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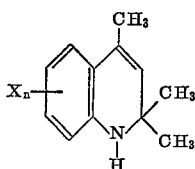
ACTIVATED DIHYDROQUINOLINES

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36 Claims. (Cl. 99-2)

This application is a continuation-in-part of application Ser. No. 218,551 filed Aug. 22, 1962.

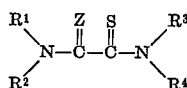
This invention relates to improved antioxidants and to methods of stabilizing substances subject to oxidative degradation. This invention further relates to animal feed compositions containing said improved antioxidants and to methods of feeding animals.

It has now been found in accordance with this invention that the antioxidant properties of well known antioxidants are significantly enhanced by admixture with certain nitrogen-containing compounds. The improved antioxidant compositions of this invention comprise a 2,2,4-trimethyl-1,2-dihydroquinoline antioxidant of the formula



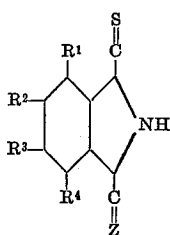
wherein n is an integer from 0 to 2 inclusive and X is selected from the group consisting of chlorine, bromine and $RO-$, wherein R is selected from the group consisting of hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the class consisting of alkyl having not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, cycloalkyl having at least 4 and not more than 7 carbon atoms, benzyl and phenyl, and wherein the substituents of not more than 4 carbon atoms on the hydrocarbyl are selected from the class consisting of alkyl, alkynyl and alkoxy, and a nitrogen-containing compound present in an amount sufficient to provide an enhanced antioxidant property, said compound having a formula selected from the group consisting of

(A)



wherein Z is selected from the group consisting of oxygen, sulfur and imino, and R^1, R^2, R^3 and R^4 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

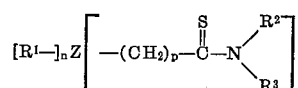
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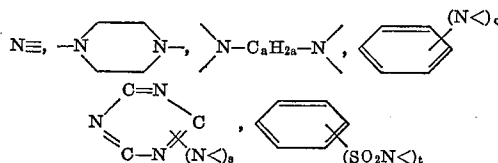
wherein Z is selected from the group consisting of oxygen, imino and sulfur, and R^1, R^2, R^3 and R^4 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, alkyl, phenyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

(C)



wherein Z contains a plurality of terminal nitrogen bonds and is selected from the group consisting of

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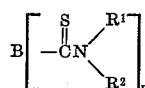


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wherein q and t are each integers from 1 to 6 inclusive, s is an integer from 1 to 3 inclusive and a is an integer from 2 to 12; R^1, R^2 , and R^3 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, m is an integer from 2 to 3, n is an integer from 0 to 10 inclusive and p is an integer from 1 to 2,

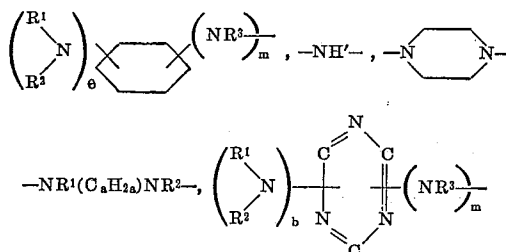
(D)

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wherein B contains a plurality of terminal nitrogen bonds and is selected from the group consisting of

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55

60

wherein m is an integer from 2 to 3, e is an integer from 0 to 4 inclusive, b is an integer from 0 to 1, a is an integer from 2 to 12 inclusive; and R^1, R^2 and R^3 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano,

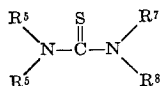
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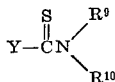
carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

(E)

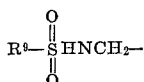


wherein R⁵, R⁶, R⁷ and R⁸ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, phenyl, cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of alkyl, nitro, hydroxyl, cyano, carboxyl, amino, alkylamino, dialkylamino, phenyl, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, provided that not more than one of R⁵ and R⁶ and not more than one of R⁷ and R⁸ are selected from the group consisting of phenyl, substituted phenyl, benzyl, cyclohexyl and substituted cyclohexyl, and

(F)



wherein R⁹ and R¹⁰ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of alkyl, nitro, hydroxyl, cyano, carboxyl, amino, alkylamine, phenyl, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, provided that not more than one of R⁹ and R¹⁰ is selected from the group consisting of phenyl, substituted phenyl, benzyl, cycloalkyl and substituted cycloalkyl; and Y is selected from the group consisting of R⁹, —SH,



and the heterocyclic group



wherein K is a heteronucleus selected from the group consisting of oxygen, sulfur, nitrogen and imino (—NH—) and D is a divalent hydrocarbon of at least three and not more than seven carbon atoms.

