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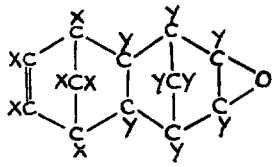
COMPLETE SPECIFICATION

Compositions comprising Halogenated Octahydro-*Endo, Endo*-Dimethano-naphthalenes and Stabiliser therefor

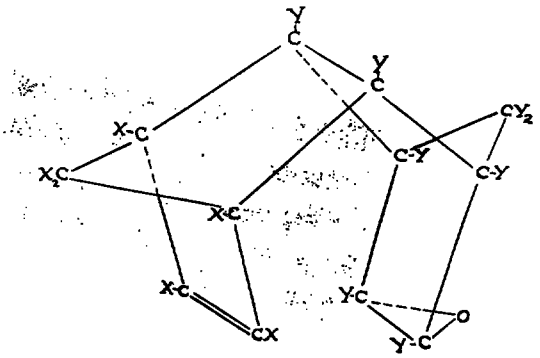
We, NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, a company organised under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel compositions comprising epoxy- and halogen-substituted octahydro - *endo,endo* - dimethanonaphthalene compounds as hereinafter defined, particularly 6,7 - epoxy - 1,2,3,4,10,10 - hexachloro-1,4,4*a*,5,6,7,8,8*a* - octahydro - 1,4,5,8 - *endo,endo*-dimethanonaphthalene, and a stabiliser therefor, and to a method of stabilising said compounds.

The epoxy- and halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene compounds used in the compositions of the invention can be represented by the planar structural formula:—



and have an *endo-endo* geometrical configuration which can be represented by the three dimensional formula:—

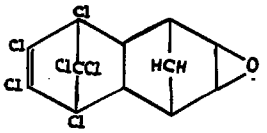


wherein each X represents a chlorine or bromine atom and each Y represents a hydrogen atom, or an alkyl, alkoxy or ester group.

Epoxy- and halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene compounds containing halogen substituents, such as 6,7-epoxy - 1,2,3,4,10,10-hexachloro-1,4,4*a*,5,6,7,8,8*a* - octahydro-1,4,5,8-*endo,endo*-dimethanonaphthalene, have recently been made known and have been found to have considerable value as insecticides. Serious difficulties have been encountered in the production and use of these compounds, however, owing to their chemical instability. These difficulties have been particularly serious with 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro - 1,4,5,8-*endo,endo*-dimethanonaphthalene. The insecticidal activity and chemical instability of these halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene com-

pounds appear to be attributable largely to their particular stereochemical configurations and to a lesser extent to the nature of the substituent groups and atoms present in the molecule. For example, under conditions where 6,7 - epoxy - 1,2,3,4,10,10-hexachloro-1,4,4*a*,5,6,7,8,8*a* - octahydro - 1,4,5,8 - *endo*, *endo*-dimethanonaphthalene undergoes irreversible, substantially complete conversion in but a few hours to products having little if any insecticidal activity, the corresponding *endo*,*exo*-isomer has been found to be substantially stable.

The compound 6,7 - epoxy-1,2,3,4,10,10-hexachloro - 1,4,4*a*,5,6,7,8,8*a* - octahydro-1,4,5,8-*endo*,*endo*-dimethanonaphthalene is the epoxide of the Diels-Alder adduct of 1,2,3,4,7,7 - hexachlorobicyclo(2.2.1) - 2,5-heptadiene and cyclopentadiene and can be represented by the planar structural formula



The geometrical configuration can be indicated by the above three-dimensional formula wherein X represents a chlorine atom and Y represents a hydrogen atom.

When an epoxy- and halogen-substituted octahydro - *endo*,*endo*-dimethanonaphthalene compound, such as 6,7-epoxy-1,2,3,4,10,10-hexachloro - 1,4,4*a*,5,6,7,8,8*a* - octahydro-1,4,5,8-*endo*,*endo*-dimethanonaphthalene, is stored at ambient temperatures or is heated for a short period it undergoes a chemical change which substantially destroys the valuable insecticidal activity of the compound. This change even occurs when the compound is in the form of crystals of a high degree of purity.

It has now been found that the chemical instability of epoxy- and halogen-substituted octahydro - *endo*,*endo*-dimethanonaphthalene compounds is due to two factors and that the stability of these compounds is substantially improved by obviating the effect of either one of these factors and still more so by obviating the effects of both factors.

One of these factors which has a profound effect on the stability of epoxy- and halogen-substituted octahydro - *endo*,*endo*-dimethanonaphthalene compounds is its acidity (or alkalinity). For example, in the presence of even a minute amount of a strong acid, 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro - 1,4,5,8-*endo*,*endo*-dimethanonaphthalene undergoes rapid and irreversible conversion to products which have little or no insecticidal activity. Traces of acid, liberated apparently by spontaneous dehydrohalogenation, tend to accelerate not only the conversion but also the liberation of further quantities of acid. As a result, the conversion of the halogen - substituted octahydro - *endo*,*endo*-dimethanonaphthalene compound into insecticidally inert materials tends to be autocatalytic. Furthermore, since the reaction is exothermic, the heat liberated accelerates the reaction still more so that it sometimes proceeds with almost explosive violence.

