, in which the UV absorber protects the other component from destruction by UV-light, and said other component inhibit the formation of free radicals and thereby extends the useful life of the UV-absorber (see, for example, J. Pospisil, P.P. Klemchuk, "Oxidation Inhibition in Organic Materials", Vol. 1&2, CRC Press, Bola Raton, 1990; G. Scott, "Atmospheric Oxidation and Antioxidants", Elsevier, A-L-NY-T, Vol 1,2,3, 1993; J. Pospisil. Angew. Macromol. Chem. 216 (1994), pp.135-46; and F. Gugumas, "Polym. Degrad. and Stab.", 44 (1994), pp.273-297 and references cited therein).

Considerable efforts have been made to develop pyrazole-containing dyes, since these compounds were found to have high light stability, mainly due to their effective UV absorbance (See, for example, B.I. Stepanov, Introduction to the Chemistry and Technology of Organic Dyes, publ. "Chemistry", Moscow, 1977. p. 253-268).
Examples of light stabilizers based on pyrazole derivatives and their metal salts or metal complexes are disclosed in Ger. Pat. No. 2,433,111; 2,410,370; 2,519,594; 2,651,272; 2,529,052; and 2,511,354, Fr. Pat. No. 2,777,826, U.S. Pat. No. 4,008,200, Swiss Pat. No. 605,796, Belg. Pat. No. 891,814, and S.U. Pat. No. 956,504; 737,401; 2,829,024; 1,427,802; 1,015,664; 1,205,543; 1,005,448; 717,043; and 786,317.

However, most of these light stabilizers do not exhibit efficient radical scavenging activity, and they lose their effectiveness under conditions of continuous and intensive irradiation.

There is thus a widely recognized need for, and it would be highly advantageous to have, a light stabilizer which incorporates the effective UV absorption of pyrazole derivatives and the efficient radical scavenging activity of hindered amine light stabilizers (HALS) such as piperidine derivatives, and which retains its effectiveness under conditions of continuous and intensive irradiation.

SUMMARY OF THE INVENTION

According to the present invention there is provided a novel chemical compound useful as a light stabilizer for polymers such as polyesters, polystyrene, polycarbonate, and polyolefins, comprising: (a) a pyrazole derivative; and (b) a piperidine derivative.

Also according to the present invention, there is provided a metal complex comprising: (a) a chemical compound, including: (i) a pyrazole derivative; and (ii) a piperidine derivative; and (b) a metal ion.

Further according to the present invention, there are provided methods for the synthesis of the metal complex, including (a) reaction of the chemical compound with metal acetate; or (b) reaction of a metal complex with a suitable derivative.

According to further features in preferred embodiments of the invention described below, the pyrazole derivative may be a 4-aminomethylene derivative of 2-pyrazolin-5-one or 2-pyrazolin-5-thione.
The pyrazole derivative may further be a derivative of 5-aminopyrazole, and may be substituted at its 4-position with CH=O, or CH=N-Aryl such as CH=NC₆H₅, CH=NC₆H₄OC₆H₅, CH=NC₆H₄COOC₄H₉ (m- or p-), and CH=NC₆H₂[p-OH,m,m'-C(CH₃)₃].

Further, the pyrazole derivative may be substituted with a phenyl group at its 1-position and a methyl group at its 3-position.

According to still further features in the described preferred embodiments, the piperidine derivative may be a 2,2',6,6'-tetramethylpiperidine derivative, and may further be substituted at its 1-position with alkyl such as methyl, a carboxyacryloyl derivative such as 3-carboxyacryloyl and 2-carboxymethylacryloyl, a carboxybenzoyl derivative such as 2-carboxybenzoyl, and a pyrazole derivative such as 3-Me-1-Ph-5-pyrazolonylmethylidene-4, and 3-Me-1-Ph-5-thiopyrazolonylmethylidene-4.

The metal complex may include a metal ion such as Ni(II), Zn(II), Cu(II), and Co(II).

The reaction of the chemical compound with a metal acetate may be carried out in ethanol or acetone. The reaction of a metal complex with a suitable derivative may be carried out in a benzene solution. The suitable derivative may be anhydride or a pyrazole derivative.

The present invention successfully addresses the shortcomings of the presently known configurations by providing a chemical compound useful as a light stabilizer, which incorporates the properties of an effective UV absorber such as a pyrazole derivative, and an efficient radical scavenger such as a piperidine derivative, and which retains its effectiveness under conditions of continuous and intensive irradiation.

Further, the present invention provides high molecular mass and highly compatible metal complexes of such chemical compounds, which incorporate the properties of UV absorbers, radical scavengers, hydroperoxide decomposers, and excited state quenchers, and which therefore feature considerable photostability and thermostability.

The present invention discloses a novel chemical compound useful as a light stabilizer which incorporate a pyrazole derivative and a piperidine
derivative, metal complexes of such chemical compound, and methods for the synthesis of such metal complexes. The chemical compounds and their metal complexes may be used as additives to polymers such as polyesters, polystyrene, polycarbonate and polyolefins. They may be added to a melted polymer by conventional mixing or blending techniques, or may be dissolved in a suitable solvent and added to the polymer as a solution.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is herein described, by way of example only, with reference to the accompanying drawings, wherein:

FIG. 1a represents the chemical structure of a compound according to the present invention, in which the pyrazole derivative is 4-aminomethylene-2-pyrazolin-5-one or -thion.

FIG. 1b represents the chemical structure of an alternative compound according to the present invention, in which the pyrazole derivative is a substituted 5-aminopyrazole.

FIG. 1c represents specific examples of the compounds shown in FIGs. 1a and b.

FIG. 2a represents the chemical structure of metal complexes of the compounds shown in FIGs. 1a, b and c, and a schematic description of a method for the synthesis of such metal complexes.

FIG. 2b represents specific examples of metal complexes which can be synthesized according to the method illustrated in FIG. 2a.

FIG. 3a is a schematic description of an alternative method for the synthesis of some of the metal complexes.

FIG. 3b represents specific examples of metal complexes which can be synthesized according to the methods illustrated in FIGs. 2a and 3a.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is of a chemical compound which can be used as a light stabilizer for various polymers, and which incorporates the properties of an effective UV absorber such as a pyrazole derivative, and an efficient radical
scavenger such as a piperidine derivative. Further, the invention is of a metal complex of such compound, and methods for the synthesis of such a metal complex.

Examples of available commercial hindered amine light stabilizer (HALS) which are based on piperidine derivatives are Tinuvin 770, Tinuvin 622, Tinuvin 292, and Chimassorb 994. The stabilizing mechanism of such compounds is described in detail in the literature (see, for example, G. Scott, "Atmospheric Oxidation and Antioxidants", Elsevier, A-L-NY-T, Vol 1.2.3, 1993), and is based on a catalytic cycle in which there is a continuous feedback of piperidinoxyl radicals which react with alkyl radicals to produce: (a) non-radical products such as olefins; and (b) hydroxylamines which are known to be effective light stabilizers. Thus, such compounds renew their radical-scavenging capabilities due to continuous decomposition and formation of piperidinoxyl radicals and hydroxylamines, and are therefore very effective light stabilizers.

The incorporation of an effective UV absorber such as a pyrazole derivative and an efficient radical scavenger such as a piperidine derivative in a single compound results in a synergistic behavior, in which the overall stabilizing effect of the pyrazole-piperidine combination is greater than the sum of the stabilizing effects of the individual components (pyrazole alone and piperidine alone), since the pyrazole protects the piperidine from destruction by UV light, and the piperidine inhibits the formation of alkyl radicals and therefore extends the useful life of the pyrazole.

Thus, compounds according to the present invention have high extinction coefficient in the region of 250-360 nm, and they show high light-stability under conditions of continuous and intensive irradiation such as Hg Lamp (400W) and sunlight (Summer, Ashkelon, Israel). Furthermore, several embodiments are thermostable up to 300°C. In addition, compounds according to the present invention show high solubility in most organic solvents and high compatibility with various polymers such as polyesters, polystyrene, polycarbonate, and polyolefins.

Metal complexes of compounds according to the present invention incorporate the properties of UV-absorbers, free radical scavengers.
hydroperoxide decomposers, and excited state quenchers. Further, they have high molecular mass and therefore are not volatile. As a result, these metal complexes exhibit spectral properties which are similar to those of the individual compounds they are built of; however, they show much higher photostability and thermostability.

