United States Patent Office 3,156,689 Patented Nov. 10, 1964

3,156,689

1,4-PHENYLENE-BIS[2-OXY-4,6-BIS(ALKYLTHIO)-5-TRIAZINES]

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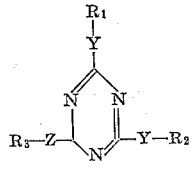
No Drawing. Original application Feb. 21, 1961, Ser. No. 87,520. Divided and this application Apr. 4, 1963, Ser. No. 273,540

2 Claims. (Cl. 260—248)

This application is a division of copending application, Serial No. 87,520, filed on February 21, 1961. Application Serial No. 87,520 is a continuation-in-part of copending application, Serial No. 47,159, filed on August 3, 1960, which is, in turn, a continuation-in-part of copending application, Serial No. 21,604 filed on April 12, 1960. Applications Serial No. 47,159 and Serial No. 21,604 are now abandoned.

This invention relates to a method of stabilization with a substituted triazine and to compositions stabilized thereby. The invention also relates to novel substituted triazines.

One class of substituted triazines, useful as stabilizers according to the invention, consists in compounds of the formula:



I

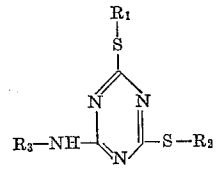
wherein

R_1 and R_2 each independetly represents an aliphatic hydrocarbon radical, preferably alkyl having from 1 to 18 carbon atoms, cycloalkyl having from 5 to 6 carbon atoms, phenyl, alkylphenyl, especially alkylphenyl having from 7 to 24 carbon atoms, e.g. methylphenyl, dimethylphenyl, ethylphenyl, propylphenyl, butylphenyl, dibutylphenyl, dioctylphenyl, octadecylphenyl, etc., substituted hydroxyphenyl, especially alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, alkylhydroxybenzyl, preferably alkylhydroxybenzyl having from 8 to 25 carbon atoms, e.g. methyl-substituted hydroxybenzyl, ethyl-substituted hydroxybenzyl, dimethyl-substituted hydroxybenzyl, butyl-substituted hydroxybenzyl, dibutyl-substituted hydroxybenzyl, etc., cyanoalkyl, preferably cyano(lower)alkyl, alkylmercaptoalkyl, preferably having from 2 to 10 carbon atoms, carbalkoxyalkyl, preferably having from 3 to 15 carbon atoms, carbalkoxyaryl, preferably carbalkoxyphenyl having from 8 to 19 carbon atoms;

R_3 represents hydroxyphenyl or substituted hydroxyphenyl, especially phenylhydroxyphenyl or alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, such as e.g. methylhydroxyphenyl, dimethylhydroxyphenyl, ethylhydroxyphenyl, butylhydroxyphenyl, dibutylhydroxyphenyl, octylhydroxyphenyl, octadecylhydroxyphenyl, etc., or alkylhydroxybenzyl, preferably as defined above; and

X, Y and Z each independently represents —S—, —O— or —NR_4—, wherein R_4 is aralkyl, preferably benzyl, alkyl, preferably lower alkyl, or hydrogen.

An especially valuable subclass of stabilizers of the Formula I comprises the dithio-substituted triazines of the Formula I(*a*):



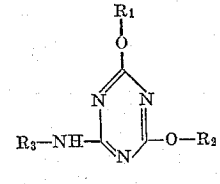
I(*a*)

wherein

R_1 and R_2 each independently represents alkyl, preferably alkyl having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, etc., cycloalkyl, preferably having from 5 to 6 carbon atoms alkylphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylphenyl, ethylphenyl, propylphenyl, butylphenyl, octylphenyl, dodecylphenyl, octadecylphenyl, dimethylphenyl, dibutylphenyl, dioctylphenyl, dioctadecylphenyl, methyldibutylphenyl, etc., phenyl, cyanoalkyl, preferably cyanoalkyl having from 2 to 7 carbon atoms, e.g. cyanomethyl, cyanoethyl, cyanopropyl, cyanobutyl, cyanohexyl, etc., alkylmercaptoalkyl, preferably having from 2 to 10 carbon atoms, e.g. methylthiomethyl, ethylthiomethyl, octylthioethyl, etc., carbalkoxyalkyl, preferably having from 3 to 15 carbon atoms, e.g. carbomethoxymethyl, carbethoxymethyl, carbethoxyethyl, carbobutoxymethyl, carbobutoxyethyl, etc., carbolauryloxymethyl, etc., carbalkoxyphenyl, preferably having from 8 to 19 carbon atoms, e.g. carbomethoxyphenyl, carbobutoxyphenyl, carbolauryloxyphenyl, etc., and

R_3 represents alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, dibutylmethylhydroxyphenyl, etc., or hydroxyphenyl, or phenylhydroxyphenyl.

Another especially useful subclass of stabilizers of the Formula I comprises the dioxy-substituted triazines of the Formula I(*b*):



I(*b*)

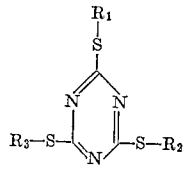
wherein

R_1 and R_2 each independently represents phenyl, alkyl especially alkylphenyl having from 7 to 24 carbon atoms, e.g. methylphenyl, ethylphenyl, propylphenyl, butylphenyl, octylphenyl, dodecylphenyl, octadecylphenyl, dimethylphenyl, dibutylphenyl, dioctylphenyl, methyldibutylphenyl, etc., or an aliphatic hydrocarbon radical, preferably alkyl having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, pentyl, octyl, dodecyl, octadecyl, etc.; and

R_3 represents alkylhydroxyphenyl having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl propylhydroxyphenyl, butylhydroxyphenyl, oc-

tylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, methyldibutylhydroxyphenyl etc.

A further valuable subclass of stabilizers of the Formula I comprises triazines of the Formula I(*c*):



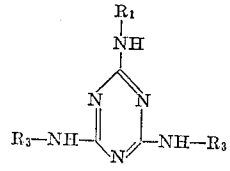
I(*c*)

Wherein

R_1 and R_2 each independently represents alkylhydroxybenzyl, preferably having from 8 to 25 carbon atoms, e.g. methylhydroxybenzyl, ethylhydroxybenzyl, propylhydroxybenzyl, butylhydroxybenzyl, octylhydroxybenzyl, dimethylhydroxybenzyl, dibutylhydroxybenzyl, octadecylhydroxybenzyl, etc., or an aliphatic hydrocarbon radical, preferably alkyl having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, pentyl, octyl, dodecyl, octadecyl, etc.; and

R_3 represents alkylhydroxyphenyl having from 7 to 24 carbon atoms e.g. methylhydroxyphenyl, ethylhydroxyphenyl, dimethylhydroxyphenyl, butylhydroxyphenyl, dibutylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenly, etc., or alkylhydroxybenzyl having from 8 to 25 carbon atoms, e.g. methylhydroxybenzyl, ethylhydroxybenzyl, propylhydroxybenzyl, butylhydroxybenzyl, octylhydroxybenzyl, dimethylhydroxybenzyl, dibutylhydroxybenzyl, octadecylhydroxybenz, dioctylhydroxybenzyl, etc.

Another valuable subclass of stabilizers of the Formula I comprises the triamino-substituted triazines of the Formula I(*d*):



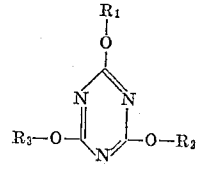
I(*d*)

wherein

R_1 and R_2 each independently represents phenyl and alkyl, preferably alkyl having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, etc.; and

R_3 represents alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, methylbutylhydroxyphenyl, etc.

Still another valuable subclass of stabilizers of the Formula I comprises triazines of the Formula I(*e*):



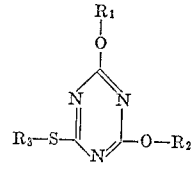
I(*e*)

wherein

R_1 and R_2 each independently represents phenyl or alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, methyldibutylhydroxyphenyl, etc.; and

R_3 represents alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, methyldibutylhydroxyphenyl, etc.

Still another valuable subclass of stabilizers of the Formula I comprises the dioxy-substituted triazines of the Formula I(*f*):



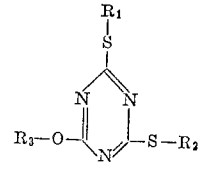
I(*f*)

wherein

R_1 and R_2 each independently represents alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, methylbutylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, methyldibutylhydroxyphenyl, etc.; and

R_3 represents alkyl, preferably having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, etc.

A further especially useful subclass of stabilizers comprises dithio-substituted triazine compounds of the Formula I(*g*):



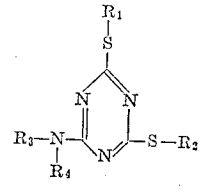
I(*g*)

wherein

R_1 and R_2 each independently represents an alkyl group, preferably having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, etc., or alkylmercaptoalkyl, preferably having from 2 to 10 carbon atoms, e.g., methylthiomethyl, methylthioethyl, butylthioethyl, octylthioethyl, etc; and

R_3 represents hydroxyphenyl or alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, dibutylhydroxyphenyl, octylhydroxyphenyl, octadecylhydroxyphenyl, methyldibutylhydroxyphenyl, etc.

Still further, another valuable class of stabilizers comprises triazine compounds of the Formula I(*h*):



I(*h*)

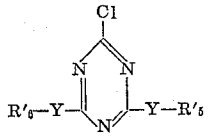
wherein

R_1 and R_2 each independently represents an aliphatic hydrocarbon radical, preferably alkyl having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, etc.,

R_3 represents hydroxyphenyl or alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, methyldibutylhydroxyphenyl, etc., and

R_4 represents benzyl or lower alkyl, e.g. methyl, ethyl, propyl, butyl, pentyl, hexyl, etc.

In another aspect of the invention, the novel monohalogen substituted triazines, particularly the monochloro substituted triazines of the formula:



II

wherein

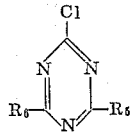
R'_5 represents substituted hydroxyphenyl, such as alkylhydroxyphenyl, especially having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, etc., or an aliphatic hydrocarbon radical, preferably alkyl having from 1 to 18 carbon atoms,

R'_6 represents hydroxyphenyl or substituted hydroxyphenyl, preferably alkylhydroxyphenyl having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, etc.; and

X and Y each independent represents —S—, —O— or —NR_4—, wherein R_4 is aralkyl, preferably benzyl, alkyl, preferably lower alkyl, or hydrogen,

are useful in stabilizing compositions of organic materials, such as e.g. polypropylene compositions, etc.

A particularly preferred stabilizer of Type II is constituted by a compound of the formula:



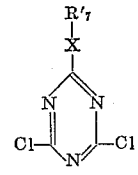
II(a)

wherein

R_5 represents substituted hydroxyphenylamino, such as alkylhydroxyphenylamino, especially having from 7 to 24 carbon atoms, e.g. methylhydroxyphenylamino, ethylhydroxyphenylamino, propylhydroxyphenylamino, butylhydroxyphenylamino, octylhydroxyphenylamino, octadecylhydroxyphenylamino, dimethylhydroxyphenylamino, dibutylhydroxyphenylamino, etc., or aliphatic hydrocarbon radical substituted mercapto, preferably alkylmercapto having from 1 to 18 carbon atoms, e.g. methylmercapto, ethylmercapto, propylmercapto, butylmercapto, octylmercapto, dodecylmercapto, octadecylmercapto, etc.; and

R_6 represents substituted hydroxyphenylamino, preferably alkylhydroxyphenylamino having from 7 to 24 carbon atoms, e.g. methylhydroxyphenylamino, ethylhydroxyphenylamino, propylhydroxyphenylamino, butylhydroxyphenylamino, octylhydroxyphenylamino, octadecylhydroxyphenylamino, dimethylhydroxyphenylamino, dibutylhydroxyphenylamino, etc.

In a further aspect of the invention, dihalogen-substituted triazines, particularly the dichloro-substituted triazines of the formula:



III

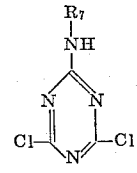
wherein

R'_7 represents substituted hydroxyaryl, preferably alkylhydroxylphenyl having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, etc.; and

X represents —S—, —O— or —NR_4—, wherein R_4 represents hydrogen, alkyl, preferably lower alkyl or aralkyl, preferably benzyl,

are useful for stabilizing compositions of organic materials, such as e.g. polypropylene, etc.

A particularly preferred stabilizer of Type III is constituted by a compound of the formula:

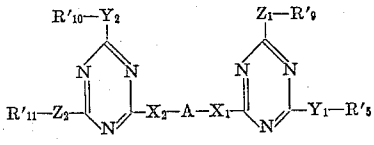


III(a)

wherein

R_7 represents alkylhydroxyphenyl having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, etc.