It has now been found that the adverse effect of acidity on the stability of halogen-substituted octahydro-*endo*,*endo*-dimethanonaphthalene compounds, particularly the solid or crystalline compounds, can be obviated by incorporating a minor proportion of an acid-binding agent.

The second factor adversely affecting the stability of epoxy- and halogen-substituted octahydro - *endo*,*endo*-dimethanonapthhalene compounds is the presence therein of traces of iron in certain chemical forms to which the dimethanonaphthalene compounds are highly susceptible. Thus, it has been found that the ferric ion acts as a rather specific and very active catalyst for the conversion of 6,7-epoxy - 1,2,3,4,10,10 - hexachloro-1,4,4*a*,5,6,7,8,8*a* - octahydro - 1,4,5,8 - *endo*,*endo* dimethanonaphthalene and related insecticidally active compounds into insecticidally inert materials. Amounts of the ferric ion even as small as 5 parts per million exert a very pronounced deleterious effect.

It has now been found that if the ferric ion is combined through coordinate valency linkages with an addendum to form a complex stable in aqueous solution, it can no longer catalyse the conversion of the epoxy- and halogen - substituted octahydro - *endo*-*endo*-dimethanonaphthalene compounds into insecticidally inert materials. The addendum may be unidentate, as in the case of the ions CN^- and SCN^- or it may be polydentate, or may contain a plurality of electron-donating groups, as is the case where the addendum is one that forms a chelated penetration complex with the ferric ion.

Accordingly, the present invention provides a composition comprising an epoxy- and halogen - substituted octahydro - *endo*,*endo*-dimethanonaphthalene compound as hereinbefore defined, and as a stabiliser therefor a minor proportion of an acid-binding agent and/or an iron complex forming agent. Advantageously, the stabiliser may be a single substance which is both an acid binding agent and an iron complex forming agent.

The acid-binding substance used as stabiliser in the compositions of the invention is suitably a base or a basic-acting substance which may be alkaline-reacting, for example, an alkali metal hydroxide or an alkaline-reacting salt of an alkali metal, such as a bicarbonate, carbonate, nitrite, basic phosphate acetate, aluminate, citrate, borate or silicate, the alkali metal carbonates and nitrites being preferred. As the alkali metal hydroxide there

may be employed the hydroxide of lithium, potassium sodium, rubidium or cæsium, potassium hydroxide and sodium hydroxide being preferred. Salts which may be advantageously employed are those whose aqueous solutions have a pH value higher than about pH 6 and preferably above pH 8, the preferred salts being the alkali metal salts of weak acids, i.e. acids having pK_a values greater than about 3. Specific salts which may be employed include salts of potassium, lithium, sodium, cæsium and rubidium and are exemplified but not limited by the following: trisodium phosphate, potassium carbonate, sodium carbonate, sodium borate, lithium carbonate, sodium citrate, potassium borate, sodium silicate, sodium aluminate, potassium acetate, and potassium basic phosphate. Bases and basic-acting compounds of the alkaline earth metals, particularly the alkaline-reacting compounds, may also be employed, including the hydroxides, oxides and basic-acting salts of calcium, magnesium, strontium and barium, for example magnesium carbonate, calcium acetate calcium hydroxide, magnesium hydroxide, lime, magnesia and calcium carbonate. The acid-binding agent used in the compositions of the invention may also be a nitrogeneous base such as urea, thiourea, guanidine or a derivative thereof, guanidine salts with weak, preferably volatile acids, such as guanidine acetate and guanidine carbonate, hexamethylenetetramine, benzyltrimethylammonium hydroxide and the various amines, such as the mono-, di- and trialkylamines, e.g. triamylamine, trioctylamine and di-2-ethylhexylamine. The preferred bases or basic-acting substances, owing to their more lasting stabilising action, are those that are essentially non-volatile at ambient temperatures, such as the inorganic salts, oxides, and hydroxides, and the normally solid nitrogenous bases and their salts.

The nitrites of nitrogenous bases have been found to be particularly effective as stabilisers in the compositions of the invention, for example, the nitrites of the primary, secondary and tertiary amines, and also of the quaternary ammonium organic bases. Of these, the nitrites of compounds containing trivalent nitrogen are in general preferred, and particularly suitable are the nitrites of secondary amines.

The nitrogenous bases, whose nitrite salts are used as stabilisers in the compositions of the invention, may be acyclic or they may contain one or more cyclic structures, for example an alicyclic or aromatic ring, or a heterocyclic ring which may or may not include the basic nitrogen atom in the ring, for example, piperidine, pyridine, morpholine, pyrrolidine and the thiazolines, or derivatives thereof containing alkyl, aryl, arylalkyl or cycloaliphatic groups as nuclear substituents.