Methods for the synthesis of metal complexes according to the present invention enable the extraction of high yields of products by using simple and inexpensive technology.

The principles and operation of the present invention may be better understood with reference to the drawings and the accompanying description.

Referring now to the drawings, FIGS. 1a, and 1b illustrate the chemical structure of a compound according to the present invention. The compound includes a pyrazole derivative and a piperidine derivative.

As shown in FIG. 1a, the pyrazole derivative may be a 4-aminomethylene derivative of 2-pyrazolin-5-one or 2-pyrazolin-5-thione, and may preferably be substituted with a phenyl group at its 1-position and a methyl group at its 3-position.

The piperidine derivative may preferably be 2,2',6,6'-tetramethylpiperidine, and may be substituted at its 1-position with substituents such as: (a) alkyl such as methyl; (b) a carboxyacryloyl derivative such as 3-carboxyacryloyl and 2-carboxymethylacryloyl; (c) a carboxybenzoyl derivative such as 2-carboxybenzoyl; and (d) a pyrazole derivative such as 3-Me-1-Ph-5-pyrazolonylmethylidene-4. and 3-Me-1-Ph-5-thiopyrazolonylmethylidene-4.

Another possible configuration is shown in FIG. 1b, wherein the pyrazole derivative may be a derivative of 5-aminopyrazole, and may be substituted at its 4-position with substituents such as CH=O, or CH=N-Aryl such as CH=NC6H5, CH=NC6H4OC6H5, CH=NC6H4COOC4H9 (m- or p-), and CH=NC6H2[p-OH,m.m'-C(CH3)2].

With continued reference to FIGS. 1a, and 1b, the chemical compounds may be synthesized according to methods described in the literature (see, for example, I. Y. Kvitko, J. Ob. Khim. 34, 2999-3005 (1964); I. Y. Kvitko, J. Org. Khim. 1, 169-173 (1966); and I. Y. Kvitko, J. Org. Khim. 5, 1685-92 (1969)).
FIG. 1c represents specific examples of the compounds shown in FIGs. 1a and b. Compounds I-IV may preferably be synthesized by reacting the corresponding 3-methyl-1-phenyl-5-hydroxy (mercapto- or chloro-) pyrazolecarboxylaldehydes with 4-amino-2,2′,6,6′-tetramethylpiperidine or 4-5 amino-1,2,2′,6,6′-pentamethylpiperidine. Compounds V-IX may preferably be synthesized by reacting compounds I, II or III, with maleic, itaconic, or phtalic anhydride in benzene solution. Compounds X-XVI may preferably be synthesized by reacting compounds I, II or III, with 3-methyl-1-phenyl-5-hydroxy-4-formylpyrazole or 3-methyl-1-phenyl-5-mercapto-4-formylpyrazole. This reaction may preferably be carried out in benzene solution, at 40°-60°C, for about 30 min.

FIG. 2a illustrates the chemical structure of metal complexes of the compounds shown in FIGs. 1a, b, and c. The metal complexes may include metal ions such as Ni(II), Zn(II), Cu(II), and Co(II).

Further, FIG. 2a shows a schematic description of a method for the synthesis of such metal complexes. Thus, the metal complex may preferably be synthesized by reacting a compound such as in FIGs. 1a, b, and c, with the corresponding metal acetate Me(OOCCH₃)₂, in ethanol or acetone.

Specific examples of metal complexes which can be synthesized according to the method illustrated in FIG. 2a are given in FIGs. 2b and 3b, where compounds XVII-XXV are metal complexes of compounds I-IV in FIG. 1c, and compounds XXVI-XLII are metal complexes of compounds V-XVI in FIG. 1c.

FIG. 3a represents an alternative method for the synthesis of a metal complex of a compound in which the piperidine derivative is substituted with, for example, a derivative of carboxyacryloyl, carboxybenzoyl, or pyrazole. Such metal complex may preferably be synthesized by reacting a metal complex of a compound in which the piperidine derivative is unsubstituted or substituted with, for example, CH₃, with the corresponding anhydride or pyrazole derivative. This reaction may preferably be carried out in benzene solution at room temperature.
Specific examples of metal complexes which can be synthesized according to the method illustrated in FIG. 3a are given in FIG. 3b. Thus, compounds XXVI-XLII may be synthesized by reacting compounds XVII-XXV, which are metal complexes of compounds I-IV in FIG. 1c, with the corresponding anhydride or pyrazole derivative as mentioned above.

Referring now to the examples, the preparation and the resulted photostabilizing activities of compounds and metal complexes according to the present invention are described.

The photostabilizing activities were evaluated using UV-spectrophotometer, in ethanolic, chloroformic and isooctaninc solutions. The absorption of compounds and metal complexes was measured before and after irradiation by: (a) a Hg Lamp (400W) for a period of 1-5 hours; (b) sunlight (summer, Ashkelon, Israel) for a period of about 10 days; and (c) a weathermeter (standard conditions) for 250 hours.

Example 1: 3-Methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4)amino-methylen-5-pyrazolinon (compound I, FIG. 1c)

To a 1 l kettle equipped with a mixer, condenser, and a bath for heating, were added: 500 ml of benzene; and 229 g of 3-methyl-1-phenyl-4-dimethylaminomethylene-5-pyrazolone which were obtained with a yield of 92% from 3-methyl-1-phenyl-5-pyrazolone, dimethylformamide and phosphoryltrichloride, using the method described in J. Ob. Khim. 32. 4050-6 (1962).

To the resulting suspension, 187 g (202 ml) of 4-amino-2,2',6,6'-tetramethylpiperidine, obtained by "Fluka", were added by mixing over a period of 10-20 min, at room temperature. The mixture was then refluxed for 12 hours. The dimethylamine formed in the condenser was sent for absorption in a vessel containing cold water. After heating, some of the benzene (~ 250 ml) was distilled, and the residue was transferred to a crystallizator. After cooling at room
temperature (~10-12 hours), the crystalline product was filtered and washed on the filter with 250 ml of petroleum ether.

The result was 285 g of yellowish crystals with a m.p. of 135-7°C. From the benzene-petroleum ether mixture, 41.4 g with a m.p. of 132-4°C were obtained. The total yield was 326.4 (96%). After crystallization from n-hexane, the m.p. was 136-7°C. Point of decomposition >290°C. The product dissolves in ethanol, methanol, chloroform, dichloromethane, benzene, acetone, n-hexane, and diethylether, and with difficulty in petroleum ether and water.

λmax in ethanol: 330; 295; and 255 nm.

Found % : C 70.45; H 7.99; N 16.32.

Gross formula: C_{20}H_{28}N_{4}O.

Calc. % : C 70.6; H 8.23; N 16.32.

The absorption results obtained before (d) and after (d’) irradiation by Hg Lamp (400W), at 50°C, for 1 hour, at a distance of 50 cm:

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<th>255</th>
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<tr>
<td>d</td>
<td>0.5</td>
<td>2.0</td>
<td>1.35</td>
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<tr>
<td>d’</td>
<td>0.45</td>
<td>1.9</td>
<td>1.30</td>
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The absorption results obtained before (d) and after (d’) irradiation by sunlight, in ethanol solution (5·10^{-5}), for 7 days, in the conditions of May 1995, Ashkelon:

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<th>λmax</th>
<th>330</th>
<th>295</th>
<th>255</th>
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<tr>
<td>d</td>
<td>0.5</td>
<td>2.0</td>
<td>1.35</td>
</tr>
<tr>
<td>d’</td>
<td>0.48</td>
<td>1.97</td>
<td>1.24</td>
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</table>

The results of color estimation according to Hardners methods before and after irradiation of a polyester plate (3 mm) in a weathermeter for 250 hours:

Before: 2;  After 250 hours: 1.
Example 2: 3-Methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4)aminomethylen-5-thiopyrazolinon (compound II. FIG 1.c).

This compound was obtained from 3-methyl-1-phenyl-4-methylaminomethylen-5-thiopyrazolinone, which was synthesized with a yield of 91% using the method of Kvitko I.Y. (J. Org. Khim. 5, 1685-9), and 4-amino-2,2',6,6'-tetramethylpiperidine, as in example 1.

The compound was obtained with a yield of 94%. The m.p. was 210-2°C. After crystallization from toluene the m.p. was 212-3°C. Point of decomposition >260°C.

This product dissolves in ethanol, methanol, chloroform, dioxane, acetone, benzene, and toluene, and by heating, in diethylether and n-hexane. However, it does not dissolve in petroleum ether.