In still another aspect of the invention, bis-substituted triazines, particularly compounds of the formula:



IV

wherein

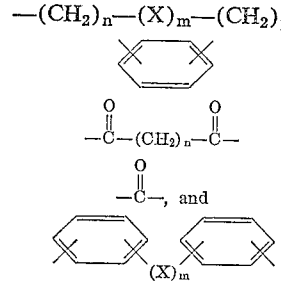
R'_8, R'_9, R'_{10} and R'_{11} each independently represents alkyl, preferably alkyl having from 1 to 18 carbon atoms, cycloalkyl having from 5 to 6 carbon atoms, aryl, preferably phenyl, substituted aryl, preferably hydroxyphenyl, alkylphenyl, preferably having from 7 to 24 carbon atoms, alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, alkylhydroxybenzyl, preferably having from 8 to 15 carbon atoms, cyanoalkyl, preferably cyano-lower alkyl, alkylmercaptoalkyl, preferably having from 2 to 10 carbon atoms, carbalkoxyalkyl, preferably having from 4 to 16 carbon atoms, carbalkoxyaryl, preferably carbalkoxyphenyl having from 8 to 19 carbon atoms,

X_1, X_2, Y_1, Y_2, Z_1 and Z_2 each independently represents —S—, —O— or —NR_4—,

wherein

R_4 is aralkyl, e.g. benzyl, alkyl, e.g. lower alkyl or hydrogen, and

A represents

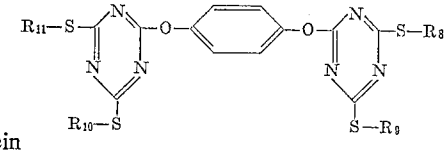


wherein

n is 0, 1, 2, 3, 4, 5 or 6,
m is 0 or 1,
p is 0, 1, 2, 3, 4, 5 or 6, and
X has the same definition as X_1 hereinabove,

are useful for stabilizing organic materials, such as e.g. polypropylene, etc.

A particularly preferred stabilizer of Type IV is constituted by a compound of the formula:

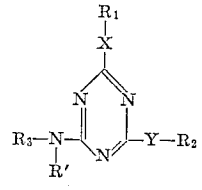


IV(*a*)

wherein

R_8, R_9, R_{10} and R_{11} each independently represents an alkyl group having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, etc.

In a further aspect of the invention, organic material, e.g. polypropylene, is stabilized with compounds of the formula:



V

wherein

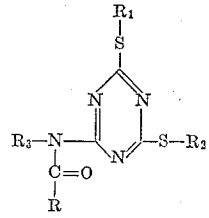
R_1 and R_2 each independently represents alkyl having from 1 to 18 carbon atoms, e.g. methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, etc.;

R_3 represents alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, dibutylmethylhydroxyphenyl, etc.;

R′ is alkanoyl, preferably having from 1 to 12 carbon atoms; and

X and Y each independently represents —S—, —O— or —NR_4—, wherein R_4 is aralkyl, preferably benzyl, alkyl, preferably lower alkyl, or hydrogen.

In this further aspect of the invention, organic materials, e.g. polypropylene, are stabilized preferably with compounds of the general Formula V(*a*):



V(*a*)

wherein

R_1 and R_2 each independently represents alkyl having

from 1 to 18 carbon atoms, e.g., methyl, ethyl, propyl, butyl, octyl, dodecyl, octadecyl, etc.;

R_3 represents alkylhydroxyphenyl, preferably having from 7 to 24 carbon atoms, e.g. methylhydroxyphenyl, ethylhydroxyphenyl, propylhydroxyphenyl, butylhydroxyphenyl, octylhydroxyphenyl, dodecylhydroxyphenyl, octadecylhydroxyphenyl, dimethylhydroxyphenyl, dibutylhydroxyphenyl, dioctylhydroxyphenyl, dibutylmethylhydroxyphenyl, etc.; and

R is an alkyl radical, preferably having from 1 to 11 carbon atoms, e.g. methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, nonyl, decyl, undecyl, etc.

In this specification, the term "lower" signifies a group having from 1 to 6 carbon atoms, and "aryl" embraces within its meaning not merely carbocyclic, e.g. phenyl, naphthyl, etc., but also heterocyclic radicals, e.g. pyridyl, thiazolyl, etc.

Up to the present time, the use of the substituted triazines of the invention in stabilizing polymeric material, e.g. polypropylene, has not been known. It has now surprisingly been found that other organic materials are stabilized, e.g. against oxidative deterioration, by incorporating therein effective quantities of one of the substituted triazines defined according to the present invention hereinabove.

Accordingly, it is a prime object of the invention to provide stable organic material, preferably stable polymeric material, e.g. polypropylene. In this specification it is understood that polymeric material means polyolefins, such as polyethylene, etc. Preferably, the polyolefins are of high molecular weight, e.g. above 1000 into the hundreds of thousands range. The polyethylenes and polypropylenes may be of high density, medium density or low density class. The preferred polymeric material for stabilization is polypropylene.

Polymeric materials, such as the foregoing, find use as thermoplastic molding or coating agents. Moreover, because of their high dielectric strength and their resistance to water, they are particularly useful as insulators or dielectrics in condensers and other such equipment. It is known that these polyolefins, e.g. polyethylene and polypropylene, are attacked by oxygen, particularly when exposed to the atmosphere and at elevated temperatures. For example, during use or manufacture the desirable properties of the polyolefins may be impaired due to oxidative deterioration. Such degradation causes loss in dielectric properties, discoloration, embrittlement, gelation, etc.

Not only homopolymeric material, but also copolymers and physical mixtures thereof are stabilized according to the present invention. For example, high impact polystyrene containing copolymers of butadiene and styrene is stabilized according to the invention.

The invention is also particularly useful in stabilizing lubricating oils of various types including aliphatic esters, such as for example dihexyl azelate, di-(2-ethylhexyl) azelate, di(3,5,5-trimethylhexyl)glutarate, di-(3,5,5-trimethylpentyl)-glutarate, di-(2-ethylhexyl)pimelate, di-(2-ethylhexyl)adipate, diisoamyl adipate, triamyl tricarballylate, pentaerythritol tetracaproate, dipropylene glycol dipelargonate, 1,5-pentanediol-di-(2-ethylhexanoate), etc.

The present invention also relates to the stabilizing of fatty materials including oils of animal and vegetable origin which tend to deteriorate on standing and exposure to atmospheric oxygen. Among the edible fats and oils within the scope of the present invention are: linseed oil, menhaden oil, cod liver oil, castor oil, olive oil, rapeseed oil, coconut oil, palm oil, corn oil, sesame oil, peanut oil, cotton seed oil, butter, fat, lard, beef tallow, etc. Other oils and fats which deteriorate on standing and exposure to oxygen in the air or oxygen at elevated temperatures, are all within the scope of the invention.

Within the scope of the invention, also, are saturated and unsaturated hydrocarbons which tend to deteriorate

on storage, such as for example, gasolines, both natural and synthetic, in particular, saturated and unsaturated gasolines, etc., jet fuel, diesel oil, mineral oil, fuel oil, drying oil, waxes, resins, etc. Such hydrocarbons are protected against gum formation, discoloration and other deterioration with the stabilizers of the present invention.

It is, therefore, an object of the present invention to provide novel substituted triazine compounds which are versatile and effective stabilizers in at least a single class of the foregoing organic materials which are normally subject to deterioration caused by exposure to light and/or heat and/or oxygen, etc.

A particularly preferred stabilizer of the invention is 6 - (4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine which is especially useful in stabilizing polyolefinic material, e.g. polypropylene and polyethylene, as well as other polymeric material, e.g. polystyrene, in particular "high impact" polystyrene. This triazine is also an effective stabilizer for other relatively unstable organic material, e.g. hydrocarbon oil of mineral origin, in particular mineral oil; gasoline, both natural and synthetic; oils of animal origin, in particular, lard; oils of vegetable origin, in particular, cotton seed oil; high temperature lubricating oils, e.g. diesters of fatty acids, in particular, diesters of fatty acids having from 5 to 15 carbon atoms per molecule. Further organic materials which are effectively stabilized by this triazine comprise: aldehydes, e.g. aliphatic, such as heptaldehydes.

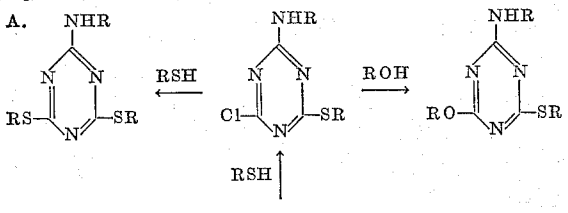
It is a prime object of the invention, therefore, to provide a method for stabilizing organic material, such as described hereinabove, by incorporating in said organic material a stabilizing amount of a triazine compound according to the invention.

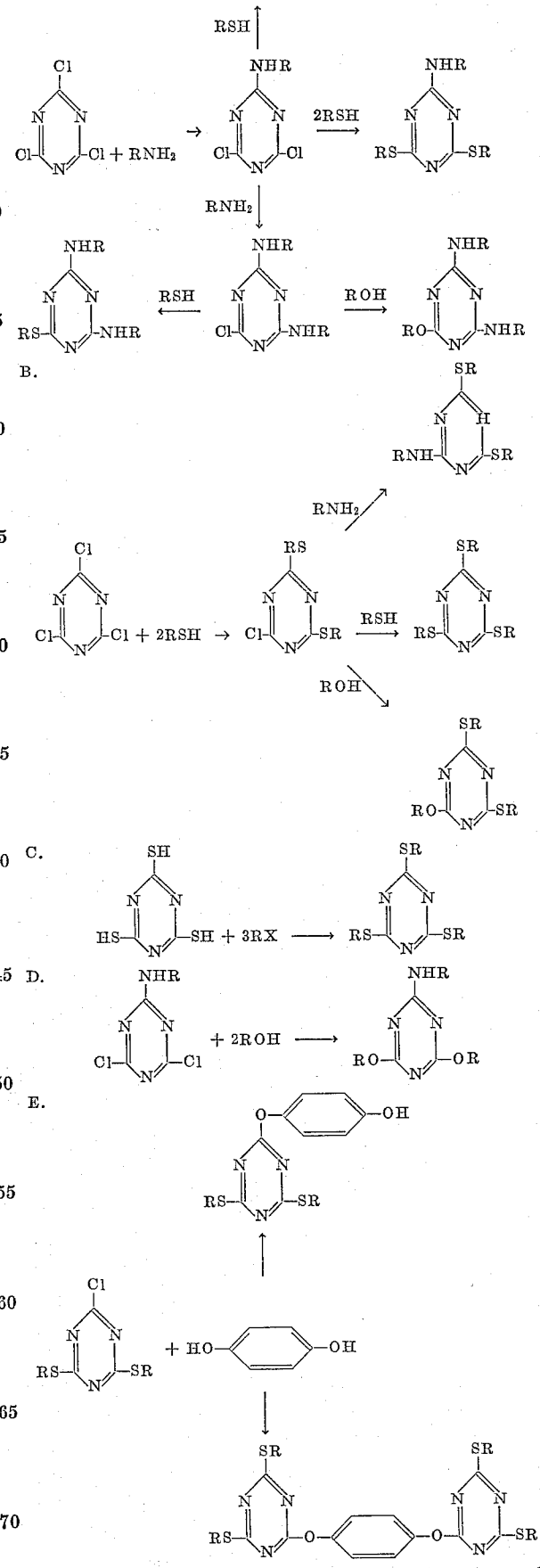
It is understood that the stabilizers of the invention are not necessarily of equivalent potency. The specific stabilizer most useful to a given unstable material will depend upon several factors for its advantages. Availability and cost of raw materials for the manufacture of the stabilizer and effective inhibitory action of the stabilizer, including duration and degree of activity, are among the factors which control the choice of a specific stabilizer for a specific substrate which is normally subject to deterioration. Toxicity, color, stability to light and/or heat and solubility are also important factors. For example, a preferred stabilized composition according to the invention comprises from about 0.001% to about 5% by weight of 6 - (4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine and polypropylene.

The compounds of this invention may be used also to stabilized organic material in combination with other additive agents, such as for example, antioxidants, pourpoint depressants, corrosion and rust inhibitors, dispersing agents, demulsifiers, antifoaming agents, carbon black, accelerators and other chemicals used in rubber compounding, plasticizers, color stabilizers, heat stabilizers, UV absorbers, dyes and pigments, etc.