Specific examples of organic nitrite salts are the primary amine nitrites, such as the nitrites of methylamine, ethylamine, isopropylamine, tertiary butylamine and the various amyl, hexyl, heptyl, octyl and higher primary aliphatic amines, cyclopentylamine, cyclohexylamine and alkyl substitution products of the same, such as the monomethylcyclohexyl amines, the dimethylcyclohexyl amines and the trimethylcyclohexyl amines; aromatic amines, such as aniline, para-ethyl aniline, 2,4,6-trimethyl aniline, naphthylamine and their homologues and analogues. The primary amine may contain one more basic nitrogen atom. Examples of primary amines which contain more than one basic nitrogen atom include ethylene diamine, trimethylene diamine, propylene diamine and hexamethylene diamine.

The secondary amines from which the preferred nitrite salts are prepared, include the various dialkylamines as well as the amines in which the nitrogen atom is substituted by either one or two cyclic radicals, such as an alicyclic or an aromatic radical. Suitable dialkylamines are, for example, dimethylamine, diethylamine, dipropylamine, diisopropylamine, diamylamine, dioctylamine, and their various homologues and analogues. Secondary amines in which the amino nitrogen atom is substituted by one or two cyclic groups include dicyclohexylamine, N-phenyl aniline, N-methyl aniline, the phenylene diamines, N-octyl aniline, N-methylcyclohexylamine and their various homologues and analogues. The secondary amine may contain more than the one nitrogen atom as in tetrahydropyrimidine, 2,2,4,4,6 - pentamethyl tetrahydro pyrimidine, diethylene triamine and triethylene tetramine.

Among the tertiary amines whose nitrite salts may be used in the compositions of the invention are the trialkylamines, such as trimethylamine, triethylamine, tri-isopropylamine, triamylamine and their homologues and analogues, as well as cyclic tertiaryamines, such as N,N-dimethyl aniline, N-ethyl piperidine, N-methyl dicyclohexylamine and triphenylamine. Guanidine nitrite and the nitrite salts of urea, thiourea and the N-substituted ureas and thioureas may also be used.

Because of their effectiveness, the nitrites of the secondary amines are particularly preferred and of these the salts wherein the amine residue contains from about 4 to about 32 carbon atoms are particularly preferred.

Compositions of the invention of very good stability are also obtained when the basic-acting substances employed therein are soluble alkalinous metal salts of acidic aromatic compounds having directly substituted in an aryl nucleus thereof both a hydroxyl group and an alkyl group, preferably a long-chain alkyl group, for example one containing from 5 to 20 carbon atoms. Preferred substances of this type are the alkalinous metal salts of the condensation products of formaldehyde with

alkyl phenols wherein the alkyl group is of sufficient chain length, or contains a sufficient number of carbon atoms, to impart to the salt solubility in organic solvents, such as mineral oil, benzene, toluene and acetone. The alkyl group thus may contain from about 5 up to about 20 carbon atoms, a particularly suitable chain length being about 8 carbon atoms. The term "alkalinous metal" is employed in the specification and appendent claims to include both are alkali metals, such as sodium, potassium lithium, rubidium and cæsium, and the alkaline earth metals, including magnesium, calcium, strontium, barium and zinc. The preferred salts are the salts of the light metals, particularly the metals of Group II-A of the Periodic Table. For most purposes the calcium salts are especially well suited for use as stabilisers in the compositions of the invention.

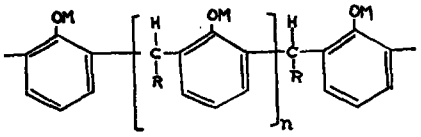
The above-mentioned condensation products of formaldehyde with alkyl phenols in general have a molecular weight in the range of from about 350 to about 2000. Suitable products can be prepared by effecting the condensation in the presence of an acid or a basic catalyst. For example, a suitable condensation product has been prepared by condensing para-octyl phenol with formaldehyde, supplied as an aqueous 37% formalin solution, in approximately 1:1 mole ratio with about 0.5 mole of lime present as the condensation catalyst.

Alkyl phenols from which the above-mentioned condensation products can be prepared include phenols having one or more alkyl groups on the aryl nucleus and at least one of the alkyl groups being a relatively long-chain alkyl group, such as one containing from 5 to 20 carbon atoms, for example, para-amyl phenol, para-hexyl phenol, para-octyl phenol, paradodecyl phenol, para-hexadecyl phenol, para-octyl cresol and para-nonyl-meta-ethyl phenol when the alkylated phenol is prepared by alkylating phenol or a substituted phenol, the long-chain alkyl group will in general occupy the para position. In order to facilitate condensation with the formaldehyde the ortho positions should in general be unsubstituted.

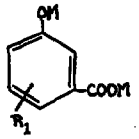
Although preferred stabilising agents are the alkalinous metal salts of the formaldehyde-alkyl phenol condensation products there may also be employed condensation products prepared equivalently, utilising other lower aliphatic aldehydes than formaldehyde, such as acetaldehyde, propionaldehyde, butyraldehyde and acrolein.