λ_max in ethanol: 385, 300, 280, and 235 nm.

Found % : C 67.15; H 7.91; N 15.48; S 9.14.

Gross Formula: C_{20}H_{28}N_{4}S.

Calc % : C 67.4; H 7.9; N 15.7; S 8.9.

The absorption results obtained before (d) and after (d') irradiation by Hg Lamp (400W), at 50°C , for 1 hour, at a distance of 50 cm:

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<tr>
<td>d'</td>
<td>0.3</td>
<td>1.4</td>
<td>1.46</td>
<td>1.09</td>
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</table>
Example 3: 3-Methyl-1-phenyl-5-(2,2’,6,6’-tetramethylpiperidyl-4)aminopyrazole-4-carboxyaldehyde (compound III, FIG. 1c)

To a 1 l kettle equipped with a mixer, thermometer, and a bath for heating, were added: 220.5 g of 3-methyl-1-phenyl-5-chloropyrazole-4-carboxaldehyde obtained by method described in J. Org. Khim 1966, 1, 169-73; 300 ml of dimethylformamide; and 234 g of 4-amino-2,2’,6,6’-tetramethylpiperidine.

The mixture was heated at 95-100°C for 8 hours. After heating the solution was transferred to a crystallizator containing 1,200 ml of water. After cooling to room temperature by mixing, the pale yellow precipitate was filtered, washed with cold water (3 x 50 ml) and air-dried. 289 g (85%) of colorless product were obtained with a m.p. of 78-82°C. After crystallization from an ethanol-water mixture and subsequently from petroleum ether, the m.p. was 95-6°C and the point of decomposition >300°C.

This product dissolves in most organic solvents, and does not dissolve in water.

λmax in ethanol: 260 nm; in isooctane: 265 nm.

The absorption results obtained before (d) and after (d’) irradiation by Hg Lamp (400W), at 50°C, for 1 hour, at a distance of 50 cm. in isooctan solution:

<table>
<thead>
<tr>
<th>λmax</th>
<th>d</th>
<th>d’</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>260</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Example 4: 3-Methyl-1-phenyl-4(1,2,2’,6,6’-pentamethylpiperidyl-4)aminomethylen-5-pyrazolinon (compound IV, FIG. 1c)

A 250 ml one-necked round bottom flask, equipped with condenser and magnetic stirrer, was filled with 46 g of 3-methyl-1-phenyl-4-dimethylaminomethylene-5-pyrazolinone (see example 1), 100 ml of benzene and 38 g of 4-amino-1,2,2’,6,6’-pentamethylpiperidine. The mixture was refluxed for 8 hours.
After cooling the precipitate was collected by filtration, washed on the filter with petroleum ether, and dried. 64 g (91%) of pale yellow product was obtained, with a m.p. of 153-4°C. After crystallization from benzene the m.p. was 155-6°C.

This compound has good solubility in most organic solvents, and does not dissolve in petroleum ether and water.

λmax in ethanol: 330, 298, and 255 nm.

Found % : C 71.46; H 8.56; N 15.64.

Gross formula: C_{21}H_{30}N_{4}O.

Calc % : C 71.2; H 8.48; N 15.82.

The absorption results obtained before (d) and after (d’) irradiation by Hg Lamp (400W), at 50°C, for 1 hour, at a distance of 50 cm. in ethanolic solution:

<table>
<thead>
<tr>
<th>λmax</th>
<th>d</th>
<th>d’</th>
</tr>
</thead>
<tbody>
<tr>
<td>330</td>
<td>0.65</td>
<td>0.60</td>
</tr>
<tr>
<td>298</td>
<td>1.92</td>
<td>1.90</td>
</tr>
<tr>
<td>255</td>
<td>1.65</td>
<td>1.60</td>
</tr>
</tbody>
</table>

Example 5: Compounds V-XIV. FIG. 1c

(A) 3-Methyl-1-phenyl-4(1-(3’-carboxyacryloyl)-2,2’,6,6’-tetramethylpiperidyl-4)aminomethylene-5-pyrazolinone (compound V, FIG. 1c)

A 250 ml one-necked round bottom flask, equipped with condenser and magnetic stirrer, was filled with 34 g of 3-methyl-1-phenyl-4-(2,2’,6,6’-tetramethylpiperidyl-4) amino-methylene-5-pyrazolinone (I), and 100 ml of benzene. After dissolving the residue, the solution was cooled at 0-5°C. and 10 g of maleic anhydride was added by mixing. The mixture was kept at these conditions for 3 hours and was left for 12 hours at room temperature.

The precipitate was collected by filtration, washed with 50 ml of petroleum ether and dried. 41 g (93%) of pale yellow powder was obtained, with a m.p. of 244-6°C. After crystallization from toluene the m.p. was 246-7°C. and the molecular mass was 438. Point of decomposition: 250°C.

λmax in ethanol: 300 and 258 nm.
(B) Compounds VI-IX, FIG. 1c

Compounds VI-IX were obtained using the same procedure as in (A), with the following yield, molecular mass, m.p., and λmax:

3-methyl-1-phenyl-4-[1-(3′-carboxymethylacryloyl)-2,2′,6,6′-tetramethylpiperidyl-4] aminomethylene-5-pyrazolinone (VI): 92%, 452, 212-4°C, λmax (ethanol) 300, 255 nm;

3-methyl-1-phenyl-4-[1-(o-carboxybenzoyl)-2,2′,6,6′-tetramethylpiperidyl-4] aminomethylene-5-pyrazolinone (VII): 92.5%, 488, 223-5°C, λmax (ethanol) 298, 260 nm;

3-methyl-1-phenyl-4-[1-(o-carboxybenzoyl)-2,2′,6,6′-tetramethylpiperidyl-4] aminomethylene-5-thiopyrazolinone (VIII): 68%, 504, 227-30°C (decomp.), λmax (ethanol) 380, 300, 280, 235 nm;

3-methyl-1-phenyl-5-[1-(3′-carboxyacryloyl)-2,2′,6,6′-tetramethylpiperidyl-4] aminopyrazole methylene-4-carboxyaldehyde (IX): 92%, 438, 193-5°C (benzene), >270°C, λmax (ethanol) 262 nm.

(C) Compounds X-XVI, FIG. 1c

Compounds X-XVI were obtained using the same procedure, but the reaction with carboxyaldehydes was carried out by heating at 40-60°C. The pertinent yield, molecular mass, m.p., point of decomp., and λmax are:

3-methyl-1-phenyl-4-[1-(3′-methyl-1′-phenyl-5′-pyrazolonylmethylidene-4)-2,2′,6,6′-tetramethylpiperidyl-4] aminomethylene-5-pyrazolinone (X): 96%, 524, 225-6°C (toluene), 260°C, λmax (ethanol) 295, 260 nm; (CHCl₃) 298, 255 nm;

3-methyl-1-phenyl-4-[1-(3′-methyl-1′-phenyl-5′-thiopyrazolonylmethylidene-4)-2,2′,6,6′-tetramethylpiperidyl-4] aminomethylene-5-pyrazolinone (XI): 93.5%, 540, 208-10°C (dioxane), >240°C, λmax (ethanol) 295, 265, 230 nm; (CHCl₃) 298, 275 nm;
3-methyl-1-phenyl-5-[1-(3'-methyl-1-phenyl-5-
pyrazolonylmethyldene-4')-2,2',6,6'-tetramethylpiperidyl-4] aminopyrazole-4-
carboxyaldehyde (XII): 83.5%, 524, 208-9°C (benzene), >230°C, \( \lambda_{\text{max}} \) (ethanol) 260 nm; 5
3-methyl-1-phenyl-5-[1-(3'-methyl-1-phenyl-5-
-thiopyrazolonylmethyldene-4')-2,2',6,6'-tetramethylpiperidyl-4] aminopyrazole-4-
carboxyaldehyde (XIII): 92.8%, 540, 245-7°C (toluene), >260°C, \( \lambda_{\text{max}} \) (ethanol) 280, 225 nm;
3-methyl-1-phenyl-5-[1-(3'-methyl-1-phenyl-5-
pyrazolonylmethyldene-4')-2,2',6,6'-tetramethylpiperidyl-4] aminopyrazole-4-
carboxy (ald(p-phenoxy)phenylimin (XIV): 58%, 152-4°C (benzene), \( \lambda_{\text{max}} \) (ethanol) 325, 260, 250 nm;
3-methyl-1-phenyl-4-[1-(3'-methyl-1-phenyl-5-
pyrazolonylmethyldene-4')-2,2',6,6'-tetramethylpiperidyl-4] aminomethylene-5-
thiopyrazolinone (XV): 96%, 540, 215-7°C (toluene), >250°C, \( \lambda_{\text{max}} \) (ethanol) 380, 300, 260 nm;
3-methyl-1-phenyl-4-[1-(3'-methyl-1-phenyl-5-
thiopyrazolonylmethyldene-4')-2,2',6,6'-tetramethylpiperidyl-4] aminomethylene-5-
thiopyrazolinone (XVI): 94%, 556, 245-6°C (dioxane), 250°C, \( \lambda_{\text{max}} \) (ethanol) 380, 20 300, 265 nm.