Compounds of the Formulae II and III are also useful as intermediates in the synthesis of valuable di- and trisubstituted triazines which are themselves useful as stabilizers.

The compounds of the present invention are advantageously prepared, for example, according to the following reactions, wherein R represents the same or different radical as defined hereinbelow (the said R radicals corresponding to the previously mentioned R_1, R_2 R_3, etc.):





In the foregoing scheme of reactions, it is understood that, while cyanuric chloride is a preferred starting material, other triazine compounds having reactive groups

other than halogen may be used. Likewise, any combination of the methods outlined in A, B, C, D, and E may be employed to attain the desired variant compound within the scope of the invention.

In the foregoing scheme also, the "H" of ROH and RSH may be replaced by a suitable reactive group or atom, as e.g. an alkali metal, such as sodium, potassium, etc., or the ammonium radical. In the case of the imino group, hydrogen may be replaced by alkyl, benzyl, etc. Also, X represents halogen, e.g., chlorine.

For reaction with a suitable triazine, the amines, mercaptans and halides of the formulae RNH_2, RSH and RX are useful. The halide may be any suitable halide, as e.g. a fluoride, iodide, bromide, and, preferably, a chloride. The R group is advantageously an alkyl group having from 1 to 18 carbon atoms, e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, and octadecyl. R is also advantageously a cycloalkyl group, e.g., cyclopentyl and cyclohexyl. In other aspects R is aryl, e.g., phenyl, hydroxyaryl, e.g. hydroxyphenyl, alkylaryl, e.g., alkylphenyl having from 7 to 24 carbon atoms, such as tolyl, ethylphenyl, propylphenyl, butylphenyl, octylphenyl, octadecylphenyl, etc.; alkylhydroxyaryl, e.g., alkylhydroxyphenyl, such as methylhydroxyphenyl, dimethylhydroxyphenyl, trimethylhydroxyphenyl, tetramethylhydroxyphenyl, ethylhydroxyphenyl, diethylhydroxyphenyl, triethylhydroxyphenyl, tetraethylhydroxyphenyl, propylhydroxyphenyl, dipropylhydroxyphenyl, butylhydroxyphenyl, dibutylhydroxyphenyl, octylhydroxyphenyl, dioctylhydroxyphenyl, octadecylhydroxyphenyl, etc.

Another useful class of R groups comprises the alkylthioalkyls, such as methylthiomethyl, methylthioethyl, methylthiopropyl, methylthiobutyl, methylthiopentyl, etc. also ethylthiopentyl, etc., propylthiomethyl, propylthioethyl, propylthiopropyl, propylthiobutyl, propylthiopentyl, etc., butylthiomethyl, butylthioethyl, butylthiopropyl, butylthiobutyl, butylthiopentyl, etc., pentylthiomethyl, pentylthioethyl, pentylthiopropyl, etc., hexylthiomethyl, hexylthioethyl, hexylthiopropyl, etc., heptylthiomethyl, heptylthioethyl, heptylthiopropyl, octylthiomethyl, octylthioethyl, etc.

Other useful R groups comprise benzyl, hydroxybenzyl and alkylhydroxybenzyl, e.g. methylhydroxybenzyl, ethylhydroxybenzyl, propylhydroxybenzyl, butylhydroxybenzyl, octylhydroxybenzyl, etc.; cyanoalkyl, e.g. cyanomethyl, cyanoethyl, cyanopropyl, cyanobutyl, cyanopentyl, cyanohexyl, etc.; carbalkoxyalkyl, e.g., carbomethoxymethyl, carbethoxyethyl, carbopropoxyethyl, carbododecanoxyethyl, etc.; carbalkoxyphenyl, e.g., carbomethoxyphenyl, carbethoxyphenyl, carbopropoxyphenyl, carbododecanoxyphenyl, etc.

Compounds of the Formula V are conveniently prepared by acylation, e.g., with acetic anhydride or acetyl chloride, etc.

The following examples are illustrative of the invention, but by no means is the invention limited thereto. In all examples parts are by weight unless otherwise noted, and the relationship between parts by weight and parts by volume is as that of grams to cubic centimeters. The temperature is in degrees centigrade.

EXAMPLE 1

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

(*a*) *4-nitroso-2,6-di-t-butylphenol.*—750 parts by volume of ethanol, cooled to 15°, are saturated with hydrogen chloride gas and then diluted by the addition of 4000 parts by volume of ethanol. 2,6-di-t-butylphenol (824 parts) is dissolved in the alcoholic solution and a solution of sodium nitrite (304 parts in 400 parts by volume of water) is added at 15–20° over a period of one hour while stirring. Stirring is continued for another 2 hours while allowing the temperature to rise to room temperature. 2000 parts by volume of water are added and the product is then separated by filtration and washed well with water. The filter cake is slurried in 3000 parts by volume of petroleum ether, filtered, washed on the filter with 1000 parts by volume of petroleum ether and dried in a vacuum oven at 70–80°. The yield of 4-nitroso-2,6-di-t-butylphenol, melting at 219°, is 848 parts (90.2%).

(*b*) *4-amino-2,6-di-t-butylphenol.*—4-nitroso - 2,6 - di-t-butylphenol (176 parts) is dissolved in 600 parts by volume of 5 N sodium hydroxide and 1200 parts by volume of water, and a solution of sodium hydrosulfite (522 parts) in 2200 parts by volume of water is added with moderate speed (about 30 minutes), during which time the temperature rises to 53°. After the addition is completed, stirring is continued for 2½ hours after which the product is filtered rapidly, washed with 4000 parts by volume of water and dried in a vacuum desiccator over phosphoric anhydride. The yield of 4-amino-2,6-di-t-butylphenol, melting at 105–108° is 162.3 parts (98.5%).

(*c*) *6-(4-hydroxy-3,5-di-t-butylanilino)-2,4 - dichloro-1,3,5-triazine.*—A solution of cyanuric chloride (18.4 parts) in boiling acetone (100 parts by volume) is poured in a thin stream while stirring into 200 parts by volume of ice-water, keeping the temperature at 0–5° with external cooling. 4-amino-2,6-di-t-butylphenol (22.1 parts) and sodium carbonate (5.3 parts) are added and the reaction mixture is stirred vigorously at 8–10° for 45 minutes. The mixture is then diluted by the addition of 100 parts by volume of acetone and stirring is continued for an additional hour at 8–10°. The suspension is then poured into 500 parts by volume of ice-water, the precipitate is filtered off and dried in vacuo. The yield of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5 - triazine is 34.8 parts (94%). The product melts at 144°.

(*d*) *6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - bis - (n-octylthio)-1,3,5-triazine.*—An alcoholic solution of sodium n-octylmercaptide (prepared by dissolving 2.3 parts of sodium in 50 parts by volume of ethanol and adding 14.6 parts of n-octylmercaptan) is added rapidly with stirring to a solution of 18.5 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine in 150 parts by volume of ethanol. The reaction mixture is stirred and refluxed for 1½ hours. After cooling to room temperature, 500 parts by volume of water are added. The precipitated product is separated by filtration and washed well with water. Purification of the product is accomplished by dissolving in 300 parts by volume of boiling ethanol, adding activated carbon, filtering and slowly recrystallizing. The 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, which crystallizes as white needles, is filtered off, washed with cold ethanol and is dried in vacuo yielding 10.6 parts melting at 92–95°. Additional 8.6 parts having the same melting point are obtained by concentration of the mother liquor. The total yield is 65.5% of the theoretical yield.

By replacing n-octylmercaptan by ethylmercaptan, cyclohexylmercaptan, n-octadecylmercaptan, tertiary-butylmercaptan and p-tertiary-butyl-thiophenol respectively, the following compounds are obtained:

6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - bis-(ethylthio)-1,3,5-triazine, M.P. 89–90° (recryst. from petroleum ether)

6-(4-hydroxy - 3,5 - di-t-butylanilino)-2,4-bis-(cyclohexylthio)-1,3,5-trazine, M.P. 171–172° (recryst. from methanol)

6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - bis-(n-octadecylthio)-1,3,5-triazine, M.P. 86–88° (recryst. from ethanol and petroleum ether)

6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(t - butylthio)-1,3,5-triazine, M.P. 169–170° (recryst. from benzene and heptane)

6-(4-hydroxy - 3,5 - di-t-butylanilino) - 2,4 - bis-p-t-butylphenylthio)-1,3,5-triazine, M.P. 87°

EXAMPLE 2

4,6-Bis-(4-Hydroxy-3,5-Di-t-Butylanilino)-2-n-Octylthio-1,3,5-Triazine

(a) *4,6-bis-(4-hydroxy-3,5-di-t-butylanilino)-2-chloro-1,3,5-triazine.*—A solution of 4.6 parts of cyanuric chloride in 100 parts by volume of boiling acetone is poured in a thin stream into 200 parts by volume of ice-water while stirring and keeping the temperature at 0–5° by means of external cooling of the mixture. 4-amino-2,6-di-t-butylphenol (16.7 parts) and sodium bicarbonate (6.3 parts) are then added and the temperature is maintained at 10° for 45 minutes while vigorously stirring; then the temperature is kept at 50° for 45 minutes, and finally at reflux for 45 minutes. The brown solid which precipitates is filtered off, washed well with water and petroleum ether and is finally recrystallized from dioxane-hexane (5:4). The product 4,6-bis(4-hydroxy-3,5-di-t-butylanilino)-2-chloro-1,3,5-triazine weighs 5.05 parts (37%) and melts under decomposition at 304°.

(b) *4,6 - bis-(4-hydroxy-3,5-di-t-butylanilino)-2-octylthio-1,3,5-triazine.*—An alcoholic solution of sodium n-octylmercaptide (prepared by dissolving 0.172 parts of sodium in 10 parts by volume of ethanol and adding 1.09 parts of n-octylmercaptan) is added to a suspension of 4.15 parts of 2,4-bis-(4-hydroxy-3,5-di-t-butylanilino)-6-chloro-1,3,5-triazine in 125 parts by volume of ethanol and the mixture is refluxed for 1 hour. The alcoholic solution is filtered hot to remove 1.2 parts of insoluble material and then flooded with 500 parts by volume of water. The solid, precipitated product is filtered off, washed with dilute NaOH and water and finally dried in vacuo. The 4,6-bis-(3,5-di-t-butyl-4-hydroxyanilino)-2-octylthio-1,3,5-triazine weights 3.1 parts (62%) and melts at 55°.

EXAMPLE 3

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(Phenylthio)-1,3,5-Triazine

A mixture of 11.1 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine [preparation described in Example 1 (*a*) through (*c*)], 6.6 parts of thiophenol and 4.74 parts of pyridine in 100 parts by volume of acetone is stirred at room temperature for 30 minutes, after which the reaction mixture is stirred and refluxed for 1½ hours. After being cooled to room temperature, the pyridine hydrochloride is filtered off and the filtrate is flooded with water, causing the formation of a gummy precipitate. The supernatant liquid is decanted and the resulting viscous mass is boiled with ethanol (100 parts by volume). On cooling, 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(phenylthio)-1,3,5-triazine separates in the form of yellow crystals. The product is filtered, washed with ethanol and dried in vacuo, yielding 10.5 parts which melt at 169–170°. A second crop of 0.5 parts is obtained by chilling the mother liquor. The total actual yield is 71.4% of the theoretical yield.

If, in the foregoing Example 3, 12.8 parts of 6-(4-hydroxyanilino)-2,4-dichloro-1,3,5-triazine are reacted in an analogous manner with 11 parts of thiophenol, dissolved in 150 parts by volume of acetone, together with 7.9 parts of pyridine, dissolved in 25 parts by volume of acetone, then there are obtained 15.33 parts (76%) of 6-(4-hydroxyanilino)-2,4-bis-(phenylthio)-1,3,5-triazine, whose melting point is 72–78°. The method of Example 3 is also modified in that, after flooding with water, the gummy precipitate, upon trituration with water and standing, solidifies. This solid is purified by redissolving in base and subsequently treating with activated carbon. The purified solution, after filtration, is neutralized with dilute hydrogen chloride, and the precipitate which forms is the desired 6-(4-hydroxyanilino)-2,4-bis-(phenylthio)-1,3,5-triazine.

The starting compound 6-(4-hydroxyanilino)-2,4-dichloro-1,3,5-triazine is prepared by reacting cyanuric chloride with 4-aminophenol in a manner analogous to the preparation described in Example 1 (*c*).