The following are representative of the nitrogen-containing compounds useful in the compositions and methods of this invention.

(A)

tetraethyldithiooxamide
N,N'-diphenyl dithiooxamide
N,N'-diphenyl thiooxamide
N,N'-dioctyldecyl dithiooxamide
N,N'-dioleyl dithiooxamide
N,N'-dicyanoethyl thiooxamide
N,N'-bis(p-nitrophenyl) dithiooxamide
dithiooxamide
N,N'-dimethyl thiooxamide
N,N'-dimethyl dithiooxamide
N,N'-bis(carboxymethyl) dithiooxamide
N,N'-bis[2(diethylamino)ethyl] dithiooxamide
thiooxanilothiooxamide
N,N'-bis(2-hydroxyethyl) dithiooxamide
N,N'-dicyclohexyl dithiooxamide

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(B)

3-methoxydithiophthalimide
5-ethoxydithiophthalimide
4,5-dinitrodithiophthalimide
4-methoxythiophthalimide
thiophthalimide
dithiophthalimide

(C)

10 bis-N(thiocarbamoylmethylene) 1,4-benzenedisulfonamide
2,4,6-tris(thiocarbamoylmethylene)-S-triazine
1,4-piperazine-bis(thioacetamide)
N,N'-bis(thiocarbamylmethylene)-p-phenylenediamine

(D)

15 dithiobiuret
N,N'-dithiocarbamoyl-1,4-piperazine
2,4,6-tris(dimethylthiocarbamyl)-S-triazine
N,N'-di(thiocarbamyl)ethylenediamine-1,2

(E)

20 thiourea
N,N-dimethyl thiourea
N,N'-di(n-propyl)thiourea
N,N'-diphenyl thiourea
25 N,N'-di(tetradecyl)thiourea

(F)

thioacetamide

30 A large number of the above described nitrogen-containing compounds which are useful in the compositions and methods of this invention are disclosed in the published literature and can be prepared by known methods. For example, the basic compound, rubeanic acid, can be prepared by reacting cyanogen with hydrogen sulfide. The rubeanic acid can be converted to other of the useful compounds by reaction with a primary or a secondary amine. Alternatively, the nitrogen containing compounds can be prepared from acid chlorides of carboxylic acids by reaction with amines, for example aniline, and thereafter converting the carbonyl groups to thiocarbonyl radicals.

The amount of nitrogen-containing compound necessary to provide enhanced antioxidant properties in the antioxidant compositions of this invention varies to some extent depending upon the specific dihydroquinoline antioxidant employed. The antioxidant compositions of this invention usually contain from about 0.05 part to about 20 parts by weight of nitrogen containing compound per one part by weight of dihydroquinoline antioxidant. Preferred compositions contain from about 0.33 part to about 10 parts by weight of nitrogen-containing compound per one part by weight of dihydroquinoline antioxidant. The improved antioxidant compositions of this invention can be incorporated into any substance which is subject to oxidative degradation in the presence of air, ozone, oxygen or various other oxidizing agents under the influence of heat, natural or artificial light, or various metals. The improved antioxidant compositions are added to the substance to be stabilized in any conventional manner.

60 The components of the improved antioxidant compositions of this invention can also be added separately to the substances to be stabilized followed by conventional mixing to form the stabilized substance. Substances subject to oxidative degradation in which the improved antioxidant compositions of this invention are useful include for example unsaturated polymers such as natural rubber; synthetic rubber, e.g. butadiene and isoprene polymers and copolymers; petroleum based resins, e.g. coumarone indene; rosin and derivatives thereof, and high impact plastics, e.g. ABS, impact polystyrene, impact acrylics and impact PVC; saturated polymers such as hydrocarbon polymers, e.g. polyethylene, polypropylene, ethylene/propylene copolymers and polyisobutylene; and food products, particularly those containing unsaturated oils,

75 vitamins and vitamin containing components.