2

(D) Data of absorption of the ethanolic solutions of compounds V- XVI (FIG. 1c)
The data of absorption obtained for the ethanolic solutions of compounds V-
XVI at the corresponding \( \lambda_{\text{max}} \) values, before (d) and after (d') irradiation by Hg
25 Lamp (400W), at 50°C:
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ (d)</th>
<th>$\lambda'_{\text{max}}$ (d')</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>300 (1.45), 258 (1.28)</td>
<td>300 (1.42), 258 (1.25)</td>
</tr>
<tr>
<td>VI</td>
<td>300 (1.62), 255 (1.46)</td>
<td>300 (1.60), 255 (1.40)</td>
</tr>
<tr>
<td>VII</td>
<td>298 (1.38), 260 (1.22)</td>
<td>298 (1.36), 260 (1.20)</td>
</tr>
<tr>
<td>VIII</td>
<td>380 (0.60), 300 (1.28)</td>
<td>380 (0.20), 300 (1.50)</td>
</tr>
<tr>
<td></td>
<td>280 (1.50), 235 (1.65)</td>
<td>280 (0.85), 235 (1.50)</td>
</tr>
<tr>
<td>IX</td>
<td>262 (1.25)</td>
<td>262 (1.20)</td>
</tr>
<tr>
<td>X</td>
<td>295 (1.16), 265 (1.67)</td>
<td>295 (1.10), 265 (1.58)</td>
</tr>
<tr>
<td>XI</td>
<td>265 (1.40), 230 (1.55)</td>
<td>265 (1.35), 230 (1.50)</td>
</tr>
<tr>
<td>XII</td>
<td>260 (1.75), 230 (1.60)</td>
<td>260 (1.70), 230 (1.50)</td>
</tr>
<tr>
<td>XIII</td>
<td>280 (1.65), 260 (1.50)</td>
<td>280 (1.35), 260 (1.60)</td>
</tr>
<tr>
<td>XIV</td>
<td>340 (1.25), 260 (1.10)</td>
<td>340 (1.20), 260 (1.10)</td>
</tr>
<tr>
<td></td>
<td>230 (1.40)</td>
<td>230 (1.35)</td>
</tr>
<tr>
<td>XV</td>
<td>380 (0.65), 300 (1.40)</td>
<td>380 (0.25), 300 (0.85)</td>
</tr>
<tr>
<td>XVI</td>
<td>260 (1.35)</td>
<td>260 (1.40)</td>
</tr>
<tr>
<td></td>
<td>380 (0.60), 300 (1.45)</td>
<td>380 (0.25), 300 (0.90)</td>
</tr>
<tr>
<td></td>
<td>265 (1.20)</td>
<td>265 (1.20)</td>
</tr>
</tbody>
</table>

Example 6: Compounds XVII-XXXI, FIGs. 2b and 3b

(A) Zinc bis [3-Methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4) aminomethylene-5-pyrazolonate (compound XVII, FIG. 2b)

170 g of 3-methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4) aminomethylene-5-pyrazolone (I) and 300 ml of acetone were added to a 1 l kettle equipped with a mixer, condenser, and bath for heating and cooling. The resulting solution was heated to 50°C and a solution of 57 g of zinc acetate dihydrate in 150 ml of water was added to it. The mixture was heated at this temperature for 30 min, and then cooled to room temperature.
After 3 hours the precipitate was collected by filtration. The precipitate was placed in a 3 l glass equipped with a mixer, and 1 l of cold water (15-20°C) was added to it. To this suspension, a solution of 26 g of sodium carbonate in 200 ml of water was added, over a period of 2 hours. After neutralization of the acetic acid, the precipitate was collected by filtration, washed with 150 ml of cold water (~10°C) and dried at 60-70°C.

The complex was obtained with a yield of 172 g (92.4%) of colorless powder, with a m.p. of 236-39°C. After crystallization from benzene the m.p. was 248-9°C. This complex dissolves well in methanol, ethanol, chloroform, toluene, acetone, and dioxane. When heated it dissolves in n-hexane and partly in petroleum ether.

λmax (ethanol): 295 and 255 nm.

Found %: C 64.25; H 7.14; N 15.28.

Gross formula: C₄₀H₅₄N₈O₂Zn.

Calc. %: C 64.60; H 7.27; N 15.09

The absorption results obtained before (d) and after (d’) irradiation by sunlight for a period of 7 days under conditions of June, 1995, Ashkelon, Israel, in ethanolic solution (5-10-5):

<table>
<thead>
<tr>
<th></th>
<th>λmax</th>
<th>d</th>
<th>d’</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>295</td>
<td>1.56</td>
<td>1.52</td>
</tr>
</tbody>
</table>

The absorption results obtained before (d) and after (d’) irradiation by Hg Lamp (400W), at 50°C, for 1 hour, in ethanol solution:

<table>
<thead>
<tr>
<th></th>
<th>λmax</th>
<th>d</th>
<th>d’</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>295</td>
<td>1.78</td>
<td>1.72</td>
</tr>
</tbody>
</table>

The results of color estimation according to Hardners method before and after irradiation of a polyester plate (3 mm) in a weathermeter for 250 hours:

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Before</td>
<td>After 250 hours</td>
<td>1</td>
</tr>
</tbody>
</table>
(B) Compounds XVIII-XXVII, FIGs. 2b and 3b

Complexes XVIII-XXVII were obtained by the same procedure as in (A), with the following yield, gross formula and molecular mass, m.p., point of decomp., and λmax:

5 Nickel bis[3-methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4)-aminomethylene-5-pyrazolonate] dihydrate (XVIII): 90.5%. C_{40}H_{54}N_{8}O_{2}Ni·2H_{2}O, 772, 236-8°C (benzene), >280°C, λmax (EtOH) 300, 275, 260 nm;

Copper bis[3-methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4)-aminomethylene-5-pyrazolonate] (XIX): 92.3%. C_{40}H_{54}N_{8}O_{2}Cu, 741, 206-8°C (benzene), >270°C;

Zinc bis[3-methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4)-aminomethylene-5-thiopyrazolonate] (XX): 90.5%. C_{40}H_{54}N_{8}S_{2}Zn, 775, 252-4°C (toluene), >290°C, λmax (ethanol) 330, 285, 260, 225 nm;

Cobalt bis[3-methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4)-aminomethylene-5-thiopyrazolonate] dihydrate (XXI): 86%. C_{40}H_{54}N_{8}S_{2}Ni·2H_{2}O, 768.7, 245-7°C (toluene), >290°C, λmax (ethanol) 340, 300, 280, 240 nm;

Copper bis[3-methyl-1-phenyl-4-(2,2',6,6'-tetramethylpiperidyl-4)-aminomethylene-5-thiopyrazolonate] (XXII): 91.5%. C_{40}H_{54}N_{8}S_{2}Cu, 773, 236-7°C (benzene), >290°C, λmax (ethanol) 330, 290, 260, 230 nm;

Zinc bis[3-methyl-1-phenyl-5-(2,2',6,6'-tetramethylpiperidyl-4)-4-carboxyaldehyde-5-aminopyrazolonate] (XXIII): 85.6%. C_{40}H_{54}N_{8}O_{2}, 743, 198-9°C (benzene-n-hexane), >290°C, λmax (ethanol) 260, 235 nm;

Nickel bis[3-methyl-1-phenyl-4-(1,2,2',6,6'-pentamethylpiperidyl-4)-aminomethylene-5-pyrazolonate] dihydrate (XXIV): 89.8%. C_{42}H_{58}N_{8}O_{2}Ni·2H_{2}O, 800.7, 242-3°C (benzene), >280°C, λmax (ethanol), 280 nm.