Instead of an alkalinous metal salt of an alkyl phenol-formaldehyde condensation product, there may be employed other soluble alkalinous metal salts of phenolic compounds, such as oil-soluble alkalinous metal salts of long-chain alkyl-substituted aromatic compounds having both a hydroxyl group and a second acidic group, such as a carboxylic group, substituted on the aryl nucleus. Such phenolic compounds may be prepared by alkylating phenol or a substituted phenol with an olefin, alcohol, alkyl halide or ether containing from about 5 to 20 carbon atoms and carboxylating the reaction product with carbon dioxide, utilising the well-known Kolbe reaction or modification thereof. Phenols from which such long-chain alkyl-substituted alkalinous metal phenate can be prepared by known methods include phenol itself, alkyl phenols, such as the cresols and mixtures thereof and naphthols. Particularly suitable substances for use in the compositions of the invention are alkalinous metal salicylates prepared by alkylating a phenol with olefins containing from 8 to 18 carbon atoms per molecule, carboxylating the alkylation product according to the Kolbe synthesis, and converting the resulting alkali metal salicylate to an alkaline earth metal (preferably calcium) salicylate by metathesis.

It is believed that the structure of the condensation products of the alkyl phenol with the aldehyde can be represented substantially as by the following formula:



wherein the aryl groups are substituted at least by a relatively long-chain alkyl group, R represents hydrogen or hydrocarbon according to the aldehyde reactant that was used, and M is the hydrogen equivalent of the alkalinous metal. The condensation products will generally contain a mixture of individual compounds having this probable formula wherein n ranges from 0 up to 5 or even more. The word "compound" as used in reference to these condensation products is not intended to exclude the presence of more than one molecular species. The alkalinous metal salts of salicylates can be represented by the following formula



in which R_1 represents the alkyl substituent.

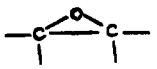
Although the alkalinous metal salts of the alkyl phenol-aldehyde condensation products or of salicylic acids constitute a preferred class of stabiliser for use in the compositions of the invention, in consideration of both effectiveness and availability, there may also be employed alkalinous metal phenates of the

relatively simpler phenols, such as the alkalinous metal phenates of such substituted phenols as para-octyl phenol, para-amyl phenol, para-dodecyl phenol, para-hexadecyl phenol and their homologues and analogues. It is particularly preferred, however, that the stabiliser be a salt possessing excess or reserve basicity; that is to say, an amount of alkalinous metal base in excess of the amount theoretically required to combine with the acidity of the acidic aromatic compound. Such excess or reserve basicity is best provided by combining lime or other alkaline earth metal hydroxide or carbonate with a solution of a long-chain alkyl salicylate, an aldehyde-alkyl phenol condensation product or equivalent phenolic material in a neutral organic solvent such as a petroleum fraction distilling in the lubricating oil range. The excess of alkalinous metal base may be present in the form of a complex with the phenolic material or in some cases it may be finely dispersed and suspended as such in the solution, for example, as a colloidal dispersion. Commercially available mineral oil solutions of the alkalinous metal salts of aldehyde-alkyl phenol condensation products, containing from 5 to 25% by weight or more of sulphate ash, have been used with particular success in the compositions of the invention.

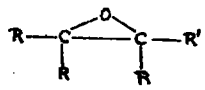
The acid-binding agent used as stabiliser in the compositions of the invention may also be an epoxy compound. Epoxy compounds which have been found very suitable for use are relatively low molecular weight compounds wherein the epoxy group is directly substituted on vicinal carbon atoms which form part of a chain of carbon atoms.

It was surprising to find that these epoxy-substituted or oxirane compounds were capable of stabilising the epoxy- and halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene compounds since the latter are themselves epoxy-substituted compounds. The fact of their instability, notwithstanding that they contain the epoxy group, would not lead one to expect that a dissimilar oxirane compound added in small amounts would lead to such a marked improvement in stability as has been realised in accordance with the invention.

The epoxy-substituted compounds which are employed as stabilisers in the compositions of the invention can be represented by the structural formula



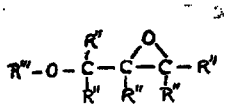
in which the free valencies depicted are each attached to hydrogen atoms or to separate univalent organic radicals. More specifically, the stabilisers can be represented by the structural formula



in which each R represents a hydrogen atom, an alkyl group or an aryl group, and R^1 represents a hydrogen atom, an alkyl group, a halogen-substituted alkyl group or an alkyl group substituted by an oxygen function such as the ether linkage (—O—) or the ester linkage (—O—CO—).

Unsubstituted epoxide compounds which can be employed are exemplified by the olefin oxides, such as ethylene oxide, propylene oxide, butylene oxide, butadiene dioxide and styrene oxide. The halogen-substituted oxirane compounds which conform to the above formula are exemplified by the epihalohydrins, specifically epichlorohydrin (1,2 - epoxy-3-chloropropane), epibromohydrin (1,2-epoxy-3-bromopropane), beta-methyl epichlorohydrin (1,2 - epoxy-3-chloro-2-methylpropane), 1,2-epoxy-4-chloro butane, 1,2-epoxy-5-chloropentane, 1-chloro-2,3-epoxy butane, 1,2-epoxy-3-chloro-2-phenyl propane, and homologous and analogous compounds containing both the *vic*-epoxy group and at least one atom of halogen (bromine or chlorine) substituted on an acyclic hydrocarbon chain.