The antioxidant compositions of this invention are particularly useful for the stabilization of animal feeds containing components subject to oxidative degradation such as unsaturated oils, dehydrated alfalfa and other forage crops, vitamin concentrates, meal from oil processing industries, proteins and antibiotics.

It is well known that the carotene in dehydrated alfalfa and other forage crops is subject to oxidative degradation and loss of vitamins, particularly vitamin A, under normal processing and storage conditions. Furthermore, animal feeds which include dehydrated forage crops and other vitamin-containing components can undergo further decomposition, such that animals to which they are fed are subject to malnutrition and more serious disabilities attributable to deficiencies in essential vitamins. It has also been found that many animals have the ability to store vitamins, and that the retention of these vitamins for future use is extended if antioxidants are included in the animal diets. The animal industry now regularly includes antioxidants as a conventional component in animal feeds.

The improved antioxidant compositions of this invention, when used in place of conventional amounts of dihydroquinoline antioxidants, give an equivalent level of antioxidant protection with less antioxidant or a more effective level of antioxidant protection with the same amount of antioxidant. Thus, the compositions of this invention are usually employed in an amount equal to or less than the amount of antioxidant which is conventionally employed in the art.

The following examples illustrate the invention. Parts and percent are by weight unless otherwise indicated.

Example

The antioxidant properties of nitrogen-containing compounds included within the scope of the generic formulae of this invention and closely related compounds not within the scope of this invention are determined by a standardized procedure using carotene emulsions and microanalysis techniques. The 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline is used as a standard for control and its antioxidant activity under identical conditions is assigned a rating of 100. The antioxidant activity of each nitrogen containing compound tested, both alone and in a one to three part admixture with the 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline standard, is expressed as a percentage of the antioxidant rating of the standard. Results and further details are given in Table I.

TABLE I

Compound	Antioxidant Activity	
	Alone	1 part compound plus 3 parts standard
Standard; 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline.	100	-----
1. Dithioamide	-3.0	184.0
2. N,N'-dimethylthiooxamide	1.5	138.6
3. N,N'-dimethyl dithiooxamide	3.0	163.6
4. Thioxanthionitrile	0.9	126.3
5. O-Zinc salt 8-allyl-N-dithiocarboxy-N-phenyl-L-alanine.	3.1	132.9
6. Thioacetamide	2.4	165.7
7. N,N'-dicyclohexyl dithiooxamide	13.6	127.2
8. Rubenic acid	0	187.7
9. N,N'-bis(2-ethyl mercaptoethyl oxamide).	3.6	110.7
10. α -Anilino thioacetamide	-4.4	126.0
11. Dithioburet	-3.3	204.9
12. Thiophthalimide	0.8	135.8
13. Dithiophthalimide	2.9	146.9
14. 2-thiopicolinamide	-1.2	145.7
15. N,N'-bis(2-hydroxyethyl) dithiooxamide.	2.6	121.5
16. N,N'-bis(carboxymethyl) dithiooxamide.	2.7	191.9
17. N,N'-dibenzyl dithiooxamide	4.7	161.0
18. 1,4-piperazine bis(thioacetamide)	0.5	137.1
19. N(thiocarbamoylmethylene)-p-toluenesulfonamide.	2.4	151.4
20. 2-dimethylamino-4,6-bis(dimethylthiocarbamyl)-S-triazine.	-1.9	240

TABLE I—Continued

Compound	Antioxidant Activity	
	Alone	1 part compound plus 3 parts standard
21. 4-ethoxy-2-thiopicolinanilide.	-5.2	198.6
22. N,N'-di(3,4-dichlorobenzyl) dithiooxamide.	3.4	164.0
23. Thioxanthiothioamide	6.4	139.0
24. N,N'-bis[2(diethylamino)ethyl] dithiooxamide.	0.9	205.1
25. Dithioburet	-4.2	116.5
26. N,N'-didodecyl dithiooxamide	0	128.2
27. N,N'-bis(thiocarbamylmethylene)-p-phenylenediamine.	-2.2	110.8

The following nitrogen-containing compounds are not within the scope of the useful compounds of the invention. The compounds have no beneficial activity and in some cases they adversely affect the antioxidant properties of the dihydroquinoline standard.