Zinc bis[3-methyl-1-phenyl-4-(1,2,2',6,6'-pentamethylpiperidyl-4)-aminomethylene-5-thiopyrazolonate] (XXV): 90.6%. C_{42}H_{58}N_{8}S_{2}Zn, 803, 256-8°C (benzene), >290°C, λmax (ethanol) 330, 288, 260, 237 nm.

SUBSTITUTE SHEET (RULE 26)
Data of absorption of the ethanolic and isoctane solutions of compounds **XVII-XXXI**. FIGs. 2b and 3b

The data of absorption obtained for the ethanolic and isoctane solutions of compounds **XVII-XXXI** at the corresponding $\lambda_{\text{max}}$ values, before (d) and after (d') irradiation by Hg Lamp (400W) at 50°C for 1 hour at a distance of 50 cm:

<table>
<thead>
<tr>
<th>Comp.</th>
<th>Ethanol</th>
<th>Isooctane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda_{\text{max}}$ (d)</td>
<td>$\lambda_{\text{max}}$ (d')</td>
</tr>
<tr>
<td>XVII</td>
<td>295 (1.55)</td>
<td>295 (1.50)</td>
</tr>
<tr>
<td></td>
<td>255 (1.28)</td>
<td>255 (1.20)</td>
</tr>
<tr>
<td>XVIII</td>
<td>300 (1.10)</td>
<td>300 (1.00)</td>
</tr>
<tr>
<td></td>
<td>275 (1.85)</td>
<td>275 (1.70)</td>
</tr>
<tr>
<td>XIX</td>
<td>280 (1.649)</td>
<td>280 (1.10)</td>
</tr>
<tr>
<td>XXVI</td>
<td>295 (1.65)</td>
<td>295 (1.60)</td>
</tr>
<tr>
<td></td>
<td>255 (1.30)</td>
<td>260 (1.28)</td>
</tr>
<tr>
<td>XXVIII</td>
<td>295 (1.65)</td>
<td>295 (1.60)</td>
</tr>
<tr>
<td></td>
<td>255 (1.55)</td>
<td>255 (1.45)</td>
</tr>
<tr>
<td></td>
<td>230 (1.35)</td>
<td>230 (1.35)</td>
</tr>
<tr>
<td>XXX</td>
<td>310 (0.75)</td>
<td>310 (0.60)</td>
</tr>
<tr>
<td></td>
<td>280 (1.85)</td>
<td>280 (1.50)</td>
</tr>
<tr>
<td>XXXI</td>
<td>305 (0.95)</td>
<td>305 (0.85)</td>
</tr>
<tr>
<td></td>
<td>225 (1.35)</td>
<td>225 (1.30)</td>
</tr>
<tr>
<td>Tin 320</td>
<td>348 (1.25)</td>
<td>348 (1.25)</td>
</tr>
<tr>
<td></td>
<td>300 (1.20)</td>
<td>300 (1.15)</td>
</tr>
</tbody>
</table>

The absorption data for Tinuvin 320 are given for comparison.
Example 7: Compounds XXVI-XXXV (FIG. 3b)

(A) Zinc bis[3-methyl-1-phenyl-4-[1-(3′-carboxyacryloyl)-2,2′.6,6′-tetramethylpiperidyl-4]-aminomethylene-5-pyrazolonate] (compound XXVI, FIG. 3b)

A 250 ml erlenmeyer flask with a magnetic stirrer was filled with 14.86 g of Zinc complex (XVII) (Example 6), and 100 ml of benzene, which were dried over CaH₂. The flask contents were heated and stirred until all the complex was dissolved. The solution was cooled to room temperature and then 4 g of maleic anydride was added. The resulting mass was stirred at room temperature for about 12 hours. Then the precipitate was collected by filtration, washed with 50 ml of petroleum ether and dried. The compound was obtained with a yield of 17.8g (94.6%), and a m.p. of 203-6°C. After crystallization from ethanol, the m.p. was 210-12°C.

λmax (ethanol): 295 and 255 nm.

Found % : C 60.94; H 6.02; N 12.06.

Gross formula: C₄₈H₅₈N₈O₈Zn.

Calc. % : C 61.32; H 6.18; N 11.93.

(B) Compounds XXVII-XXXV (FIG. 3b)

Complexes XXVII-XXXV were obtained using the same procedure as in (A), with the following yield, gross formula, molecular mass, m.p., point of decomp., and λmax:

Zinc bis{3-methyl-1-phenyl-4-[1-(2-carboxymethylacryloyl)-2,2′.6,6′-tetramethylpiperidyl-4] aminomethylene-5-pyrazolonate} (XXVII): 89%, C₅₀H₆₂N₈O₈Zn, 967, 199-201°C, >240°C, λmax 295, 255 nm;

Nickel bis{3-methyl-1-phenyl-4-[1-(o-carboxybenzoyl)-2,2',6,6'-tetramethylpiperidyl-4] aminomethylene-5-pyrazololate} dihydrate (XXIX): 88.4%, \( \text{C}_{56}\text{H}_{62}\text{N}_{8}\text{O}_{8}\text{Ni}-2\text{H}_{2}\text{O} \), 1068-1067, 243-245°C, >260°C. \( \lambda_{\text{max}} \) 300, 260 nm.

Zinc bis{3-methyl-1-phenyl-4-[1-(3-methyl-1-phenyl-5-
5 pyrazolonylmethylidene-4)-2,2',6,6'-tetramethylpiperidyl-4] aminomethylene-5-
pyrazololate} (XXX): 92%, \( \text{C}_{62}\text{H}_{70}\text{N}_{12}\text{O}_{4}\text{Zn} \), III, 194-5°C, >250°C. \( \lambda_{\text{max}} \) (ethanol) 310, 280, 220 nm.

Zinc bis{3-methyl-1-phenyl-4-[1-(3-methyl-1-phenyl-5-
-thiopyrazolonylmethylidene-4)-2,2',6,6'-tetramethylpiperidyl-4] aminomethylene-5-
-thiopyrazololate} (XXXI): 85%, \( \text{C}_{62}\text{H}_{70}\text{N}_{12}\text{O}_{4}\text{S}_{2}\text{Zn} \), 1147, 153-5°C, >270°C. \( \lambda_{\text{max}} \) (ethanol) 305, 270, 225 nm.

Cobalt bis{3-methyl-1-4-[1-(3-methyl-1-phenyl-5-
pyrazolonylmethylidene-4)-2,2',6,6'-tetramethylpiperidyl-4] aminomethylene-5-
pyrazololate} dihydrate (XXXII): 89%, \( \text{C}_{62}\text{H}_{70}\text{N}_{12}\text{O}_{4}\text{Co}-2\text{H}_{2}\text{O} \), 1141, 186-8°C, >240°C. \( \lambda_{\text{max}} \) 300, 280, 220 nm.

Copper bis{3-methyl-1-phenyl-4-[1-(3-methyl-1-phenyl-5-
pyrazolonylmethylidene-4)-2,2',6,6'-tetramethylpiperidyl-4] aminomethylene-5-
pyrazololate} (XXXIII): 91%, \( \text{C}_{62}\text{H}_{70}\text{N}_{12}\text{O}_{4}\text{Cu} \), 1109, 186-9°C, >250°C. \( \lambda_{\text{max}} \) (ethanol) 300, 280, 225 nm.

Zinc bis{3-methyl-1-phenyl-4-[1-(3-methyl-1-phenyl-5-
thiopyrazolonylmethylidene-4)-2,2',6,6'-tetramethylpiperidyl-4] aminomethylene-5-
thiopyrazololate} (XXXIV): 90.5%, \( \text{C}_{62}\text{H}_{70}\text{N}_{12}\text{S}_{4}\text{Zn} \), 1175, 241-3°C (toluene), 270°C, \( \lambda_{\text{max}} \) 330, 300, 260, 225 nm.