EXAMPLE 4

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-4-n-Octylthio-2-Chloro-1,3,5-Triazine

An alcoholic solution of sodium n-octylmercaptide (prepared by dissolving 0.23 part of sodium in 10 parts by volume of ethanol and adding 1.46 parts of n-octylmercaptan) is added rapidly to a slurry of 3.69 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine [preparation described in Example 1, (*a*) through (*c*)] in 10 parts by volume of ethanol. An immediate exothermic reaction ensues, but external cooling is applied and the reaction mixture is kept at room temperature for ½ hour, after which said mixture is poured into 50 parts by volume of water and an oil separates which solidifies upon cooling. The 6-(4-hydroxy-3,5-di-t-butylanilino)-4-n-octylthio-2-chloro - 1,3,5 - triazine, thus obtained, is filtered, washed with water until free of chloride ion, and finally recrystallized twice from hexane. The purified compound weighs 2.04 parts (42.5%) and melts at 119–120°.

EXAMPLE 5

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(Anilino)-1,3,5-Triazine

A cold (—5°) solution of 14.75 parts of 6-(4-hydroxy - 3,5 - di - t - butylanilino) - 2,4 - dichloro - 1,3,5-triazine [preparation described in Example 1, (*a*) through (*c*)] and 7.6 parts of aniline in 100 parts by volume of acetone is allowed to slowly warm up to 25° while maintaining the pH between 7 and 8 by the addition of 5 N sodium hydroxide. When the pH remains constant, 200 parts by volume of water are added and the reaction mixture is heated to boiling, allowing the acetone to distil off, while keeping the pH between 7 and 8 by the addition of 5 N sodium hydroxide. After the theoretical amount of alkali has been added the pH remains at 7 and refluxing is continued for an additional 45 minutes. The solid obtained is filtered off from the hot suspension, washed copiously with water, air dried and finally triturated with hexane. In this manner 17.8 parts (92.5%) of 6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis-(anilino)-1,3,5-triazine is obtained in the form of a white solid. The product melts at 192–194°. Purification is accomplished by recrystallization from isopropyl alcohol. The melting point remains the same.

EXAMPLE 6

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(n-Octylamino)-1,3,5-Triazine

12.9 parts of n-octylamine, 18.5 parts of 6-(4-hydroxy-3,5 - di - t - butylanilino) - 2,4 - dichloro - 1,3,5 - triazine [preparation described in Example 1 (*a*) through (*c*)] and 5.3 parts of sodium carbonate are added to 200 parts by volume of water and the mixture is heated at reflux for ½ hour. Methyl cellosolve (200 parts by volume) is then added and reflux is continued for an additional 6 hours. 300 parts by volume of water are added and on standing the oily layer which separates becomes a thick resinous mass. 100 parts by volume of 5 N hydrochloric acid are added and the product is extracted into ether. The resultant ether solution is washed with water, dilute sodium hydroxide and again with water; it is then dried over anhydrous sodium sulfate, filtered and the ether is removed by evaporation. The 6-(4-hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis - (n - octylamino)-1,3,5-triazine so obtained, melts at 42–45°. The yield is 9.0 parts (32.6%).

EXAMPLE 7

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(Phenoxy)-1,3,5-Triazine

A solution of 7.36 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine [preparation described in Example 1 (*a*) through (*c*)] in 50 parts by volume of ethanol is added while stirring to an alcoholic solution of sodium phenoxide (prepared by dissolving 0.92 part of sodium in 25 parts by volume of ethanol and adding 3.76 parts of phenol). After the exothermic reaction has subsided, the reaction mixture is refluxed for 2 hours. The sodium chloride is removed by filtration and the filtrate is flooded with water giving a gummy yellow solid which on trituration with petroleum ether gives a white solid weighing 6.6 parts. After recrystallization from methanol-water (5:1) the 6-(4-hydroxy-3,5 - di - t - butylanilino) - 2,4 - bis - (phenoxy) - 1,3,5-triazine weighs 4.3 parts and melts at 160–161°.

EXAMPLE 8

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(Ethoxy)-1,3,5-Triazine

A solution of 10 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine [preparation described in Example 1, (*a*) through (*c*)] in 25 parts by volume of ethanol is added rapidly with stirring to a solution of 1.24 parts of sodium in 50 parts by volume of ethanol. The reaction mixture is stirred and refluxed for 1 hour after which the sodium chloride salt is removed by filtration and the filtrate purified with active carbon, filtered and flooded with water. The oil which is separated is extracted into ether, dried over anhydrous magnesium sulfate and finally, the ether is removed by evaporation. When the last traces of solvent are removed under high vacuum, the resinous oil 6-(4-hydroxy-3,5 - di - t - butylanilino) - 2,4 - bis - (ethoxy) - 1,3,5-triazine becomes an amorphous solid weighing 6.9 parts (66%) and melting at 54°.

EXAMPLE 9

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(n-Octyloxy)-1,3,5-Triazine

10 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine [preparation described in Example 1, (*a*) through (*c*)] are added to a solution of 1.24 parts of sodium in 50 parts by volume of n-octyl alcohol while stirring. An exothermic reaction ensues and the temperature is not allowed to rise above 60°. Stirring is continued at 60° for 15 minutes and then the excess octyl alcohol is removed by distillation under high vacuum with a maximum bath temperature of 95°. The product obtained is a resinous oil weighing 10.2 parts. Purification is accomplished by dissolving the product in hexane and by placing the same on a silica gel column, afterwards eluting first with hexane-benzene (1:1) and then with benzene. The 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octyloxy)-1,3,5-triazine, a resinous oil, is recovered from the benzene eluate.

Analysis.—Calculated for $C_{33}H_{56}O_3N_4$: C, 71.19%; H, 10.14%; N, 10.05%. Found: C, 71.13%; H, 10.12%; N, 10.07%.

EXAMPLE 10

2,4,6-Tris-(4-Hydroxy-3,5-Di-t-Butylbenzylthio)-1,3,5-Triazine

(*a*) *4-hydroxy-3,5-di-t-butylbenzyl chloride.*—A mixture of 103 parts of 2,6-di-t-butylphenol and 100 parts by volume of 37% formalin is stirred at 30° and 100 parts of anhydrous zinc chloride are added portionwise during 5 minutes, while keeping the temperature below 30°. Dry hydrogen chloride is then passed through the mixture rapidly in a stream while stirring and maintaining the temperature at 30–35° with external cooling. After about 1½ hours, the reaction ceases. The oily layer is separated and taken up in ether, washed well with water, with 10% sodium bicarbonate and again with water. The resultant ether solution is dried over anhydrous magnesium sulfate. The magnesium sulfate is then filtered off and the ether is removed by distillation. The residue is vacuum distilled. The 4-hydroxy-3,5-di-t-butylbenzyl chloride so obtained boils at 118° under 0.1 mm. Hg and weighs 65.25 parts (51.5%).

Analysis.—Calculated for $C_{15}H_{23}OCl$: C, 70.1%; H, 9.1%. Found: C, 70.64%; H, 8.90%.

(*b*) *2,4,6 - tris - (4 - hydroxy-3,5-di-t-butylbenzylthio)-1,3,5-triazine.*—A solution of 10.2 parts of 4-hydroxy-3,5-di-t-butylbenzyl chloride in 25 parts by volume of ethanol is added while stirring to an alcoholic solution of trisodium trithiocyanurate (prepared by dissolving 0.92 part of sodium in 25 parts by volume of ethanol and adding 2 parts of trithiocyanuric acid. After the exothermic reaction has subsided, the mixture is heated to boiling on a steam bath, and then allowed to cool. Finally the sodium chloride salt is filtered off and the filtrate is flooded with water after which the oily layer is extracted into ether, dried and the ether is removed by distillation, the residue being recrystallized from methanol-water. The 2,4,6-tris- (4-hydroxy-3,5-di-t-butylbenzylthio) - 1,3,5 - triazine, so obtained, weighs 1.45 parts (15.4%) and melts at 96–98°.

EXAMPLE 11

6-(2-Hydroxy-3-t-Butyl-5-Methylanilino)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

(*a*) *2,4-bis-(n-octylthio)-6-chloro-1,3,5-triazine.*—A solution of 36.8 parts of cyanuric chloride, 58.4 parts of n-octylmercaptan and 0.3 part by volume of pyridine in 100 parts by volume of xylene is refluxed for 6 hours while passing nitrogen through the reactants, until the evolution of hydrogen chloride has ceased. The solution is filtered from a small amount of insoluble material and the solvent is stripped off with a water pump and finally the residue is vacuum distilled. The 2,4-bis-(n-octylthio)-6-chloro-1,3,5-triazine, weighing 43 parts (53.5%), distills at 206–208° under 0.075 mm. Hg.

(*b*) *6 - (2-hydroxy-3-t-butyl-5-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine.*—A mixture of 10.1 parts of 6-chloro-2,4-bis-(n-octylthio)-1,3,5-triazine, 4.7 parts of 2-amino-4-methyl-6-t-butylphenol [Albert, H. E., J. Am. Chem. Soc. 76, 4985 (1954)] and 100 parts by volume of water is gradually warmed with stirring under a nitrogen atmosphere to 70° and at the same time the pH is maintained at 7–8 by the addition of 5N sodium hydroxide. When the pH remains constant, the oily layer is extracted with ether, the extract is dried over anhydrous magnesium sulfate. The magnesium sulfate is then filtered off and the ether is removed by evaporation. The residue weighs 11.6 parts. Purification is effected by dissolving the crude 6-(2 - hydroxy - 3 - t-butyl-5-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine in petroleum ether and placing the mixture on a silica gel chromatographic column and afterward eluting with benzene. After removal of the benzene, the compound, a resinous oil, weighs 8.2 parts (60%).

Analysis.—Calculated for $C_{30}H_{50}N_4S_2O$: C, 65.91%; H, 9.22%; N, 10.24%. Found: C, 66.06%; H, 9.24%; N, 10.45%.

In a similar manner, 6-(4-hydroxy - 3,5 - di - isopropylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine is prepared by substituting 4-amino-2,6-di-isopropylphenol [prepared by the method described for the preparation of 4-amino-2,6-di-t-butylphenol in Example 1, (*a*) through (*b*)] for the 2-amino-4-methyl-6-t-butylphenol. This product is also obtained as a resinous oil after similar purification using a silica gel column.

Analysis.—Calculated for $C_{30}H_{52}ON_4S_2$: C, 66.37%; H, 9.35%; N, 9.99%. Found: C, 66.06%; H, 9.17%; N, 10.27%.

In a similar manner, 6-(4-hydroxy-3-methyl-5-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine is prepared by

substituting 4-amino-2-methyl-6-t-butylphenol [prepared by the method described for the preparation of 4-amino-2,6-di-t-butylphenol in Example 1, (*a*) through (*b*)] for the 2-amino-4-methyl-6-t-butylphenol. This product is also obtained as a resinous oil after chromatographic purification.

Analysis.—Calculated for $C_{30}H_{50}N_4S_2O$: C, 65.91%; H, 9.22%; N, 10.24%. Found: C, 66.07%; H, 8.87%; N, 10.40%.

In a similar manner, 6-(4-hydroxyanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine is prepared by substituting p-aminophenol for the 2-amino-4-methyl-6-t-butylphenol. In this case, the product is a solid. Thus, it is not necessary to use chromatography for purification. The product after crystallization from petroleum ether is obtained in 41% yield and melts at 62–63°.

In a similar manner as well, 6-(4-hydroxy-3,5-dimethylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine is prepared by substituting 4-amino-2,6-dimethylphenol [prepared by nitrosation of 2,6-dimethylphenol as in Example 1, (*a*) and catalytic reduction using palladium on carbon catalyst] for the 2-amino-4-methyl-6-t-butylphenol. In this case, the product is a solid and it is not necessary to use chromatography for purification. The product after two crystallizations from petroleum ether is obtained in 40% yield and melts at 70–71°.

EXAMPLE 12

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(n-Octylthioethylthio)-1,3,5-Triazine

An alcoholic solution of sodium n-octylthioethyl mercaptide [prepared by dissolving 0.92 part of sodium in 20 parts by volume of ethanol and adding 8.58 parts of n-octylthioethyl mercaptan prepared according to the method described by Reid, "Organic Chemistry of Bivalent Sulphur," Chemical Publishing Co., N.Y., N.Y., 1958, p. 394] is added while stirring to a slurry of 7.38 parts of 6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - dichloro-1,3,5-triazine [preparation described in Example 1, (*a*) through (*c*)] in 20 parts by volume of ethanol. After the exothermic reaction has subsided, the reaction mixture is heated on a steam bath for 1 hour, cooled to room temperature and the precipitated sodium chloride is removed by filtration. On standing overnight, the product crystallizes from the filtrate. A second crop is obtained by carefully adding water to the mother liquor until crystallization occurs to produce a total yield of 10.7 parts (75%). The 6 - (4 - hydroxy - 3,5 - di-t-butylanilino)-2,4-bis-(n-octylthioethylthio)-1,3,5-triazine, obtained after recrystallization from hexane, is a waxy solid which melts at 69–71°.