TABLE II

Compound	Antioxidant Activity	
	Alone	1 Part compound plus 3 Parts standard
Standard; 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline.	100	-----
28. Oxamide	0	103.0
29. N,N'-bis-3-methoxypropyloxamide	4.6	55.3
30. 1,1'-dithiodiformamidine dihydrochloride.	0	97.5
31. Dihexyl dithiooxalimidate	-3.4	88.6
32. Thiododecanamide	3.4	97.5
33. N,N'-dimethyl oxamide	0.9	103.9
34. N,N'-dimethyl oxamide	3.5	103.9
35. Dimethylloxalimidate	3.9	105.2

The antioxidant activity of various admixtures of rubenic acid with the 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline standard is determined in order to demonstrate the relationship of the nitrogen-containing compounds to the antioxidant with respect to proportions of each. Results and further details are given below in Table III.

TABLE III

Parts		Wt. percent RA	Antioxidant Activity Standard=100
Rubenic Acid	Standard Antioxidant		
.5	15	3	122.4
1.0	15	6	123.7
5.0	15	25	287.1
15	15	50	293.4
45	15	75	318.4
225	15	94	206.6
450	15	97	159.2

The antioxidant compositions of this invention can be incorporation into any or all components of animal feed compositions in any convenient manner. Conventional animal feed compositions generally comprise at least about 2 percent plant ingredients such as hay, straw, silage, yellow corn, pasturage, ground corn cobs, cottonseed hulls, cotton mill wastes, beet pulp, corn meal, soybean oil meal, wheat bran, wheat middlings, dehydrated alfalfa, ground oats, millet, linseed oil meal, coconut oil meal, distillers dried grains, peanut oil meal, cottonseed meal and the like plant products. Most animal feed compositions also contain up to about 2 percent mineral ingredients such as bone meal, limestone, salt (NaCl) and the various trace minerals including salts of zinc, copper, manganese, cobalt, iodine, iron and the like. Other materials which can be

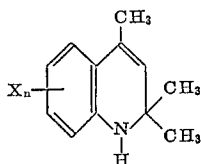
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incorporated into animal feed compositions in varying amounts include animal ingredients such as fish meal, meat and bone scraps, dried milk, animal fats, dried whey solubles and the like; vitaminaceous ingredients such as vitamins A, B₁₂, D and K, as well as the B vitamins such as riboflavin, niacin, pantothenic acid or salts thereof, choline, pyridoxine, thiamine, nicotinic acid or salts thereof, biotin, folic acid and the like; amino acids such as methionine, phenylalanine, arginine, glycine, histidine, isoleucine, leucine, lysine, threonine, tryptophan, valine and the like, and medicaments such as antibiotics, steroids, arsenicals, ant-helmintics and the like.

Although the invention is described with respect to specific modifications, the details thereof are not to be construed as limitations except to the extent indicated in the following claims.

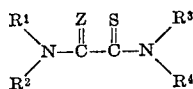
What is claimed is:

1. Antioxidant composition comprising an antioxidant of the formula



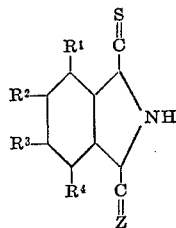
wherein n is an integer from 0 to 2 inclusive and X is selected from the group consisting of chlorine, bromine and $RO-$, wherein R is selected from the group consisting of hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the class consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, cycloalkyl having at least 4 and not more than 7 carbon atoms, benzyl and phenyl, and wherein the substituents of not more than 4 carbon atoms on the hydrocarbyl are selected from the class consisting of alkyl, alkynyl and alkoxy and a compound present in an amount sufficient to provide an enhanced antioxidant property, said compound having a formula selected from the group consisting of

(A)



wherein Z is selected from the group consisting of oxygen, sulfur and imino, and R^1 , R^2 , R^3 and R^4 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

(B)