Epoxy-substituted aliphatic compounds conforming to the above formula and containing an additional oxygen function include in particular glycidol and glycidyl ethers and glycidyl esters, e.g. the oxirane compounds conforming to the structural formula



in which each R^{11} represents a hydrogen atom or an alkyl group, preferably the hydrogen atom, and R^{111} represents an alkyl, aryl, alkaryl, alkoxyaryl, aryloxyaryl, aryloxyalkyl, alkoxyalkyl or acyl group. The alkyl groups may be unsubstituted alkyl groups or they may be alkyl groups substituted by epoxy oxygen. For example suitable glycidyl ethers are diglycidyl ether, and the various unsubstituted glycidyl alkyl ethers, such as glycidyl ethyl ether, glycidyl propyl ether, glycidyl sec-butyl ether, glycidyl t-butyl ether, and glycidyl amyl ether. Glycidyl ethers of phenols may be employed, such as glycidyl phenyl ether, glycidyl cresyl ethers, and glycidyl tolyl ether. The glycidyl compound may contain a plurality of glycidyl units as in the glycidyl ethers of glycols or polyhydric phenols. These polyfunctional glycidyl ethers are illustrated by the glycidyl ether of glycerine, ethylene glycol diglycidyl ether, resorcinol diglycidyl ether and diglycidyl ethers of such bisphenols

as 2,2-bis(*p*-hydroxyphenyl) propane, 2,2-bis-(*p* - hydroxyphenyl) butane and 1,1-bis(*p*-hydroxyphenyl) ethane. The glycidyl esters which may be employed include in particular the glycidyl esters of the lower aliphatic carboxylic acids, such as glycidyl acetate, glycidyl propionate, glycidyl butyrate, glycidyl ethoxy acetate, and glycidyl caproate.

Because of their effectiveness two particularly preferred stabilisers are phenyl glycidyl ether and chlorohydrin. Another stabilising agent which warrants particular mention is allyl glycidyl ether.

The amount of basic-acting substance required to impart a substantially improved stability need be but a minor amount based upon the weight of the epoxy- and halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene compound. In general, amounts of the basic-acting material between about 0.05% and about 25% by weight of the epoxy- and halogen-substituted octahydro-*endo,endo* - dimethanonaphthalene compound are employed, a preferred range being from about 0.5% to about 5% by weight.

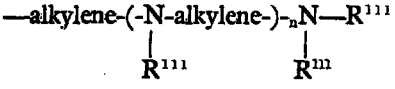
The iron complex forming agents used as stabilisers in the composition of the invention may be compounds yielding unidentate addenda such as cyanide, thiocyanate and cyanate ions. Compounds yielding such addenda include metal cyanides, such as alkali metal, particularly potassium, sodium and lithium, and alkaline earth metal cyanides, cyanates and thiocyanates.

The iron complex forming agents used as stabilisers in the compositions of the invention may also be compounds which yield polydentate addenda and are thereby capable of chelating the ferric ion, i.e. of combining with the ferric ion to form a pentatomic or hexatomic heterocyclic ring containing iron as one of the ring atoms. Stabilisers of this type which are preferably employed are compounds preferably aliphatic compounds, which contain at least two functional groups selected from the class consisting of amino, hydroxyl, and carboxyl groups, the said two functional groups being separated from each other by two or three carbon atoms which preferably are arranged in an open-chain structure and which include the carboxyl carbon atom where the functional group is the carboxyl group. Examples of such stabilisers are oxalic acid and geminate dicarboxylic acids such as malonic acid, ethylmalonic acid, diethylmalonic acid, isopropylmalonic acid, methylmalonic acid, *n*-propylmalonic acid and phenylmalonic acid. Further examples of such stabilisers are ethylenediamine and trimethylene diamine and their substitution products such as diacetonediamine, diethylenetriamine, N,N-diethylethylenediamine, triethylenetetramine, propylenediamine, tris(2 - aminoethyl)amine, 1,2,3-triaminopropane, N(3 - amino - 2-hydroxypropyl) - 2 - hydroxy - 1,3 - propanediamine, 2 - hydroxy-1,3-propanediamine, and N,N^1-bis - (3 - amino-2-hydroxypropyl)-2-hydroxy-1,3 - propanediamine. Aromatic heterocyclic polyamines having the nitrogen separated by two or three carbon atoms and in different heterocyclic rings may also be employed, such as dipyridyl and *o*-phenanthroline. Stabilisers which contain both amino and carboxyl groups are typified by the naturally occurring amino acids as well as synthetic alpha- and beta-amino acids, e.g. glycine, alanine, beta-alanine asparagine, glutamic acid, glycylglycine and phenylalanine. The acids may be used in the form of the free acid or in the partially or wholly neutralised form, such as a sodium, potassium or other alkali metal or ammonium salt. The amino acids which contain one amino group and one carboxyl group may also be employed in the form of their inner salts, or zwitter-ions. The amino acid may contain a plurality of nitrogen atoms and/or a plurality of carboxyl groups, for example ammonia diacetic acid, ammonia triacetic acid, ethylene-diamine-tetra-acetic acid, ammonia dipropionic acid, ethylenediamine dipropionic acid, 1,3-diaminocyclohexane-N,N^1-tetra-acetic acid, 3-sulphoaniline diacetic acid, aniline diacetic acid, 4-aminobenzoic acid-N,N-diacetic acid, beta-aminoethylphosphonic acid - N,N - diacetic acid, glycine-N-propionic acid, N-benzylethylenediamine triacetic acid, and methylamine-N,N-diacetic acid.