EXAMPLE 13

6-(4-Hydroxy-3,5-Di-t-Butyl-N-Benzylanilino)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

(*a*) *4-(n-benzylidineamino) - 2,6 - di-t-butylphenol.*—A solution of 22.1 parts of 4-amino-2,6-di-t-butylphenol [prepared as described above in Example 1] and 11.66 parts of benzaldehyde in 100 parts by volume of dry benzene is refluxed until 1.8 parts of water is azeotropically collected in a Dean-Stark trap. After cooling the reflux mixture, the crystalline mass which forms is filtered off, washed with cold heptane and dried in vacuo. The 4-N-benzylidineamino-2,6-di-t-butylphenol so obtained, weighs 22.0 parts and melts at 151–153°. A second crop of crystalline product, weighing 4.3 parts and having the same melting point, is obtained by concentrating the filtrates. The total yield is 85.27% of theory.

(*b*) *4-(N - benzylamino) - 2,6 - di-t-butylphenol.*—A solution of 15.45 parts of 4-(N-benzylidineamino)-2,6-di-t-butylphenol in 250 parts by volume of glacial acetic acid is charged to a hydrogenation vessel, 0.2 part of 10% palladium on charcoal added and the whole mixture is shaken under a hydrogen atmosphere until the theoretical amount of hydrogen had been absorbed. The catalyst is then removed by filtration and the free acetic acid is removed by distillation under reduced pressure over a hot water bath at 50–60°. 100 parts of water is added to the residue from distillation; the pH is adjusted to 12 with 5 N sodium hydroxide and the resultant amine is extracted into 250 parts by volume of ether. The ether solution is washed with water and dried over anhydrous magnesium sulfate. After removal of the magnesium sulfate by filtration, the ether is evaporated and the residue is triturated with 50 parts by volume of cold petroleum ether and then washed twice with 25 parts by volume of cold petroleum ether each time. After drying, the 4-(N-benzylamino)-2,6-di-t-butylphenol weighs 5.67 parts (36.5% yield) and melts at 90–94°.

(*c*) *6-(4-hydroxy - 3,5 - di-t-butyl-N-benzylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine.*—This synthesis is carried out in a manner similar to that described above for the preparation of 6-(2-hydroxy-3-t-butyl - 5 - methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Example 11) by substituting 4-(N-benzylamino)-2,6-di-t-butylphenol for 2-amino-4-methyl-di-t-butylphenol. After purification with a silica gel column, the 6-(4-hydroxy-3,5-di-t-butyl-N-benzylanilino) - 2,4 - bis-(n-octylthio)-1,3,5-triazine is obtained as a waxy solid melting at 36°. The yield is 36% of theory.

EXAMPLE 14

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(Cyanoethylthio)-1,3,5-Triazine

This synthesis is carried out in a manner similar to that described above for 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine in Example 1 by substituting for n-octylmercaptan, β-mercapto-propionitrile, [prepared according to Marvel et al. I and EC 45, 2090 (1953)]. The yield of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(cyanoethylthio) - 1,3,5-triazine melting at 100–103° was 39% of theory.

EXAMPLE 15

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(4-t-Butylphenoxy)-1,3,5-Triazine

An alcoholic solution of sodium p-t-butylphenoxide (prepared by dissolving 9.2 parts of sodium in 750 parts by volume of ethanol and adding 60 parts of p-t-butylphenol) is added rapidly with stirring to a slurry of 74 parts of 6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - dichloro-1,3,5-triazine [preparation as in Example 1 (*c*) hereinabove] in 250 parts of ethanol. After the exothermic reaction subsides, the reaction is allowed to stand for several hours, then poured into 2000 parts of water. The gummy solid is separated by filtration and purification is accomplished by recrystallization from methanol-water (100:7). The 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(4-t-butylphenoxy)-1,3,5-triazine after filtration, washing and drying weighs 63.6 parts (53.5%) and melts at 119–121°.

By replacing p-t-butylphenol by p-t-octylphenol, n-dodecyl-β-mercaptopropionate, n-decyl-β-mercaptopropionate, n-dodecyl thioglycolate, n-decyl thioglycolate and n-dodecyl-2-mercaptobenzoate (prepared by esterification of 2-mercaptobenzoic acid: b.p. 180–184°/.050 mm. Hg) respectively, the following compounds are obtained in an analogous manner:

6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis-(4-t-octylphenoxy)-1,3,5-triazine, M.P. 99–101° (recrystallized from methanol);

6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis-(carbo - n - dodecyloxyethylthio) - 1,3,5 - triazine (intractable oil isolated by ether extraction).

Analysis.—Calculated for $C_{47}H_{80}O_5N_4S_2$: S, 7.58%. Found: S, 7.27%.

6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis-(carbo - n - decyloxyethylthio) - 1,3,5 - triazine (intractable oil isolated by ether extraction).

Analysis.—Calculated for $C_{43}H_{27}O_5N_4S_2$: S, 8.13%. Found: S, 7.98%.

6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis-(carbo - n - decyloxymethylthio) - 1,3,5 - triazine (viscous oil, purified by stripping under reduced pressure and at oil bath temperature).

Analysis.—Calculated for $C_{41}H_{66}O_5N_4S_2$: S, 8.42%. Found: S, 8.36%.

6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis-(carbo - n - dodecyloxymethylthio) - 1,3,5 - triazine (intractable oil isolated by ether extraction).

Analysis.—Calculated for $C_{45}H_{76}O_5N_4S_2$: S, 7.84%. Found: S, 7.78%.

6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis-(2 - carbo - n - dodecyloxyphenylthio) 1,3,5 - triazine (isolated by elution chromatography using a silica gel column).

Analysis.—Calculated for $C_{55}H_{80}O_5N_4S_2$: C, 70.17%; H, 8.56%; N, 5.95%. Found: C, 69.68%; H, 9.02%; N, 6.06%.

If, in the foregoing Example 15, 0.4 mole of sodium carbomethoxymethyl mercaptide are substituted for sodium p-t-butylphenoxide, then 6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - bis - (carbomethoxymethylthio) - 1, 3,5-triazine is obtained.

If, in Example 15, 0.4 mole of sodium 2-carbomethoxythiophenolate are substituted for sodium p-t-butylphenoxide, then 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(2-carbomethoxyphenylthio)-1,3,5-triazine is obtained.

If, in Example 15, 0.4 mole of sodium p-octadecylphenolate are substituted for sodium p-t-butylphenoxide, then 6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4-bis-(p-octadecylphenoxy)-1,3,5-triazine is obtained.

If, in Example 15, 2.3 moles of sodium methylmercaptide is substituted for sodium p-t-butylphenolate, then 6-(4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4 - bis - (methylthio)-1,3,5-triazine is obtained.

If, in Example 15, 2.3 moles of sodium cyclopentylmercaptide is substituted for sodium p-t-butylphenolate, then 6 - (4 - hydroxy - 3,5 - di - t - butylanilino) - 2,4-bis-(cyclopentylthio)-1,3,5-triazine is obtained.

EXAMPLE 16

6-(4-Hydroxy-5-Methylanilino)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

A mixture of 10.1 parts of 2,4-bis-(n-octylthio)-6-chloro-1,3,5-triazine [prepared according to Example 11 (*a*) hereinabove]. 3.08 parts of 2-methyl-4-aminophenol and 100 parts of water is gradually warmed with stirring under a nitrogen atmosphere to 90° and at the same time the pH is maintained at 6–7 by the addition of 5 N sodium hydroxide. When the pH remains constant, the reaction is complete. The product is removed by filtration, washed with water and purified by recrystallization from hexane. The 6-(4-hydroxy-5-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine is obtained in 67% yield as colorless needles melting at 67–68°.

By replacing 2-methyl-4-aminophenol by 2-amino-4-methylphenol, m-aminophenol, p-methylaminophenol sulfate, o-aminophenol, 2-t-butyl-4-aminophenol, 3,5-dimethyl - 4 - aminophenol, 2 - amino - 4,6 - di - t - butylphenol, 2 - amino - 3 - methyl - 4,6 - di - t - butylphenol, 2 - amino-4-t-butylphenol, and 2-amino-4-phenylphenol respectively, the following compounds are obtained in an analogous manner:

6-(2-hydroxy-5-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 99–101° (recrystl. from ethanol and heptane);

6-(3-hydroxyanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 55–57° (recrystl. from petroleum ether);

6-(4-hydroxy-N-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 55–57° (recrystl. from hexane, heptane and petroleum ether);

6-(2-hydroxyanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 103° (recrystl. from benzene-hexane and methanol-water);

6-(4-hydroxy-5-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 75° (isolated by elution chromatography using a silica gel column, then recrystl. from petroleum ether);

6-(4-hydroxy-2,6-dimethylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 122–123° (recrystl. from heptane);

6-(2-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 74° (recrystl. from ethanol-water and methanol);

6-(2-hydroxy-3,5-di-t-butyl-6-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (intractable oil isolated by elution chromatography);

Analysis.—Calculated for $C_{34}H_{58}N_4S_2O$: C, 67.72%; H, 9.69%; N, 9.29%; S, 10.64%. Found: C, 67.47%; H, 9.41%; N, 9.05%; S, 10.46%.

6-(2-hydroxy-5-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 101° (recryst. from methanol);

6-(2-hydroxy-5-phenylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, M.P. 119–120° (recryst. from isopropanol).

If, in Example 16, 0.025 mole of 3-octadecyl-4-aminophenol is substituted for 2-methyl-4-aminophenol, then 6 - (4 - hydroxy-2-octadecylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine is obtained.

EXAMPLE 17

6-(4-Hydoxy-3,5-Di-t-Butylphenylthio)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

An alcoholic solution of sodium 4-hydroxy-3,5-di-t-butylphenyl mercaptide (prepared by dissolving 23 parts of sodium in 2000 parts by volume of ethanol and adding 238 parts of 4-mercapto-2,6-di-t-butylphenol [Hotelling et al. J. Org. Chem. 24, 1598 (1959)]) is added with mixing to a solution of 404 parts of 2,4-bis-(n-octylthio)-6-chloro-1,3,5-triazine in 2000 parts by volume of ethanol. After the exothermic reaction has subsided the reaction is allowed to stand at room temperature for several hours; the salt is removed by filtration and the ethanol removed from the filtrate by evaporation. The oily residue therefrom is then dissolved in hexane and adsorbed on a silica gel column. After removing impurities by eluting with hexane, the product, 6-(4-hydroxy-3,5-di-t-butylphenylthio)-2,4-bis-(n-octylthio)-1,3,5-triazine is eluted with 50% by volume of benzene-hexane. Evaporation of the solvent leaves a light viscous oil.

Analysis.—Calculated for $C_{33}H_{55}ON_3S_3$: C, 65.4%; H, 9.15%; N, 6.93%; S, 15.88%. Found: C, 65.29%; H, 9.15%; N, 6.73%; S, 16.16%.

By replacing 4-mercapto-2,6-di-t-butylphenol by 4-mercapto-2,6-dimethylphenol [Hotelling et al., J. Org. Chem. 24, 1598 (1959)], the following compound is obtained in an analgous manner:

6 - (4 - hydroxy-3,5-dimethylphenylthio)-2,4-bis-(n-octylthio)-1,3,5-triazine (isolated by elution chromatography using a silica gel column and eluting wth 75% benzene-hexane).

Analysis.—Calculated for $C_{27}H_{43}ON_3S_3$: C, 62.15%; H, 8.31%; N, 8.05%; S, 18.44%. Found: C, 62.13%, H, 7.93%; N, 7.63%; S, 18.37%.

In a manner analogous to the preparation in Example 17, 6 - (4 - hydroxy - 3,5-di-t-butylanilino)-2,4-bis-(2,3-dimethylphenylthio)-1,3,5-triazine is obtained, when 7.4 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine in 100 parts by volume of ethanol are mixed with 8.4 parts of 2,3-dimethylbenzenethiol (66% pure oil) and 0.92 part of sodium dissolved in 50 parts by volume of ethanol. The resultant mixture is allowed to stand for 2 hours, after which the salt which forms is filtered off and steam is blown through the filtrate to remove volatiles, including ethanol. Upon removal of the volatiles from the reaction mixture, the residual oil solidi-

fies and the aqueous layer is decanted. The residual solid resin is dissolved in petroleum ether and the resultant mixture is dried over magnesium sulfate. Upon evaporation of the petroleum ether, 8.5 parts of the crude 6-(4-hydroxy - 3,5 - di-t-butylanilino) - 2,4-bis-(2,3-dimethylphenylthio)-1,3,5-triazine are obtained, which upon purification by dissolution in hexane and chromatography on a silica gel column (eluant is 50% benzene/hexane), yields 4.3 parts of a buff colored resinous powder (37.7% of theory).