Nickel bis{3-methyl-1-phenyl-5-thiopyrazolonylmethylidene-4)- 2,2',6,6'-
tetramethylpiperidyl-4} aminomethylene-5-thiopyrazololate} dihydrate (XXXV): 82%, \( \text{C}_{62}\text{H}_{70}\text{N}_{12}\text{S}_{4}\text{Ni}-2\text{H}_{2}\text{O} \), 1203-1207, 191-4°C, >240°C. \( \lambda_{\text{max}} \) (ethanol) 300, 275, 260 nm.
Example 8: Compounds XXXVI-XLII, FIG. 3b

(A) Cooper bis{3-methyl-1-phenyl-4-carboxyaldehydeiminine-5-[1-(3-methyl-1-phenyl-5-pyrazolonymethylidene-4)-2,2',6,6'-tetramethylpiperidyl-4 aminopyrazolonate} (compound XXXVI, FIG. 3b)

A 250 ml erlenmeyer flask with a magnetic stirrer was filled with 10.48 g of 3-methyl-1-phenyl-5-[1-(3-methyl-1-phenyl-5-pyrazolonymethylidene-4)-2,2',6,6'-tetramethylpiperidyl-4] aminopyrazole-4-carboxyaldehyde (compound XII), 100 ml of ethanol, and 2 g of aniline. The flask contents were heated to 60°C and stirred until the entire product was dissolved. To this solution, a solution of 2 g of copperacetate monohydrate in 30 ml of water was added. The resulting reaction mixture was stirred at 60°C for 30 min and then was cooled to 15-20°C, and the precipitate was collected by filtration. The precipitate was washed on the filter with 50 ml of cold water and dried at 60-70°C.

The compound was obtained with a yield of 11.6 g (91%). The m.p. was 193-6°C. After crystallization from dioxane the m.p. was 198-200°C.

λmax: 330, 280, and 240 nm.

Found %: C 69.96, H 6.40, N 15.74.

Gross formula: C_{74}H_{82}N_{14}O_{2}Cu.

Calc. %: C 70.42, H 6.53, N 15.54.

(B) Compounds XXXVII-XLII (FIG. 3b)

Complexes XXXVII-XLII were obtained using the same procedure as in (A), with the following yield, gross formula, m.p., point of decomp., and λmax:

Zinc bis{3-methyl-1-phenyl-4-carboxyaldehydeiminine-5-[1-(3-methyl-1-phenyl-5-pyrazolonymethylidene-4)-2,2',6,6'-tetramethylpiperidyl-4] aminopyrazolonate} (XXXVII): 85%. C_{86}H_{90}N_{14}O_{4}Zn. 260-2°C (dioxane), >290°C, λmax 335, 300, 280, 225 nm.

Zinc bis{3-methyl-1-phenyl-4-carboxyaldehydeiminine-5-[1-(3-methyl-1-phenyl-5-thiopyrazolonymethylidene-4)-2,2',6,6'...
tetramethylpiperidyl-4]aminopyrorazolonate\} (XXXVIII): 76\%. C\textsubscript{74}H\textsubscript{82}N\textsubscript{14}S\textsubscript{2}Zn, 225-7°C (dioxane), >290°C. λmax 330, 300, 280, 225 nm.

Copper bis\{3-methyl-1-phenyl-4-carboxylid(\text{n-phenoxo)phenylimine}- 5-[1-(3- methyl-1-phenyl-5-thiopyrazolonylmethylidine)-4]-2,2',6,6'-tetramethylpiperidyl-4]aminopyrazolonate\} (XXXIX): 88\%. C\textsubscript{86}H\textsubscript{90}N\textsubscript{14}O\textsubscript{2}S\textsubscript{2}Cu, 254-5°C (dioxane), >290°C, λmax (EtOH) 340, 300, 270, 235 nm.

Copper bis\{3-methyl-1-phenyl-4-carboxyalid(\text{n-butylcarboxy)- phenylimine}-5- [1-(3-methyl-1-phenyl-5-pyrazolonylmethylidene)-4]-2,2',6,6'-tetramethylpiperidyl-4] aminopyrazolonate\} (XL): 87.3\%, C\textsubscript{84}H\textsubscript{94}N\textsubscript{14}O\textsubscript{6}Cu. 256-8°C (dioxane), >280°C. 10 λmax (EtOH) 350, 305, 270, 235 nm.

Copper bis\{3-methyl-1-phenyl-4-carboxylid(\text{n-phenylamino)phenylimine}-5- [1-(3-methyl-1-phenyl-5-pyrazolonylmethylidene)-4]-2,2',6,6'-tetramethylpiperidyl-4] aminopyrazolonate\} (XLI): 85\%, C\textsubscript{86}H\textsubscript{92}N\textsubscript{16}O\textsubscript{2}Cu, 270-3°C (dioxane), >290°C, λmax 370, 320, 280, 245 nm.

Copper bis\{3-methyl-1-phenyl-carboxyalid(\text{N-hydroxy-m, m'-ditrebutyl)phenylimine}- 5-[1-(3-methyl-1-phenyl-5-pyrazolonylmethylidene)-4]-2,2',6,6'-tetramethylpiperidyl-4] aminopyrazolonate\} (XLII): 90\%, C\textsubscript{90}H\textsubscript{114}N\textsubscript{14}O\textsubscript{4}Cu, 238-240°C (dioxane), >270°C, λmax (EtOH) 350, 330, 280, 235 nm.

Example 9:

(A) The light-stabilizing effect of Tinuvin P, complex II as in S.U. Pat. No. 956504, and compounds XVII and XX. on polystyrene films:

M\textsubscript{θ} - the molecular mass of polystyrene, estimated by viscosimetry method.

M - the molecular mass of polystyrene (film thickness 0.04-0.045 mm) after irradiation by Hg Lamp (400W) at 50°C, for 0, 20, 40, and 60 hours.
<table>
<thead>
<tr>
<th>Mol. mass of polystyrene/hours</th>
<th>Tinuvin P</th>
<th>Complex II</th>
<th>XVII</th>
<th>XX</th>
</tr>
</thead>
<tbody>
<tr>
<td>M / M₀</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>M₂₀ / M₀</td>
<td>79.3</td>
<td>87.3</td>
<td>89.8</td>
<td>92.5</td>
</tr>
<tr>
<td>M₄₀ / M₀</td>
<td>55.6</td>
<td>78.0</td>
<td>80.2</td>
<td>82.5</td>
</tr>
<tr>
<td>M₆₀ / M₀</td>
<td>38.5</td>
<td>74.0</td>
<td>78.0</td>
<td>80.3</td>
</tr>
</tbody>
</table>

(*) Complex II as in S.U. Pat. No. 956504: Nickel bis[3-methyl-1-phenyl-4-phenylamino-methylene-5-thiopyrazolone].

10 (B) The light-stabilizing effect of Tinuvin 320 and compounds I, III, XVII, and XVIII on polycarbonate films

The absorption results obtained before (d) and after (d') irradiation of polycarbonate films (thickness 0.04-0.05 nm) by a Hg Lamp (400 W) at 50°C. for 3 hours:

<table>
<thead>
<tr>
<th></th>
<th>Tin 320</th>
<th>I</th>
<th>III</th>
<th>XVII</th>
<th>XVIII</th>
</tr>
</thead>
<tbody>
<tr>
<td>λmax(d)</td>
<td>340(1.55)</td>
<td>295(2.0)</td>
<td>260(1.8)</td>
<td>295(2.0)</td>
<td>275(1.4)</td>
</tr>
<tr>
<td></td>
<td>300(1.46)</td>
<td>255(1.35)</td>
<td></td>
<td></td>
<td>255(1.78)</td>
</tr>
<tr>
<td>λ'_max(d')</td>
<td>340(1.5)</td>
<td>295(1.85)</td>
<td>260(1.75)</td>
<td>295(1.92)</td>
<td>275(1.35)</td>
</tr>
<tr>
<td></td>
<td>300 (1.40)</td>
<td>255 (1.28)</td>
<td></td>
<td></td>
<td>255 (1.70)</td>
</tr>
</tbody>
</table>

While the invention has been described with respect to a limited number of embodiments, it will be appreciated that many variations, modifications and other applications of the invention may be made.
WHAT IS CLAIMED IS:

1. Substituted pyrazoles of the formula I,

\[
\text{R}_1 \quad \text{N} \quad \text{N} \quad \text{X} \quad \text{N} \quad \text{R}_3 \\
\text{R}_2 \quad \text{CH} \quad \text{X} \quad \text{H} \quad \text{CH}_3 \\
\]

where

- \( \text{R}_1 \) and \( \text{R}_2 \) are identical or different and each denotes hydrogen or alkyl or aryl.
- \( \text{X} \) is oxygen or sulphur, and
- \( \text{R}_3 \) is hydrogen, alkyl, a derivative of carboxyacryloyl or carboxybenzoyl, or a derivative of pyrazole.