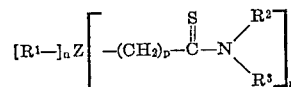


wherein Z is selected from the group consisting of oxygen, imino and sulfur, and R^1 , R^2 , R^3 and R^4 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms,

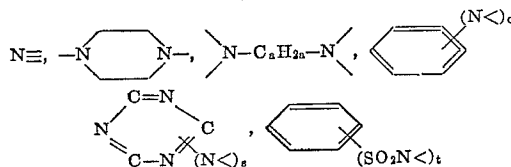
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alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, alkyl, phenyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

(C)

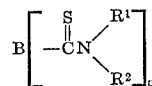


wherein Z contains a plurality of terminal nitrogen bonds and is selected from the group consisting of

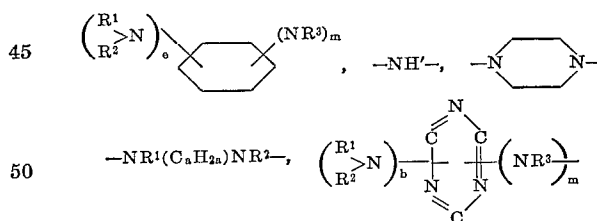


wherein q and t are each integers from 1 to 6 inclusive, s is an integer from 1 to 3 inclusive and a is an integer from 2 to 12; R^1 , R^2 , and R^3 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, m is an integer from 2 to 3, n is an integer from 0 to 10 inclusive and p is an integer from 1 to 2,

(D)

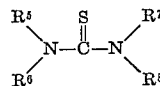


wherein B contains a plurality of terminal nitrogen bonds and is selected from the group consisting of



wherein m is an integer from 2 to 3, e is an integer from 0 to 4 inclusive, b is an integer from 0 to 1, a is an integer from 2 to 12 inclusive; and R^1 , R^2 and R^3 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

(E)

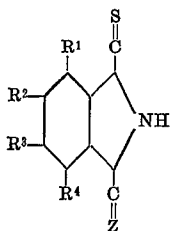


wherein R^5 , R^6 , R^7 and R^8 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon

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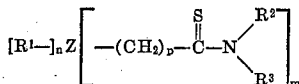
alkyl moieties of said substituents having not more than 4 carbon atoms,

(B)

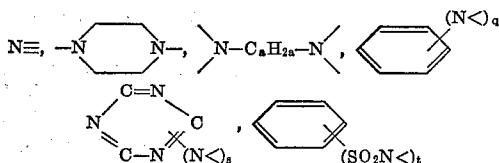


wherein Z is selected from the group consisting of oxygen, imino and sulfur, and R¹, R², R³ and R⁴ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, alkyl, phenyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

(C)

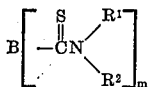


wherein Z contains a plurality of terminal nitrogen bonds and is selected from the group consisting of

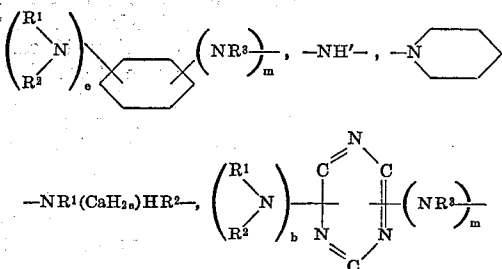


wherein q and t are each integers from 1 to 6 inclusive, s is an integer from 1 to 3 inclusive and a is an integer from 2 to 12; R¹, R², and R³ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, m is an integer from 2 to 3, n is an integer from 0 to 10 inclusive and p is an integer from 1 to 2,

(D)



wherein B contains a plurality of terminal nitrogen bonds and is selected from the group consisting of



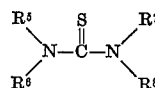
wherein m is an integer from 2 to 3, e is an integer from 0 to 4 inclusive, b is an integer from 0 to 1, a is an integer

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from 2 to 12 inclusive; and R¹, R² and R³ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

(E)