Analysis.—Calculated for $C_{33}H_{40}N_4SO_2$: C, 69.2%; H, 7.04%; N, 9.78%; S, 11.19%. Found: C, 69.52%; H, 7.6%; N, 9.65%; S, 11.62%.

EXAMPLE 18

6-(4-Hydroxy-3,5-Di-t-Butylphenoxy)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

An alcoholic solution of sodium 4-hydroxy-3,5-di-t-butylphenoxide [prepared by dissolving 60 parts of sodium in 5000 parts by volume of ethanol and adding 666 parts of 2,6-di-t-butylhydroquinone (U.S. Patent No. 2,927,932)] is added rapidly while stirring to a solution of 1212 parts of 2,4-bis-(n-octylthio)-6-chloro-1,3,5-triazine in 2500 parts by volume of ethanol. After the exothermic reaction subsides, the reaction mixture is allowed to stand several hours before removing the salt by filtration. The filtrate is treated with activated carbon, filtered, and the filtrate is concentrated to dryness under vacuum. The oily residue therefrom is dissolved in hexane, absorbed on a silica gel column and eluted with 50% benzene/hexane. After evaporation of the solvent therefrom, the 6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-bis-(n-octylthio)-1,3,5-triazine is obtained as a light colored viscous oil in 67% yield.

Analysis.—Calculated for $C_{33}H_{55}O_2N_3S_2$: C, 67.19%; H, 9.4%; N, 7.12%. Found: C, 66.84%; H, 9.11%; N, 7.26%.

By replacing 2,6-di-t-butylhydroquinone with hydroquinone, the chromatographic separation is unnecessary, since the crude reaction product is precipitated by the addition of water. Fractional crystallization from ethanol separates two products, which are obtained in 21.5 and 15.4% yields, respectively. Said products are, respectively:

1,4 - phenylene - bis-[2-oxy-4,6-bis(n-octylthio)]-1,3,5-triazine; M.P. 98° (recrystl. from ethanol);

6 - (4 - hydroxyphenoxy)-2,4-bis-(n-octylthio)-1,3,5-triazine; M.P. 79–80°.

EXAMPLE 19

6-(4-Hydroxy-3,5-Di-t-Butylbenzylthio)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

(*a*) *2,4 - bis - (n - octylthio)-6 - chloro-1,3,5-triazine.*—Preparation of this compound is described in Example 3 above.

(*b*) *2,4 - bis - (n - octylthio) - 6 - mercapto-1,3,5-triazine.*—A mixture of 4.04 parts of 2,4-bis-(n-octylthio)-6-chloro-1,3,5-triazine, 0.76 part of thiourea and 25 parts by volume of dioxane is heated at reflux until solution results. A small amount of insolubles is removed by filtration, 10 parts by volume of 2 N sodium hydroxide added and heating continued for 2 hours. The reaction mixture is then acidified to pH of 4 with 5 N hydrochloric acid and an oil which solidifies on cooling separates. The mushy solid is separated by filtration and dissolved in 12 parts by volume of hot acetic acid and recrystallized. The recrystallized product is filtered, washed with acetic acid and then with water and dried in vacuo over phosphoric anhydride. In this manner, 1.72 parts of 2,4-bis-(n-octylthio)-6-mercapto-1,3,5-triazine melting at 83–86° is obtained. Recrystallization from boiling heptane raises the melting point to 87–88°.

(*c*) *4-hydroxy-3,5-di-t-butylbenzyl chloride.*—A mixture of 103 parts of 2,6-di-t-butylphenol and 100 parts by volume of 57% formalin is stirred at 30° and 100 parts of anhydrous zinc chloride are added portionwise during 5 minutes, while keeping the temperature below 30°. Dry hydrogen chloride is then passed through the mixture rapidly in a stream while stirring and maintaining the temperature at 30–35° with external cooling. After about 1½ hours, the reaction ceases. The oily layer is separated and taken up in ether, washed well with water, with 10% sodium bicarbonate and again with water. The resultant ether solution is dried over anhydrous magnesium sulfate. The magnesium sulfate is then filtered off and the ether is removed by distillation. The residue is vacuum distilled. The 4-hydroxy-3,5-di-t-butylbenzyl chloride so obtained boils at 118° under 0.1 mm. Hg and weighs 65.25 parts (51.5%).

Analysis.—Calculated for $C_{15}H_{23}OCl$: C, 70.1%; H, 9.1%. Found: C, 70.64%; H, 8.90%.

(*d*) *6 - (4 - hydroxy - 3,5 - di - t - butylbenzylthio)-2,4-bis-(n-octylthio)-1,3,5-triazine.*—A mixture of 8.1 parts of 2,4-bis-(n-octylthio)-6-mercapto-1,3,5-triazone, 4 parts by volume of 5 N sodium hydroxide and 5.01 parts of 4-hydroxy-3,5-di-t-butylbenzyl chloride in 100 parts by volume of dioxane is stirred and refluxed for 1 hour during which time the solution becomes neutral. The dioxane is removed by distillation under reduced pressure, 200 parts by volume of water are added and the product extracted into 150 parts by volume of hexane. The hexane solution is dried and the product adsorbed on a silica-gel column. After preliminary washing of the column, the product is eluted with 25% benzene in hexane. The 6-(4-hydroxy-3,5 - di - t-butylbenzylthio)-2,4-bis-(n-octylthio)-1,3,5-triazine is recovered as a light lemon colored oil (6.5 parts).

Analysis.—Calculated for $C_{34}H_{57}S_3N_3O$: C, 65.86%; H, 9.27%; S, 15.52%. Found: C, 66.18%; H, 8.87%; S, 15.38%.

EXAMPLE 20

4,6-Bis-(4-Hydroxy-3,5-Di-t-Butylphenoxy)-2-n-Octylthio-1,3,5-Triazine

(*a*) *4,6 - dichloro-2-n-octylthio-1,3,5-triazine.*—A solution of 184.4 parts of cyanuric chloride, 146 parts of n-octyl mercaptan and 0.5 part by volume of pyridine in 500 parts by volume of xylene is refluxed while passing nitrogen through the reactants, until the evolution of hydrogen chloride has ceased. The solution is filtered from a small amount of insoluble material and the solvent stripped off with a water pump and finally the residue is vacuum distilled. The 4,6-dichloro-2-n-octylthio-1,3,5-triazine, weighing 200 parts (68%), distills at 147–148° at 0.050 mm. Hg.

(*b*) *4,6 - bis - (4 - hydroxy-3,5-di-t-butylphenoxy)-2-n-octylthio-1,3,5-triazine.*—A solution of 8.82 parts of 4,6-dichloro-2-n-octylthio-1,3,5-triazine and 13.32 parts of 2,6-di-t-butyl-1,4-hydroquinone in 50 parts by volume of ethanol is stirred vigorously and a solution of 1.38 parts of sodium in 100 parts by volume of ethanol is added dropwise over a period of 30 minutes. The reaction mixture is refluxed for an additional 30 minutes, cooled and the salt removed by filtration. The filtrate is reheated to boiling and 20 parts by volume of water are added. On cooling, the product crystallizes. After filtering and drying the product, 4,6-bis-(4-hydroxy-3,5-di-t-butylphenoxy)-2-n-octylthio-1,3,5-triazine, weighs 15.8 parts (80% yield) and melts at 129–134°. Recrystallization from ethanol-water raises the melting point to 133–134°.

If 5.88 parts of 4,6-dichloro-2-n-octylthio-1,3,5-triazine are reacted with 6.64 parts of mono-t-butyl-1,4-hydroquinone in an analogous manner to the preparation described in the foregoing Example 20, then 4,6-bis-(4-hydroxy-3-t-butylphenoxy)-2-n-octylthio-1,3,5-triazine is produced. This product is isolated by elution chromatography on a silica gel column using benzene as eluant. The so-obtained hard-glass product in 6.34 parts yield has the following composition.

Analysis.—Calculated for $C_{31}H_{43}O_4N_3S$: C, 67.25%; H,

7.83%; N, 7.59%. Found: C, 67.01%; H, 7.82%; N, 7.95%.

EXAMPLE 21

6-(4-Hydroxy-3,5-Di-t-Butylanilino)-2-n-Octylthio-4-Phenylthio-1,3,5-Triazine

(*a*) *6-(4-hydroxy-3,5-di-t-butylanilino)-4-n-octylthio-2-chloro-1,3,5-triazine.*—An alcoholic solution of sodium n-octylmercaptide (prepared by dissolving 0.23 part of sodium in 10 parts by volume of ethanol and adding 1.46 parts of n-octylmercaptan) is added rapidly to a slurry of 3.69 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine [preparation described in Example 1, (*a*) through (*c*)] in 10 parts by volume of ethanol. An immediate exothermic reaction ensues, but external cooling is applied and the reaction mixture is poured into 50 parts by volume of water and an oil separates, which solidifies upon cooling. The 6-(4-hydroxy-3,5-di-t-butylanilino)-4-n-octylthio-2-chloro-1,3,5-triazine, thus obtained, is filtered, washed with water until free of chloride ion, and finally recrystallized twice from hexane. The purified compound weighs 2.04 parts (42.5%) and melts at 119–120°.

(*b*) *6-(4-hydroxy-3,5-di-t-butylanilino)-2-n-octylthio-2-n-octylthio-4-phenylthio-1,3,5-triazine.*—6.55 parts of 6-(4 - hydroxy-3,5-di-t-butylanilino)-4-n-octylthio-2-chloro-1,3,5-triazine are dissolved in 50 parts by volume of warm ethanol and the sodium mercaptide [prepared from 1.65 parts of thiophenol dissolved in a previously prepared solution of 0.32 part of sodium metal in 120 parts by volume of ethanol]. The reaction mixture is allowed to stand for 2 hours when the pH is 7.0. The salt is removed by filtration and the ethanol solution is treated with steam, whereupon the oily residue is extracted with ether. The dried ether extract is concentrated under reduced pressure and the yellow resin resulting is recrystallized from isopropanol-water to yield crystalline 6-(4-hydroxy - 3,5 - di-t-butylanilino)-2-n-octylthio-4-phenylthio-1,3,5-triazine in quantity of 1.56 parts, melting at 99–101°.

If 9.58 parts of the 6-(4-hydroxy-3,5-di-t-butylanilino)-4-n-octylthio-2-chloro-1,3,5-triazine, in a manner analogous to Example 21, are reacted with 4.44 parts of 2,6-di-t-butyl-1,4-hydroquinone, then there is produced the crude 6 - (4-hydroxy-3,5-di-t-butylanilino)-4-(4-hydroxy-3,5-di-t-butylphenoxy) - 2 - n - octylthio - 1,3,5 - triazine, which is recrystallized from heptane, the purified crystalline product being obtained in yield of 3.88 parts, melting at 182–183°.

EXAMPLE 22

6-(4-Hydroxy-3,5-Di-t-Butylbenzylthio)-2,4-Bis-(Ethylamino)-1,3,5-Triazine

(*a*) *2,4 - bis-(ethylamino)-6-mercapto-1,3,5-triazine.*—A mixture of 20 parts of 2,4-bis-(ethylamino)-6-chloro-1,3,5-triazine, 7.6 parts of thiourea and 100 parts by volume of dioxane is heated until a clear solution results. 100 parts by volume of dioxane and 100 parts by volume of 2 N sodium hydroxide are added and the reaction mixture is heated on a steam bath for 2 hours. After cooling to room temperature, a small amount of solids is removed by filtration and the filtrate is acidified to a pH of 4.5 with 5 N hydrochloric acid. The product, 2,4-bis-(ethylamino)-6-mercapto-1,3,5-triazine, is separated by filtration and washed with water until free of chloride ion. After drying, the product weighs 16.2 parts and melts with decomposition at 254–257°. After recrystallization from glacial acetic acid, the melting point is 269–270°.