2. Compounds of the formula I as in claim 1, where \( \text{R}_1 \) is phenyl, \( \text{R}_2 \) is methyl, \( \text{X} \) is oxygen or sulphur, and \( \text{R}_3 \) is \( \text{H}, \text{CH}_3, \text{COCH} = \text{CHCOOH}, \text{CO-C-CH}_2\text{COOH}, \text{CH}_2 \text{COC}_5\text{H}_4\text{COOH(o-)}, \text{3-Me-1-Ph-5-pyrazolonylmethylidene-4}, \) or \( \text{3-Me-1-Ph-5-thiopyrazolonylmethylidene-4}. \)

3. Substituted pyrazoles of the formula II,

\[
\text{R}_1 \quad \text{N} \quad \text{N} \quad \text{H} \quad \text{CH}_3 \\
\text{R}_2 \quad \text{CH} \quad \text{Z} \quad \text{N} \quad \text{R}_3 \\
\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3
\]

SUBSTITUTE SHEET (RULE 26)
where

$R_1$ and $R_2$ are identical or different and each denotes hydrogen or alkyl
or aryl,

$Z$ is oxygen or N-aryl, and

$R_3$ is hydrogen, alkyl, a derivative of carboxyacryloyl or carboxybenzoyl,
or a derivative of pyrazole.

4. Compounds of the formula II as in claim 3, where $R_1$ is phenyl,
$R_2$ is methyl,
$Z$ is O, NC$_6$H$_5$, NC$_6$H$_4$OC$_6$H$_5$, NC$_6$H$_4$COOC$_4$H$_9$ (m- or p-), or
NC$_6$H$_2$(p-OH,m,m'-C(CH$_3$)$_3$), and
$R_3$ is H, CH$_3$, COCH=CHCOOH, CO-C-CH$_2$COOH,

\[
\text{CH}_2
\]
COC$_6$H$_4$COOH(o-), 3-Me-1-Ph-5-pyrazolonylmethylidene-4,
or 3-Me-1-Ph-5-thiopyrazolonylmethylidene-4.

5. Metal complexes of the formula III,

\[
\text{(III)}
\]

where

$R_1$, $R_2$, $R_3$ and $R_4$ are identical or different and each denotes hydrogen or
alkyl or aryl,

$X$ is oxygen or sulphur.
R₄ and R₅ are identical or different and selected from the group consisting of hydrogen, alkyl, a derivative of carboxyacryloyl or carboxybenzoyl, and a derivative of pyrazole, and 
Me is a metal ion selected from the group consisting of Ni(II), Zn(II), 
Cu(II) and Co(II).

6. Metal complexes of the formula III as in claim 5, where R₁ is phenyl. 
R₂ is methyl. 
R₃ is phenyl. 
R₄ is methyl, 
X is oxygen or sulphur, 
R₅ and R₆ are identical and selected from the group consisting of H, CH₃- 
COCH=CHCOOH, CO-C-CH₂COOH, COC₆H₄COOH(o-), 

\[
\text{CH₂}
\]

3-Me-1-Ph-5-pyrazolonylmethylidene-4, and 3-Me-1-Ph-5-thiopyrazolonylmethylidene-4, and 
Me is a metal ion selected from the group consisting of Ni(II), Zn(II). 
Cu(II) and Co(II).

7. Metal complexes of the formula IV,

\[
\text{(IV)}
\]

where 
R₁, R₂, R₃ and R₄ are identical or different and each denotes hydrogen or alkyl or aryl,
Z is oxygen or N-aryl, and
R₂ and R₆ are identical or different and selected from the group consisting of hydrogen, alkyl, a derivative of carboxyacryloyl or carboxybenzoyl, and a derivative of pyrazole, and
Me is a metal ion selected from the group consisting of Ni(II), Zn(II), Cu(II) and Co(II).

8. Metal complexes of the formula IV as in claim 7, where R₁ is phenyl,
R₂ is methyl,
R₃ is phenyl,
R₄ is methyl,
Z is O, NC₆H₅, NC₆H₄OC₆H₅, NC₆H₄COOC₆H₅(m- or p-), or
NC₆H₂(p-OH,m,m'-C(CH₃)₃),
R₅ and R₆ are identical and selected from the group consisting of H, CH₃,
COCH=CHCOOH, CO-C-CH₂COOH, COC₆H₄COOH(o-),
CH₂
3-Me-1-Ph-5-pyrazolonymethylidene-4, and 3-Me-1-Ph-5-thiopyrazolonymethylidene-4, and
Me is a metal ion selected from the group consisting of Ni(II), Zn(II),
Cu(II) and Co(II).

9. Light stabilizers containing a substituted pyrazole, of the formula I.

where
R₁ and R₂ are identical or different and each denotes hydrogen or alkyl or aryl.

X is oxygen or sulphur, and

R₃ is hydrogen, alkyl, a derivative of carboxyacryloyl or carboxybenzoyl, or a derivative of pyrazole.

10. Light stabilizers containing a substituted pyrazole, of the formula II.

\[ \text{Diagram II} \]

where

R₁ and R₂ are identical or different and each denotes hydrogen or alkyl or aryl.

Z is oxygen or N-aryl, and

R₃ is hydrogen, alkyl, a derivative of carboxyacryloyl or carboxybenzoyl, or a derivative of pyrazole.

11. Light stabilizers containing a substituted pyrazole, of the formula III.

\[ \text{Diagram III} \]

where
R₁, R₂, R₃ and R₄ are identical or different and each denotes hydrogen or alkyl or aryl,
X is oxygen or sulphur.
R₅ and R₆ are identical or different and selected from the group consisting of hydrogen, alkyl, a derivative of carboxyacryloyl or carboxybenzoyl, and a derivative of pyrazole, and
Me is a metal ion selected from the group consisting of Ni(II), Zn(II), Cu(II) and Co(II).

12. Light stabilizers containing a substituted pyrazole, of the formula IV.

![Formula IV](image)

where
R₁, R₂, R₃ and R₄ are identical or different and each denotes hydrogen or alkyl or aryl,
Z is oxygen or N-aryl.
R₅ and R₆ are identical or different and selected from the group consisting of hydrogen, alkyl, a derivative of carboxyacryloyl or carboxybenzoyl, and a derivative of pyrazole, and
Me is a metal ion selected from the group consisting of Ni(II), Zn(II), Cu(II) and Co(II).

13. A method for the synthesis of metal complexes as claimed in claim 5, which includes the reaction of:
(a) a compound as claimed in claim 1; and
(b) metal acetate, wherein the metal ion is selected from the group consisting of Ni(II), Zn(II), Cu(II) and Co(II).

14. A method for the synthesis of metal complexes as claimed in claim 7, which includes the reaction of:
   (a) a compound as claimed in claim 3; and
   (b) metal acetate, wherein the metal ion is selected from the group consisting of Ni(II), Zn(II), Cu(II) and Co(II).

15. A method for the synthesis of metal complexes as claimed in claim 5, wherein said R₅ and R₆ are selected from the group consisting of a derivative of carboxyacryloyl or carboxybenzoyl, and a derivative of pyrazole, which includes the reaction of:
   (a) a metal complex as claimed in claim 5, wherein said R₅ and R₆ are selected from the group consisting of hydrogen and alkyl; and
   (b) anhydride or derivative of pyrazole.

16. A method for the synthesis of metal complexes as claimed in claim 7, wherein said R₅ and R₆ are selected from the group consisting of a derivative of carboxyacryloyl or carboxybenzoyl, and a derivative of pyrazole, which includes the reaction of:
   (a) a metal complex as claimed in claim 7, wherein said R₅ and R₆ are selected from the group consisting of hydrogen and alkyl; and
   (b) anhydride or derivative of pyrazole.

17. A method for the synthesis of metal complexes as claimed in claim 6, which includes the reaction of:
   (a) a compound as claimed in claim 2; and
(b) metal acetate of the formula Me(OOCCH$_3$)$_2$, wherein the metal ion is selected from the group consisting of Ni(II), Zn(II), Cu(II) and Co(II).

18. A method for the synthesis of metal complexes as claimed in claim 8, which includes the reaction of:
   (a) a compound as claimed in claim 4; and
   (b) metal acetate of the formula Me(OOCCH$_3$)$_2$, wherein the metal ion is selected from the group consisting of Ni(II), Zn(II), Cu(II) and Co(II).