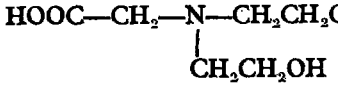
Mixtures of acid binding and iron complex forming agents may advantageously be used as stabilisers in the compositions of the invention since both factors adversely affecting the stability of the dimethanonaphthalene compounds are thereby obviated.

Especially suitable stabilisers for use in the compositions of the invention are those compounds which possess both acid-binding and iron complex forming properties and which obviate both factors adversely affecting the stability of the dimethanonaphthalene compounds. The incorporation of but a small amount, preferably not over about 5% by weight of a single stabiliser of this type in the solid epoxy- and halogen-substituted octahydro - *endo,endo* - dimethanonaphthalene compound provides compositions which are noteworthy for their stability under conditions encountered during manufacture, storage or shipment of the epoxy- and halogen-substituted octahydro - *endo,endo*-dimethanonaphthalene compound. The preferred stabilisers of this type are aliphatic polyfunctional compounds which contain amino nitrogen, the carboxyl group, and the hydroxyl group and in which the functional groups are located in beta positions to each other, or are separated from each other by two carbon atoms, inclusive of the carboxyl carbon atom. The preferred stabilisers can be defined by the structural formula $RR^1R^{11}N$ in which R repre-

sents a 2-hydroxy-alkyl group, R^1 represents a 1-carboxyalkyl or 1-metalloxyalkyl group, the metal being an alkali metal or ammonium, and R^{11} represents a hydrogen atom, or a 2-hydroxyalkyl, 1-carboxyalkyl or 1-metalloxyalkyl group (the metal being alkali metal or ammonium) or the group represented by the formula



in which alkylene denotes a 1,2-alkylene group, each R^{111} represents a hydrogen atom, or a 2-hydroxyalkyl, 1-carboxyalkyl or 1-metalloxyalkyl group, the metal being an alkali metal or ammonium, and n is O or a small integer. Illustrative preferred stabilisers which conform to this structural formula include N-2-hydroxyethyl-iminodiacetic acid, N,N^1-dihydroxyethyl - ethylenediamine-diacetic acid, N-hydroxyethyl-ethylenediamine-triacetic acid, N,N,N^1 - tri - hydroxyethyl ethylenediamine-acetic acid, and N,N^1,N^{11}-tri-hydroxyethyl-diethylenetriamine-diacetic acid. Especially desirable as the stabiliser is N,N-di-hydroxyethyl glycine which has the structural formula



which preferably is employed in the form of an alkali metal salt.

The stabilisers may be incorporated with the epoxy- and halogen-substituted octahydro-*endo,endo* - dimethanonaphthalene compound by any suitable method to provide the novel compositions of the invention. Where the epoxy- and halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene compound is a solid, such as a flaked product or a crystalline material, the stabiliser may be incorporated by dry mixing, or by blending a solution of the stabiliser, preferably in a volatile solvent, with the solid epoxy- and halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene compound and thereafter permitting the solvent to evaporate. A particularly effective method, which has been employed with advantage in the preparation of stable compositions comprising crystalline 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4,5,8-*endo,endo* - dimethanonaphthalene (known as endrin), is to add the stabiliser to a solution of the epoxy- and halogen-substituted octahydro-*endo,endo* - dimethanonaphthalene in an organic solvent for such compound and to crystallise the epoxy- and halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene compound from solution in the presence of the added stabiliser. It appears that the stabiliser is occluded in the crystals of the dimethanonaphthalene compound and that this occlusion may account for the remarkable stabilities which have been obtained by proceeding in this manner. The solvent used may be, for example, benzene, toluene, carbon tetrachloride, isooctane or other inert volatile organic solvent for the dimethanonaphthalene compound. The concentration of the dimethanonaphthalene compound in the solution may vary between about 10 and 40%, although these figures are not critical. The stabiliser is added to the solution in an amount preferably between about 0.5 and about 5% based upon the solids content of the solution. The crystallisation of the dimethanonaphthalene compound in the presence of the added stabiliser may be carried out by conventional methods.

The amount of stabiliser incorporated should in general be within the range of from about 0.05% to about 25% by weight and preferably of from 0.1 to 5% by weight, of the epoxy- and halogen-substituted octahydro-*endo,endo* - dimethanonaphthalene compound. Where the dimethanonaphthalene compound to be stabilised is technical endrin, and the stabiliser is N,N-di-2-hydroxyethyl glycine or a salt thereof, notably effective results have been obtained with amounts of the stabiliser between about 0.1 and 1% by weight of the technical endrin.