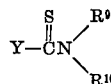
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wherein R⁵, R⁶, R⁷ and R⁸ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, phenyl, cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of alkyl, nitro, hydroxyl, cyano, carboxyl, amino, alkylamino, dialkylamino, phenyl, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, provided that not more than one of R⁵ and R⁶ and not more than one of R⁷ and R⁸ are selected from the group consisting of phenyl, substituted phenyl, benzyl, cyclohexyl and substituted cyclohexyl, and

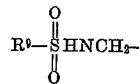
(F)

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wherein R⁹ and R¹⁰ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of alkyl, nitro, hydroxyl, cyano, carboxyl, amino, alkylamino, phenyl, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, provided that not more than one of R⁹ and R¹⁰ is selected from the group consisting of phenyl, substituted phenyl, benzyl, cycloalkyl and substituted cycloalkyl; and Y is selected from the group consisting of R⁹, —SH,

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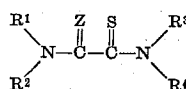
and the heterocyclic group



wherein K is a heteronucleus selected from the group consisting of oxygen, sulfur, nitrogen and imino (—NH—) and D is a divalent hydrocarbon of at least three and not more than seven carbon atoms.

15. Method of claim 14 wherein the antioxidant is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and the compound is represented by the formula

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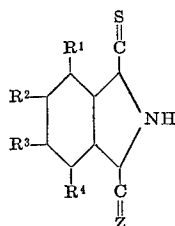
wherein Z is selected from the group consisting of oxygen, sulfur and imino, and R¹, R², R³ and R⁴ are each se-

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lected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, and wherein the compound is present in an amount from about 0.05 part to about 20 parts by weight per one part by weight of the antioxidant.

16. Method of claim 15 wherein the compound is 15 rubeanic acid.

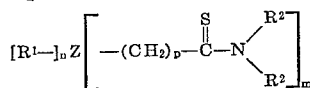
17. Method of claim 14 wherein the antioxidant is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and the compound is represented by the formula



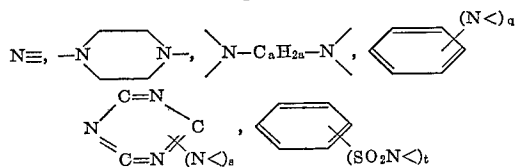
wherein Z is selected from the group consisting of oxygen, imino and sulfur, and R¹, R², R³ and R⁴ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, alkyl, phenyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, and wherein the compound is present in an amount from about 0.05 part to about 20 parts by weight per one part by weight of the antioxidant.

18. Method of claim 17 wherein the compound is dithiophthalimide.

19. Method of claim 14 wherein the antioxidant is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and the compound is represented by the formula



wherein Z contains a plurality of terminal nitrogen bonds and is selected from the group consisting of



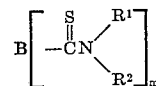
wherein q and t are each integers from 1 to 6 inclusive, s is an integer from 1 to 3 inclusive and a is an integer from 2 to 12; R¹, R², and R³ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hy-

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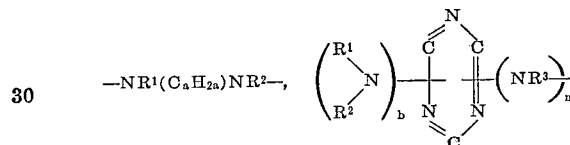
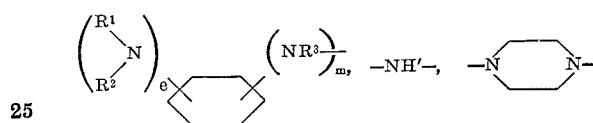
drocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, m is an integer from 2 to 3, n is an integer from 0 to 10 inclusive and p is an integer from 1 to 2, and wherein the compound is present in an amount from about 0.05 to about 20 parts by weight per one part by weight of the antioxidant.

20. Method of claim 19 wherein the compound is 1,4-piperazine bis(thioacetamide).

21. Method of claim 14 wherein the antioxidant is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and the compound is represented by the formula



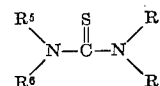
wherein B contains a plurality of terminal nitrogen bonds and is selected from the group consisting of



wherein m is an integer from 2 to 3, e is an integer from 0 to 4 inclusive, b is an integer from 0 to 1, a is an integer from 2 to 12 inclusive; and R¹, R² and R³ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, and wherein the compound is present in an amount from about 0.05 part to about 20 parts by weight per one part by weight of the antioxidant.