19. A method for the synthesis of metal complexes as claimed in claim 6, wherein said R$_5$ and R$_6$ are selected from the group consisting of
   COCH=CHCOOH, CO-C-CH$_2$COOH, COC$_6$H$_4$COOH(o-),
   CH$_2$
   3-Me-1-Ph-5-pyrazolonylmethylidene-4, and 3-Me-1-Ph-5-thiopyrazolonylmethylidene-4, which includes the reaction of:
   (a) a metal complex as claimed in claim 6, wherein said R$_5$ and R$_6$ are selected from the group consisting of H and CH$_3$; and
   (b) components selected from the group consisting of maleic, itaconic or phthalic anhydride, 3-Me-1-Ph-5-hydroxypyrazole-4-carboxyaldehyde, and 3-Me-1-Ph-5-mercaptopyrazole-4-carboxyaldehyde.

20. A method for the synthesis of metal complexes as claimed in claim 8, wherein said R$_5$ and R$_6$ are selected from the group consisting of
   COCH=CHCOOH, CO-C-CH$_2$COOH, COC$_6$H$_4$COOH(o-),
   CH$_2$
   3-Me-1-Ph-5-pyrazolonylmethylidene-4, and 3-Me-1-Ph-5-thiopyrazolonylmethylidene-4, which includes the reaction of:
   (a) a metal complex as claimed in claim 8, wherein said R$_5$ and R6 are selected from the group consisting of H and CH$_3$; and
(b) components selected from the group consisting of maleic, itaconic or phthalic anhydride, 3-Me-1-Ph-5-hydroxypyrazole-4-carboxyaldehyde, and 3-Me-1-Ph-5-mercaptopyrazole-4-carboxyaldehyde.
FIG. 1c

I  \( R = H, X = 0; \)

II \( R = H, X = S; \)

III \( R = H, Z = 0; \)

IV \( R = CH_3, X = 0; \)

V \( R = COCH=CHCOOH, X = 0; \)

VI \( R = CO-C-CH_2COOH, X = 0; \)

\[
\begin{array}{c}
\text{CH}_2 \\
\end{array}
\]

VII \( R = COC_6H_4COOH (o-), X = 0; \)

VIII \( R = COC_6H_4COOH (o-), X = S; \)

IX \( R = COC_6H_4COOH (o-), Z = 0; \)

X \( R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4}, X = 0; \)

XI \( R = 3\text{-Me-1-Ph-5-thiopyrazolonylmethylidene-4}, X = 0; \)

XII \( R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4}, Z = 0; \)

XIII \( R = 3\text{-Me-1-Ph-5-thiopyrazolonylmethylidene-4}, Z = 0; \)

XIV \( R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4}, Z = NC_6H_4OC_6H_5; \)

XV \( R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4}, X = S; \)

XVI \( R = 3\text{-Me-1-Ph-5-thiopyrazolonylmethylidene-4}, X = S. \)
FIG. 2A

A Pyrazole-containing compound
FIG. 2b

XVII  \( R = H, X = 0, Me = Zn \);
XVIII \( R = H, X = 0, Me = Ni \);
XIX \( R = H, X = 0, Me = Cu \);
XX \( R = H, X = S, Me = Zn \);
XXI \( R = H, X = S, Me = Co \);
XXII \( R = H, X = S, Me = Cu \);
XXIII \( R = H, Z = 0, Me = Zn \);
XXIV \( R = CH_3, X = 0, Me = Ni \);
XXV \( R = CH_3, X = S, Me = Zn \).
FIG. 3b

XXVI \[ R = \text{COCH}=\text{CHCOOH}, \quad X = 0, \text{Me} = \text{Zn}; \]

XXVII \[ R = \text{CO}-\text{C}-\text{CH}_{2}\text{COOH}, \quad X = 0, \text{Me} = \text{Zn}; \]

XXVIII \[ R = \text{COC}_{6}\text{H}_{4}\text{COOH (o-)}, \quad X = 0, \text{Me} = \text{Zn}; \]

XXIX \[ R = \text{COC}_{6}\text{H}_{4}\text{COOH (o-)}, \quad X = 0, \text{Me} = \text{Ni}; \]

XXX \[ R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4,} \]
\[ X = 0, \text{Me} = \text{Zn}; \]

XXXI \[ R = 3\text{-Me-1-Ph-5-thiopyrazolonylmethylidene-4,} \]
\[ X = 0, \text{Me} = \text{Zn}; \]

XXXII \[ R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4,} \]
\[ X = 0, \text{Me} = \text{Co}; \]

XXXIII \[ R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4,} \]
\[ X = 0, \text{Me} = \text{Cu}; \]

XXXIV \[ R = 3\text{-Me-1-Ph-5-thiopyrazolonylmethylidene-4,} \]
\[ X = 0, \text{Me} = \text{Cu}; \]

XXXV \[ R = 3\text{-Me-1-Ph-5-thiopyrazolonylmethylidene-4,} \]
\[ X = 0, \text{Me} = \text{Ni}; \]

XXXVI \[ R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4,} \]
\[ Z = \text{NC}_{6}\text{H}_{5}, \text{Me} = \text{Cu}; \]

XXXVII \[ R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4,} \]
\[ Z = \text{NC}_{6}\text{H}_{4}\text{OC}_{6}\text{H}_{5}, \text{Me} = \text{Zn}; \]

XXXVIII \[ R = 3\text{-Me-1-Ph-5-thiopyrazolonylmethylidene-4,} \]
\[ Z = \text{NC}_{6}\text{H}_{5}, \text{Me} = \text{Zn}; \]

XXXIX \[ R = 3\text{-Me-1-Ph-5-thiopyrazolonylmethylidene-4,} \]
\[ Z = \text{NC}_{6}\text{H}_{4}\text{OC}_{6}\text{H}_{5}, \text{Me} = \text{Cu}; \]

XL \[ R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4,} \]
\[ Z = \text{NC}_{6}\text{H}_{4}\text{COOC}_{6}\text{H}_{9 (m-)}, \text{Me} = \text{Cu}; \]

XLI \[ R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4,} \]
\[ Z = \text{NC}_{6}\text{H}_{4}\text{NHC}_{6}\text{H}_{5 (p-)}, \text{Me} = \text{Cu}; \]

XLII \[ R = 3\text{-Me-1-Ph-5-pyrazolonylmethylidene-4,} \]
\[ Z = \text{NC}_{6}\text{H}_{2}[p\text{-OH,m,m'}\text{-C(CH}_{3}_{2})_{2}], \text{M} = \text{Cu}. \]
# INTERNATIONAL SEARCH REPORT

## A. CLASSIFICATION OF SUBJECT MATTER

- **IPC(6):** C07F 1/08, 3/06; C07D 401/02, 401/12, 401/14
- **US CL:** 546/6, 11, 211

According to International Patent Classification (IPC) or to both national classification and IPC.

## B. FIELDS SEARCHED

- **Minimum documentation searched (classification system followed by classification symbols):**
  - **U.S.:** 546/6, 11, 211

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched.

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used):

- **APS**

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 3,975,382 A (AVAR et al) 17 August 1976, see entire document.</td>
<td>1-20</td>
</tr>
<tr>
<td>A</td>
<td>US 4,146,540 A (AVAR et al) 27 March 1979, see entire document.</td>
<td>1-4</td>
</tr>
<tr>
<td>A</td>
<td>US 4,194,989 A (IRICK et al) 25 March 1980, see entire document.</td>
<td>1-20</td>
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<tr>
<td>A</td>
<td>US 4,231,921 A (MOSER) 04 November 1980, see entire document.</td>
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Further documents are listed in the continuation of Box C. See patent family annex.

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<th>S</th>
<th>Special categories of cited documents:</th>
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<tr>
<td>A</td>
<td>document defining the general state of the art which is not considered to be of particular relevance</td>
</tr>
<tr>
<td>E</td>
<td>earlier document published on or after the international filing date</td>
</tr>
<tr>
<td>L</td>
<td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td>
</tr>
<tr>
<td>O</td>
<td>document referring to an oral disclosure, use, exhibition or other means</td>
</tr>
<tr>
<td>P</td>
<td>document published prior to the international filing date but later than the priority date claimed</td>
</tr>
</tbody>
</table>

| T | Later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
| X | Document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone |
| Y | Document of particular relevance; the claimed invention cannot be considered as involving an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art |
| &amp; | Document member of the same family |

**Date of the actual completion of the international search:**

03 FEBRUARY 1997

**Date of mailing of the international search report:**

17 MAR 1997

**Name and mailing address of the ISA/US Commissioner of Patents and Trademarks**

Box PCT  
Washington, D.C. 20231  
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