The stabilisers may be employed in solid form or in the form of solutions in water or organic solvents.

The novel, stable, solid (crystalline) compositions of this invention, consisting essentially of the epoxy- and halogen-substituted octahydro - *endo,endo* - dimethanonaphthalene compound and the stabiliser or stabilisers may be stored with notably greater safety than can the same dimethanonaphthalene compounds in the absence of such stabilising agents. The new compositions may be employed for the preparation of insecticidal dusts, wettable powders, sprays (which may be simple solutions or may be polyphase compositions, e.g., emulsions) by methods already known for the preparation of insecticidal compositions from these epoxy- and halogen-substituted octahydro-*endo,endo*-dimethanonaphthalene compounds. The insecticidal compositions prepared from the novel compositions of this invention have notably increased stabilities in compounding storage, shipment and use. The presence of the stabiliser has not been found to exert any deleterious effect on the insecticidal or other properties.

The following examples illustrate the invention.

EXAMPLE I.

To a sample of recrystallised 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4,5,8-*endo,endo* - dimethanonaphthalene there was added 5% by weight of solid sodium carbonate and the mixture was well blended. A sample of the mixture was placed

in a 22 × 175 mm. glass test tube and the test tube was suspended in a constant temperature bath maintained at 100° C. In a second like test tube suspended in the bath there was placed for comparative purposes another sample of the dimethanonaphthalene compound without stabiliser. While the two samples were maintained at 100° C., small portions of each sample were withdrawn at intervals and their content of 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro - 1,4,5,8 - *endo,endo* - dimethanonaphthalene determined by infrared analysis. The results obtained are shown in the following table and clearly demonstrate the stability of the compositions of the invention as compared with the unstabilised dimethanonaphthalene compound.

Time of Heating, Hours	Content of 6,7-Epoxy-1,2,3,4,10,10-Hexachloro-1,4,4*a*,5,6,7,8,8*a*-Octahydro-1,4,5,8-*endo,endo*-Dimethanonaphthalene, % by weight	
	6,7-Epoxy-1,2,3,4,10,10-Hexachloro-1,4,4*a*,5,6,7,8,8*a*-Octahydro-1,4,-5,8 *endo,endo*-Dimethanonaphthalene + 5% Na_2CO_3	Control
0	90.9	94.2
20	88.0	—
25	—	92.6
45	84.4	—
50	—	39.7
69	86.0	—
76	—	2.4
92	86.0	—
116	83.5	—

EXAMPLE II.

To a sample of technical endrin containing 89.3% by weight 6,7-epoxy-1,2,3,4,10,10-hexachloro - 1,4,4*a*,5,6,7,8,8*a* - octahydro-1,4,5,8-*endo,endo*-dimethanonaphthalene and 8 parts per million of iron, there was added by dry mixing 10% by weight of potassium hydroxide. The potassium hydroxide was added to the solid endrin in the form of a methanol solution and after mixing the methanol was evaporated. The sample then was placed in a one-half pint vacuum jacketed thermos liner and a sensitive thermocouple was inserted below the surface of the sample. The sample was heated to 75° C. by immersing the container in a constant temperature bath and the temperature of the sample was measured through the thermocouple by means of a calibrated recording potentiometer. There was no noticeable evolution of heat within the sample. The sample was maintained at 75° C. for 270 hours. At the end of this time the content of 6,7-epoxy-1,2,3,4,10,10-hexachloro-1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4,5,8-*endo,endo*-dimethanonaphthalene (determined by infrared analysis) was 70.9% by weight.

When the experiment was repeated for comparative purposes using a further quantity of the same lot of endrin but without addition of stabiliser, the temperature of the sample began to rise spontaneously and rapidly once the sample had been heated to 65° to 75° C. and continued to rise until a maximum temperature of from 260° to 280° C. was attained. By infrared analysis the content of 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4,5,8-*endo,endo* - dimethanonaphthalene was found to have decreased to below 5% after 6 to 7 hours' heating.

EXAMPLE III.

A solution of technical endrin in benzene, containing about 20% by weight of technical endrin, was washed by shaking with water and the separated organic phase then was filtered through cotton to remove remaining traces of water. The filtrate contained less than about 2 parts per million of iron based on the solids

content. To a portion of the filtered benzene solution there was added 1% by weight of thiourea based upon the solids content of the solution. The benzene was then removed by evaporation to obtain solid technical endrin stabilised by thiourea intimately admixed therewith.

A portion of the stabilised solid endrin was stored in a glass container at 100° C. The sample was analysed periodically during the time of storage at 100° C., utilising the absorption spectrum in the infrared to determine the content of 1,8,9,10,11,11-hexachloropentacyclo - (6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$)dodecan - 5-one in the sample. This latter product is a primary decomposition product of endrin. Its concentration in the sample affords a convenient measure of the extent of decomposition of the endrin.