(*b*) *6-(4-hydroxy - 3,5 - di-t-butylbenzylthio)-2,4-bis-(ethylamino)-1,3,5-triazine.*—6.0 parts of 2,4-bis-(ethylamino)-6-mercapto-1,3,5-triazine, obtained as described in part (*a*) above, are reacted with 7.65 parts of 4-hydroxy-3,5-di-t-butylbenzyl chloride and 6 parts by volume of 5 N sodium hydroxide in 100 parts by volume of dioxane at reflux for 1 hour. When the reaction mixture becomes neutral, 300 parts by volume of water are added and the resultant oil is extracted into ether. The ether solution, after drying, is concentrated, and the residue is dissolved in hexane and adsorbed on a silica gel column. 10 parts of a resinous material are eluted from the column with 25% methanol in benzene and said material is recovered by stripping off the methanol/benzene solvent, yielding a residue which is recrystallized from isopropanol/water and then from hexane. The so-obtained 6 - (4-hydroxy - 3,5 - di-t-butylbenzylthio)-2,4-bis-(ethylamino)-1,3,5-triazine in amount of 1.56 parts melts at 99–101°.

EXAMPLE 23

6-(4-Hydroxy-3,5-Di-t-Butylphenoxy)-2,4-Bis-(Phenoxy)-1,3,5-Triazine

6 parts of 2,4 - bis-phenoxy-6-chloro-1,3,5-triazine [J.A.C.S. 73, 2992 (1951)], dissolved in ethanol are reacted with a solution of 4.4 parts of 2,6-di-t-butyl-1,4-hydroquinone in sodium ethoxide [previously prepared by dissolving sodium metal (0.46 part) and 30 parts by volume of ethanol]. After filtration of the sodium chloride, the filtrate is flooded with water and the resulting solid is washed with water and filtered, dried and recrystallized from hexane, yielding 2.5 parts of 6-(4-hydroxy-3,5-di-t-butylphenoxy) - 2,4 - bis-(phenoxy) - 1,3,5-triazine, melting at 145–147°.

EXAMPLE 24

2,4,6-Tris-(4-Hydroxy-3,5-Di-t-Butylphenoxy)-1,3,5-Triazine

3.68 parts of cyanuric chloride dissolved in 50 parts by volume of acetone are cooled to 20° and 13.3 parts of 2,6-di-t-butyl-1,4-hydroquinone are added thereto. The resultant mixture is stirred for 1 hour at 20°, during which time 12 parts of 5 N sodium hydroxide in 50 parts of water are added dropwise, and the reaction mixture is then heated for 30 minutes at 60°. 50 parts of water are added and the reaction mixture is heated further for an hour at 70° until a pH of 7.0 is obtained after cooling, the solid precipitate which forms is filtered and washed copiously with water. The crude produce is recrystallized from boiling dioxane and water, the crystalline material being dried under reduced pressure at 125° to remove the solvent of crystallization. The so-obtained 2,4,6-tris-(4-hydroxy-3,5-di-t-butylphenoxy) - 1,3,5-triazine melts at 298–299° and the yield is of 10.93 parts.

If, in the foregoing Example 24, 9.2 parts of cyanuric chloride are used and, in place of 2,6-di-t-butyl-1,4-hydroquinone, 27.5 parts of mono-t-butyl-1,4-hydroquinone are used, then 13.8 parts of 2,4,6-tris-(3-t-butyl-4-hydroxyphenoxy)-1,3,5-triazine, melting at 128–134°, are obtained (recrystallized from dioxane and water).

EXAMPLE 25

6-(4-Hydroxy-3,5-Di-t-Butylphenoxy)-2,4-Bis-(-n-Octylthioethylthio)-1,3,5-Triazine

(*a*) *6 - (4 - hydroxy - 3,5 - di - t - butylphenoxy)-2,4-dichloro-1,3,5-triazine.*—18.4 parts of cyanuric chloride are dissolved in 250 parts by volume of acetone and cooled to 5° and stirred. To this mixture 22.2 parts of 2,6-di-t-butyl-1,4-hydroquinone are added, whereupon 20 parts by volume of 5 N sodium hydroxide in 250 parts by volume of water are added dropwise with stirring over a period of 30 minutes at 5°, and stirring is continued for a further 30 minutes at 5°. Then 250 parts by volume of water are added and the reaction mixture is stirred at 5° for 3 hours. The solid precipitate which forms is filtered, washed with ice-water, dried in vacuo, yielding 32.2 parts of the intermediate 6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-dichloro-1,3,5-triazine, which can be recrystallized from warm isopropanol to give a pure crystalline material, melting at 103–104°.

(*b*) *6 - (4 - hydroxy-3,5-di-t-butylphenoxy)-2,4-bis-(n-octylthioethylthio)-1,3,5-triazine.*—1.38 parts of sodium metal is dissolved in 75 parts by volume of ethanol

and 13.0 parts of n-octylthioethyl mercaptan are added. This solution is rapidly added to a stirred solution of 12.6 parts of the crude 6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-dichloro-1,3,5-triazine (obtained in step (*a*) above as 88% pure material) in 75 parts by volume of ethanol. The initial reaction is exothermic, and the reaction mixture is heated and stirred under nitrogen for 15 minutes until the pH becomes 7.0. The reaction mixture is treated with steam to remove solvent and the resulting yellow oil is extracted into 100 parts by volume of hexane, which after drying over magnesium sulfate is adsorbed on a silica gel column. The product, 6-(4-hydroxy-3,5-di-t-butylphenoxy) - 2,4 - bis-(n-octylthioethylthio)-1,3,5-triazine, is eluted with 50% benzene in hexane and, on removal of solvent, 9.62 parts of a resinous oil are obtained, which are identified by microanalysis.

Analysis.—Calculated for $C_{37}H_{63}O_2S_4N_5$, C, 62.56%; H, 8.94%; N, 5.92%; S, 18.06%. Found: C, 62.30%; H, 8.65%; N, 5.89%; S, 18.37%.

EXAMPLE 26

6-(N-Methyl-4-Hydroxy-3,5-Di-t-Butylbenzylamino)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

(*a*) *N - methyl-4-hydroxy-3,5-di-t-butylbenzylamine.*—33.9 parts of an aqueous solution of methylamine (33.7% by weight solution) in 50 parts by volume of ethanol are cooled to 5° and a solution of 20.2 parts formalin (37% by weight solution) in 50 parts by volume of ethanol is added dropwise thereto, keeping the temperature at 5–10°. After the addition is completed, the resultant mixture is allowed to stand at 25° for 3 hours, whereupon a solution of 51.5 parts of 2,6-di-t-butylphenol in 100 parts by volume of ethanol is added dropwise to said mixture and the whole is refluxed for 2 hours. On standing overnight at room temperature, a white precipitate forms in the reaction mixture. This precipitate is removed by filtration [analysis indicates to be N,N-bis-(4-hydroxy-3,5-di-t-butylbenzyl)-methylamine].

The filtrate from the reaction mixture is poured into 300 parts by volume of water and extracted twice with 100 parts by volume portions of ether. The ether extracts are combined, washed with water, dried over magnesium sulfate and saturated with anhydrous hydrogen chloride. A white solid precipitates and the so-obtained hydrochloride of N-methyl-4-hydroxy-3,5-di-t-butylbenzylamine is employed without further purification in the following step (*b*).

(*b*) *6-(N-methyl-4-hydroxy - 3,5 - di-t-butylbenzylamino)-2,4-bis-(n-octylthio)-1,3,5-triazine.*—In a manner analogous to Example 11(*b*) above, 40.4 parts of 6-chloro-2,4-bis-(n-octylthio)-1,3,5-triazine are reacted with 28.6 parts of N-methyl-4-hydroxy-3,5-di-t-butylbenzylamine hydrochloride [obtained as in Example 26(*a*) above]. Purification of the so-obtained 6-(N-methyl-4-hydroxy - 3,5-di-t-butylbenzylamino)-2,4-bis-(n - octylthio)-1,3,5-triazine is effected by elution chromatography.

EXAMPLE 27

6-(4-Hydroxy-3,5-Di-t-Butylbenzyloxy)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

(*a*) *6 - hydroxy - 2,4 - bis - (n-octylthio)-1,3,5-triazine.*—40.4 parts of 6-chloro-2,4-bis-(n-octylthio)-1,3,5-triazine are mixed with 100 parts by volume of 5 N aqueous sodium hydroxide and sufficient 2-ethoxy-1-ethanol is added to form a homogeneous solution. The resultant solution is refluxed until the chloride ion concentration is constant in the reaction mixture. Upon acidification with 6 N hydrogen chloride, the so-obtained 6-hydroxy-2,4-bis-(n-octylthio)-1,3,5-triazine which separates is purified by distillation.

(*b*) *6 - (4 - hydroxy - 3,5 - di-t-butylbenzyloxy)-2,4-bis-(n-octylthio)-1,3,5-triazine.*—4.2 parts of 6-hydroxy-2,4-bis-(n-octylthio)-1,3,5-triazine and 0.23 part of sodium, dissolved in 25 parts by volume of ethanol, are reacted with 2.55 parts of 4-hydroxy-3,5-di-t-butylbenzyl chloride, dissolved in 25 parts by volume of ethanol and the whole mixture is refluxed for 3 hours, after which the sodium chloride which forms is separated by filtration and the so-obtained 6-(4-hydroxy-3,5-di-t-butylbenzyloxy)-2,4-bis-(n-octylthio)-1,3,5-triazine is recovered from the filtrate, after stripping off the ethanol by elution chromatography on a silica gel column.

EXAMPLE 28

6 -(N-Acetyl-4-Hydroxy-3,5-Di-t-Butylanilino)-2,4-Bis-(n-Octylthio)-1,3,5-Triazine

23.5 parts of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine and 200 parts by volume of acetic anhydride are heated at 130° for 2½ hours, after which the volatile materials are stripped from the reaction mixture under high vacuum (0.05 mm. Hg) at water bath temperature. The viscous lemon colored liquid which remains in the distillation pot is dissolved in 150 parts by volume of ether, washed with 10% (by weight) sodium bicarbonate solution, and then washed with water and finally dried over anhydrous magnesium sulfate. Thereafter, the ether is removed by evaporation on the steam bath and the residue is finally stripped at 130° and 0.05 mm. Hg. The so-obtained product weighs 22.5 parts. This product, 6-(N-acetyl-4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine, has the following analysis:

Calculated for $C_{35}H_{58}N_4O_2S_2$: C, 66.6%; H, 9.27%; N, 8.88%. Found: C, 66.52%; H, 9.09%; N, 8.99%.

If in Example 28, valeric anhydride is substituted for acetic anhydride, then 6-(N-valeroyl-4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio) - 1,3,5 - triazine is obtained.

Further, if in Example 28, lauric anhydride is substituted for acetic anhydride, then 6-(N-lauroyl-4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine is obtained.

Other substituted triazines which are useful according to the invention are prepared analogously to the methods illustrated in the foregoing examples. The following are some further examples of how such substituted triazines are prepared:

If, in Example 1(*c*), 4-amino-2-methylphenol is substituted for an equimolar amount of 4-amino-2,6-di-t-butylphenol, then 6-(4-hydroxy-3-methylanilino)-2,4-dichloro-1,3,5-triazine is obtained. Alternatively, if in the same example, 4-amino-2-octadeylphenol is employed instead, then 6-(4-hydroxy-3-octadecylanilino)-2,4-dichloro-1,3,5-triazine is obtained.

If, in Example 2(*b*), an equimolar quantity of sodium p-octadecylphenyl mercaptide is substituted for sodium n-octyl mercaptide, then 4,6-bis-(3,5-di-t-butyl-4-hydroxyanilino)-2-p-octadecylphenylthio - 1,3,5 - triazine is obtained.

If, in Example 4, an equimolar amount of methyl mercaptan is employed in place of octyl mercaptan, then 6 - (4 - hydroxy - 3,5 - di-t-butylanilino)-4-methylthio-2-chloro-1,3,5-triazine is obtained. Then, if this compound is reacted with a sodium alkylhydroxyphenyl mercaptide, e.g. 3-methyl-4-hydroxyphenyl mercaptide and 3-octadecyl-4-hydroxyphenyl mercaptide, then, e.g. 6-(4-hydroxy - 3,5 - di-t-butylanilino)-4-methylthio-2-(3-methyl-4-hydroxyphenylthio)-1,3,5-triazine and 6-(4-hydroxy-3,5-di-t-butylanilino) - 4 - methylthio - 2 - (3-octadecyl-4-hydroxyphenylthio) - 1,3,5 - triazine, respectively, are obtained.

If, in Example 4, octadecyl mercaptan is employed instead of methyl mercaptan as mentioned above, then respectively, the following are obtained:

6-(4-hydroxy-3,5-di-t-butylanilino) - 4 - octadecylthio-2-chloro-1,3,5-triazine;

6-(4-hydroxy-3,5-di-t-butylanilino) - 4 - octadecylthio-2-(3-methyl-4-hydroxyphenylthio)-1,3,5-triazine; and

6-(4-hydroxy-3,5-di-t-butylanilino) - 4 - octadecylthio-2-(3-octadecyl-4-hydroxyphenylthio)-1,3,5-triazine.