22. Method of claim 21 wherein the compound is 2-dimethylamino-4,6-bis(dimethylthiocarbamyl)-S-triazine.

23. Method of claim 14 wherein the antioxidant is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and the compound is represented by the formula



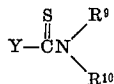
wherein R⁵, R⁶, R⁷ and R⁸ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, phenyl, cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of alkyl, nitro, hydroxyl, cyano, carboxyl, amino, alkylamino, dialkylamino, phenyl, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, provided that not more than one of R⁵ and R⁶ and not more than one of R⁷ and R⁸ are selected from the group consisting of phenyl, substituted phenyl, benzyl, cyclohexyl and substi-

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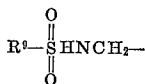
tuted cyclohexyl, and wherein the compound is present in an amount from about 0.05 part to about 20 parts by weight per one part by weight of the antioxidant.

24. Method of claim 23 wherein the compound is diphenyl thiourea.

25. Method of claim 14 wherein the antioxidant is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and the compound is represented by the formula



wherein R^9 and R^{10} are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of alkyl, nitro, hydroxyl, cyano, carboxyl, amino, alkylamino, phenyl, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, provided that not more than one R^9 and R^{10} is selected from the group consisting of phenyl, substituted phenyl, benzyl, cycloalkyl and substituted cycloalkyl; and Y is selected from the group consisting of R^9 . —SH.



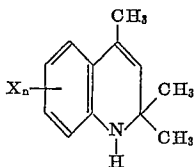
and the heterocyclic group



wherein K is a heteronucleus selected from the group consisting of oxygen, sulfur, nitrogen and imino ($-\text{NH}-$) and D is a divalent hydrocarbon of at least three and not more than seven carbon atoms, and wherein the compound is present in an amount from about 0.05 part to about 20 parts by weight per one part by weight of the antioxidant. 45

26. Method of claim 25 wherein the compound is thioacetamide.

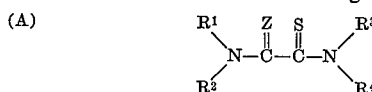
27. Animal feed composition containing as an essential ingredient therein an antioxidant composition comprising
an antioxidant of the formula



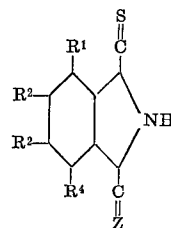
wherein *n* is an integer from 0 to 2 inclusive and X is selected from the group consisting of chlorine, bromine and RO—, wherein R is selected from the group consisting of hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the class consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, cycloalkyl having at least 4 and not more than 7 carbon atoms, benzyl and phenyl, and wherein the substituents of not more than 4 carbon atoms on the hydrocarbyl are selected from the class consisting of alkyl, alkynyl and alkoxy, and a compound present in an amount sufficient to provide an en-

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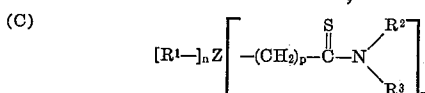
hanced antioxidant property, said compound having a formula selected from the group consisting of



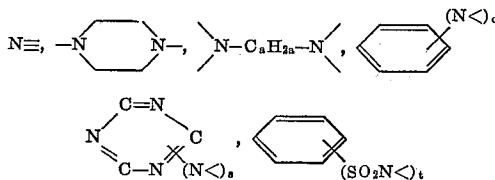
wherein Z is selected from the group consisting of oxygen, sulfur and imino, and R¹, R², R³ and R⁴ are each selected from the group consisting of hydrogen, hydrocarbonyl and substituted hydrocarbonyl wherein the hydrocarbonyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbonyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms.



wherein Z is selected from the group consisting of oxygen, imino and sulfur, and R¹, R², R³ and R⁴ are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, alkyl, phenyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms.



wherein Z contains a plurality of terminal nitrogen bonds and is selected from the group consisting of

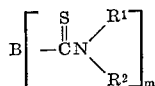


wherein q and t are each integers from 1 to 6 inclusive, s is an integer from 1 to 3 inclusive and a is an integer from 2 to 12; R^1 , R^2 , and R^3 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4

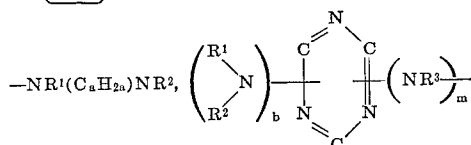
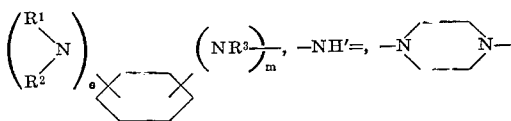
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carbon atoms, m is an integer from 2 to 3, n is an integer from 0 to 10 inclusive and p is an integer from 1 to 2,

(D)

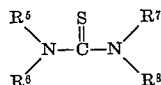


wherein B contains a plurality of terminal nitrogen bonds and is selected from the group consisting of



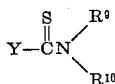
wherein m is an integer from 2 to 3, e is an integer from 0 to 4 inclusive, b is an integer from 0 to 1, a is an integer from 2 to 12 inclusive; and R^1 , R^2 and R^3 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms,

(E)



wherein R^5 , R^6 , R^7 , and R^8 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, phenyl, cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of alkyl, nitro, hydroxyl, cyano, carboxyl, amino, alkylamino, dialkylamino, phenyl, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, provided that not more than one of R^5 and R^6 and not more than one of R^7 and R^8 are selected from the group consisting of phenyl, substituted phenyl, benzyl, cyclohexyl and substituted cyclohexyl, and

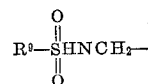
(F)



wherein R^9 and R^{10} are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 12 carbon atoms, alkenyl of not more than 12 carbon atoms, alkynyl of not more than 12 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of alkyl, nitro, hydroxyl, cyano, carboxyl, amino, alkylamino, phenyl, dialkylamino, alkoxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, provided that not

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more than one of R^9 and R^{10} is selected from the group consisting of phenyl, substituted phenyl, benzyl, cycloalkyl and substituted cycloalkyl; and Y is selected from the group consisting of R^9 , —SH ,

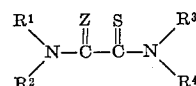


and the heterocyclic group



wherein K is a heteronucleus selected from the group consisting of oxygen, sulfur, nitrogen and imino (—NH—) and D is a divalent hydrocarbon of at least three and not more than seven carbon atoms.

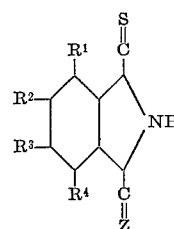
28. Animal feed of claim 27 wherein the antioxidant is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and the compound is represented by the formula



wherein Z is selected from the group consisting of oxygen, sulfur and imino, and R^1 , R^2 , R^3 and R^4 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, phenyl, alkyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, and wherein the compound is present in an amount from about 0.05 part to about 20 parts by weight per one part by weight of the antioxidant.

29. Animal feed of claim 28 wherein the compound is rubenic acid.

30. Animal feed of claim 27 wherein the antioxidant is 6-ethoxy-2,2,4-trimethyl-1,2-dihydroquinoline and the compound is represented by the formula



wherein Z is selected from the group consisting of oxygen, imino and sulfur, and R^1 , R^2 , R^3 and R^4 are each selected from the group consisting of hydrogen, hydrocarbyl and substituted hydrocarbyl wherein the hydrocarbyl is selected from the group consisting of alkyl of not more than 18 carbon atoms, alkenyl of not more than 18 carbon atoms, alkynyl of not more than 18 carbon atoms, phenyl and cycloalkyl of at least 4 and not more than 7 carbon atoms, and wherein the substituents on the hydrocarbyl are selected from the group consisting of nitro, hydroxyl, cyano, carboxyl, amino, alkyl, phenyl, alkylamino, dialkylamino, alkyloxy and alkylthio, the alkyl moieties of said substituents having not more than 4 carbon atoms, and wherein the compound is present in an amount from about 0.05 part to about 20 parts by weight per one part by weight of the antioxidant.

31. Animal feed of claim 30 wherein the compound is dithiophthalimide.

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H. H. KLARE, *Examiner.*