If, in Example 10(*b*), an equimolar quantity of 4-hydroxy-3-methylbenzyl chloride is employed in place of 4-hydroxy-3,5-di-t-butylbenzyl chloride, then 2,4,6-tris-(4-hydroxy-3-methylbenzylthio)-1,3,5-triazine is obtained.

If, in Example 12, an equimolar quantity of sodium methylthiomethyl mercaptide is used in place of sodium n-octylthioethyl mercaptide, then 6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - bis - (methylthiomethylthio) - 1,3,5-triazine is obtained.

If, in Example 14, an equimolar quantity of mercaptoacetonitrile is used instead of β-mercapto-propionitrile, then 6 - (4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(cyanomethylthio)-1,3,5-triazine is obtained.

If, in Example 14, an equimolar quantity of ω-mercapto-n-heptanonitrile is used in place of the β-mercaptopropionitrile, then 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(cyanohexylthio)-1,3,5-triazine is obtained.

EXAMPLE 29

Unstabilized polypropylene powder (Hercules Profax 6501) is thoroughly blended with 0.5% by weight of 6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - bis - (n-octylthio)-1,3,5-triazine made according to Example 1. The blended material is then milled on a two roller mill at 182° for 10 minutes, after which time the stabilized polypropylene is sheeted from the mill and allowed to cool.

The milled polypropylene sheet is then cut into small pieces and pressed for 7 minutes on a hydraulic press at 218° and 2000 pounds per square inch pressure. The resultant sheet of 25 mil thickness is then tested for resistance to accelerated aging in a forced draft oven at 149°. The resultant composition of 0.5% by weight of 6-(4-hydroxy-3,5-di-t-butylanilino) - 2,4 - bis - (n-octylthio)-1,3,5-triazine and polypropylene is stabilized against oxidative deterioration for 375 hours. The unstabilized polypropylene deteriorates after only 3 hours.

In like manner as in the foregoing example, stable compositions of polypropylene are prepared having 0.5% by weight of each the compounds which are listed at the end of Example 36 below.

In like manner stable compositions of polypropylene are prepared with 0.1% by weight of 6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio) - 1,3,5-triazine. In like manner also, stable compositions of polypropylene are prepared with 0.1% of each of the stabilizers listed at the end of Example 36.

Similarly, all the compounds according to Examples 1–28, are incorporated into low-pressure polyethylene in an amount of 0.1% by weight by milling at 121–127° for 10 min. The resultant compositions are stabilized against oxidative deterioration.

Similarly also, all the compounds according to Examples 1–28 are incorporated into high impact polystyrene (Foster Grant Tuflex®, X11516) by milling at 155° in an amount of 0.1% by weight. The resultant compositions are stabilized against oxidative deterioration.

EXAMPLE 30

A stabilized mineral oil composition is prepared by incorporating into white mineral oil (U.S.P.) 0.005% by weight of the stabilizer 6 - (4 - hydroxy - 3,5 - di-t-butylanilino)-2,4-bis-(n-octylthio) - 1,3,5-triazine (Example 1) in 100 parts of total composition. The mixture is heated for 5 hours at 115° in the presence of air. A similar amount of unstabilized mineral oil is also heated for 5 hours at 115°. The stabilized mineral oil is odorless, while the unstabilized mineral oil exhibits a strong odor.

EXAMPLE 31

A stabilized gasoline is prepared by incorporating into Texas cracked gasoline having no additives therein, 0.05% by weight of the stabilizer used in Example 30. The gasoline, with and without stabilizer, is tested by the oxygen bomb induction period method (ASTM D525–55), with the result that the gasoline with stabilizer fails after 65 hours, and the blank after 4 hours.

EXAMPLE 32

Stabilized lard is prepared by incorporating in lard 0.01% by weight of the stabilizer used in Example 30. Air is bubbled through both the stabilized and the unstabilized lard for 25.5 hours at 100°. The peroxide value of the stabilized lard after this aeration is 28, while the unstabilized lard has a peroxide value of 556.

EXAMPLE 33

A stabilized high temperature lubricating oil is prepared by incorporating 2% by weight of the stabilizer used in Example 30 into the lubricant, which comprises diisoamyladipate (Rohm and Haas, Plexol 268). The stabilized composition is compared with the unstabilized lubricant by heating at 175° in the presence of air and metallic catalysts according to the test method described in Military Specification Mil–L–7808c. After 72 hours the blank contains 83% sludge and has increased very greatly in viscosity. The stabilized lubricant, however, is very slightly less viscous than originally and contains less than 1% of sludge.

EXAMPLE 34

Heptaldehyde is stabilized by incorporating into the freshly distilled aldehyde 0.01% by weight of the stabilizer used in Example 30. The stabilized heptaldehyde is shaken in an oxygen atmosphere under normal pressure at room temperature (23°). The time necessary for absorption of 30 parts by volume of oxygen in 25 parts of heptaldehyde is 11 hours for the stabilized heptaldehyde, but only ¼ hour for heptaldehyde alone.

EXAMPLE 35

Cyclohexene, freshly distilled, is stabilized by addition thereto of 0.001% by weight of the stabilizer used in Example 30. The effectiveness of this stabilizer in cyclohexene is tested by the ASTM D525–55 oxidation test with the modification that only 10 parts by volume of cyclohexene are used in each bomb. The stabilized cyclohexene runs 90 minutes to failure, while unstabilized cyclohexene fails after 35 minutes.

EXAMPLE 36

Paraffin wax is stabilized by incorporating therein 0.001% by weight of the stabilizer of Example 30. The effective stabilization is illustrated by the odor test of Example 30. After 20 hours there is no perceptible odor for the stabilized wax. The unstabilized wax, however, exhibits a distinct odor.

It is understood that in the foregoing Examples 29–36 inclusive, compositions which comprise the unstabilized material of each of Examples 29–36 are stabilized by effective amounts, e.g. from 0.001 to 1% by weight, of at least one of the following compounds:

6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-dichloro-1,3,5-triazine (Ex. 1)

6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(ethylthio)-1,3,5-triazine (Ex. 1)

6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(cyclohexylthio)-1,3,5-triazine (Ex. 1)

6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(octadecylthio)-1,3,5-triazine (Ex. 1)

6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(p-t-butylphenylthio)-1,3,5-triazine (Ex. 1)

6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(t-butylthio)-1,3,5-triazine (Ex. 1)

4,6-bis-(4-hydroxy-3,5-di-t-butylanilino)-2-n-octylthio-1,3,5-triazine (Ex. 2)

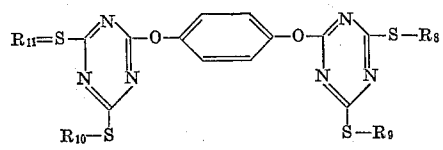
4,6-bis-(4-hydroxy-3,5-di-t-butylanilino)-2-chloro-1,3,5-triazine (Ex. 2)

6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(phenylthio)-1,3,5-triazine (Ex. 3)
6-(4-hydroxyanilino)-2,4-bis-(phenylthio)-1,3,5-triazine (Ex. 3)
6-(4-hydroxy-3,5-di-t-butylanilino)-4-n-octylthio-2-chloro-1,3,5-triazine (Ex. 4)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(anilino)-1,3,5-triazine (Ex. 5)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylamino)-1,3,5-triazine (Ex. 6)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(phenoxy)-1,3,5-triazine (Ex. 7)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(ethoxy)-1,3,5-triazine (Ex. 8)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octyloxy)-1,3,5-triazine (Ex. 9)
2,4,6-tris-(4-hydroxy-3,5-di-t-butylbenzylthio)-1,3,5-triazine (Ex. 10)
6-(2-hydroxy-3-t-butyl-5-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 11)
6-(4-hydroxy-3,5-di-isopropylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 11)
6-(4-hydroxy-3-methyl-5-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 11)
6-(4-hydroxyanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 11)
6-(4-hydroxy-3,5-dimethylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 11)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthioethylthio)-1,3,5-triazine (Ex. 12)
6-(4-hydroxy-3,5-di-t-butyl-N-benzylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 13)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(cyanoethylthio)-1,3,5-triazine (Ex. 14)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(4-t-butylphenoxy)-1,3,5-triazine (Ex. 15)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(4-t-octylphenoxy)-1,3,5-triazine (Ex. 15)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(carbo-n-dodecyloxyethylthio)-1,3,5-triazine (Ex. 15)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(carbo-n-decyloxymethylthio)-1,3,5-triazine (Ex. 15)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(carbo-n-decyloxyethylthio)-1,3,5-triazine (Ex. 15)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(carbo-n-dodecyloxymethylthio)-1,3,5-triazine (Ex. 15)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(2-carbo-n-lauryloxyphenylthio)-1,3,5-triazine (Ex. 15)
6-(4-hydroxy-5-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(2-hydroxy-5-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(2-hydroxy-5-phenylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(3-hydroxyanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(4-hydroxy-N-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(2-hydroxyanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(4-hydroxy-5-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(4-hydroxy-2,6-dimethylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(2-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(2-hydroxy-3,5-di-t-butyl-6-methylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)

6-(2-hydroxy-5-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 16)
6-(4-hydroxy-3,5-di-t-butylphenylthio)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 17)
6-(4-hydroxy-3,5-dimethylphenylthio)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 17)
6-(4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(2,3-dimethylphenylthio)-1,3,5-triazine (Ex. 17)
6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 18)
1,4-phenylene-bis-[2-oxy-4,6-bis-(n-octylthio)-1,3,5-triazine] (Ex. 18)
6-(4-hydroxyphenoxy)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 18)
6-(4-hydroxy-3,5-di-t-butylbenzylthio)-1,3,5-triazine (Ex. 19)
4,6-bis-(4-hydroxy-3,5-di-t-butylphenoxy)-2-(n-octylthio)-1,3,5-triazine (Ex. 20)
2,4-bis-(4-hydroxy-3-t-butylphenoxy)-6-(n-octylthio)-1,3,5-triazine (Ex. 20)
6-(4-hydroxy-3,5-di-t-butylanilino)-2-(n-octylthio)-4-(phenylthio)-1,3,5-triazine (Ex. 21)
6-(4-hydroxy-3,5-di-t-butylanilino)-2-(n-octylthio)-4-(4-hydroxy-3,5-di-t-butylphenoxy)-1,3,5-triazine (Ex. 21)
6-(4-hydroxy-3,5-di-t-butylbenzylthio)-2,4-bis-(ethylamino)-1,3,5-triazine (Ex. 22)
6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-bis-(phenoxy)-1,3,5-triazine (Ex. 23)
2,4,6-tris-(4-hydroxy-3,5-di-t-butylphenoxy)-1,3,5-triazine (Ex. 24)
2,4,6-tris-(4-hydroxy-3-t-butylphenoxy)-1,3,5-triazine (Ex. 24)
6-(4-hydroxy-3,5-di-t-butylphenoxy)-2,4-bis-(n-octylthioethylthio)-1,3,5-triazine (Ex. 25)
6-(4-hydroxy-3,5-di-t-butyl-N-methyl-benzylamino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 26)
6-(4-hydroxy-3,5-di-t-butylbenzyloxy)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 27)
6-(N-acetyl-4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-n-octylthio)-1,3,5-triazine (Ex. 28)
6-(N-valeroyl-4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 28)
6-(N-lauroyl-4-hydroxy-3,5-di-t-butylanilino)-2,4-bis-(n-octylthio)-1,3,5-triazine (Ex. 28)

What is claimed is:

1. A compound of the formula



wherein each of R_8,R_9, R_{10} and R_{11} is alkyl of 1 to 18 carbon atoms.

2. 1,4-phenylene-bis - [2 - oxy - 4,6 - bis-(n-octylthio)-1,3,5-triazine].

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,156,689 November 10, 1964

Martin Dexter et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 20, line 30, for "4-Hydoxy-", in italics, read -- 4-Hydroxy- --, in italics; column 21, line 30, for "absorbed" read -- adsorbed --; column 22, line 1, for "57%" read -- 37% --; line 20, for "-triazone" read -- -triazine --; column 23, line 46, for "from heptane" read -- from n-heptane --; column 24, line 41, for "produce" read -- product --; column 25, line 17, for "$C_{37}H_{63}O_2S_4N_5$" read -- $C_{37}H_{63}O_2S_4N_3$ --; column 30, line 41, for "n-octylthio)-" read -- (n-octylthio)- --.

Signed and sealed this 27th day of July 1965.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

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