After 11 days storage of the stabilised solid technical endrin at 100° C. the content of this decomposition product was found to be 3%.

For purposes of comparison, a second portion of solid technical endrin was prepared by the same method except that addition of the stabiliser was omitted. Upon heating at 100° C. the content of 1,8,9,10,11,11-hexachloropentacyclo(6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$)dodecan - 5-one in this unstabilised sample rose to 8.8% at the end of 24 hours' heating and to 72.1% at the end of 48 hours' heating.

Example IV.

This example illustrates the use of urea as the stabiliser.

In one series of tests there were employed further portions of the washed and filtered benzene solution of technical endrin described in the preceding example (solution A). In another test there was employed a solution of technical endrin in benzene, the washing and filtration being omitted (solution B). The iron content of solution B was about 20 parts per million based on the solids content.

Urea was added to each of the test solutions in the amounts shown in the following table. The solutions were then evaporated to dryness and the stability of the solid technical endrin was determined as in the preceding example. The results are shown in the following table:

Amount of Urea, % wt., Based on the Technical Endrin	Solution	Time of Heating at 100°C.	% Decomposition of Endrin
none	A	24 hours	8.8*)
none	A	48 hours	72.1*)
none	B	22 hours	100
1	A	25 days	3*)
0.5	B	22 days	3*)

*) Per cent conversion to 1,8,9,10,11,11-hexachloropentacyclo (6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$) dodecan-5-one as determined by infrared analysis.

Example V.

To a sample of the endrin employed in Example II there was added 10% by weight of urea and the mixture was thoroughly blended by dry mixing. When tested in the manner described in Example II there was no noticeable evolution of heat. The heating was continued until the content of 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro-1,4,5,8-*endo*,*endo* - dimethanonaphthalene in the sample had decreased to 37.8% by weight. This required 315 hours. Without addition of urea, the content of 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro - 1,4,5,8 - *endo*,*endo* - dimethanonaphthalene in this lot of endrin fell to less than 5% in 6 to 7 hours.

Example VI.

To a further portion of the technical endrin employed in Example II there was added 5% by weight of potassium thiocyanate as stabiliser. The stabiliser was incorporated by dissolving the endrin in acetone, adding the potassium thiocyanate to the solution and then evaporating the solvent. Upon heating the stabilised sample at 75° C. and removing samples periodically for infrared analysis, the results shown in the following table were obtained: they show clearly the marked stability of this composition.

Time of Heating, Hours	Content of 6,7-Epoxy-1,2,3,4,10,10-Hexachloro-1,4,4*a*,5,6,7,8,8*a*-Octahydro-1,4,5,8-*endo*,*endo*-Dimethanonaphthalene, % by weight
0	84.7
168	80.9
400	84.1
600	71.5
900	70.3

EXAMPLE VII.

To a further portion of the washed and filtered benzene solution of endrin described in Example III there was added as the stabiliser 1% by weight of potassium thiocyanate based upon the solids content of the solution. The solution was then evaporated to dryness and the stabilised solid technical endrin, containing the added potassium thiocyanate as stabiliser, was heated at 100° C. until the content of 1,8,9,10,11,11-hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan - 5-one, determined by infrared analysis, had risen to 3% by weight. This required 6 days' heating. In a control sample containing no added stabiliser, the content of 1,8,9,10,11,11-hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan-5-one rose to 8.8% after only 24 hours' heating at 100° C. showing, by comparison with the stabilised sample, the marked improvement that is provided by the present invention.

EXAMPLE VIII.

The technical endrin used in this experiment had a purity of about 95%. When heated at 100° C. a sample decomposed spontaneously to carbonaceous materials within 15 minutes. A further sample, however, was successfully stabilised using the tetrasodium salt of ethylene-diaminetetra-acetic acid. The stabiliser was incorporated by dissolving the technical endrin in benzene and adding to the solution about 0.6% by weight of a 27% by weight aqueous solution of the tetrasodium salt of ethylenediaminetetra-acetic acid, based on the technical endrin. The resulting mixture was washed with water, the phases were separated, and the stabilised endrin was recovered by evaporation of the benzene from the separated organic phase. A sample of the stabilised endrin, which contained residual amounts of the stabiliser not removed by the water washing, was heated at 100° C. There was no visible evidence of decomposition. After 5 days at 100° C., the content of 1,8,9,10,11,11-hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan-5-one in the sample, as measured by infrared spectroscopy, had not exceeded 3%, evidencing the markedly enhanced stability that was obtained.

EXAMPLE IX.

This example describes two additional experiments utilising the tetrasodium salt of ethylenediamine tetra-acetic acid as the stabilising agent. Two different samples of technical endrin were used. To separate solutions of the respective samples in benzene there was added an aqueous 27% by weight solution of the stabiliser and the benzene was then removed by evaporation. The resulting stabilised solid samples were heated at 100° C. and the content of 1,8,9,10,11,11-hexachloropentacyclo-(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan-5-one was determined periodically by infrared spectroscopy. The time required for the content of this conversion product to reach 3% was noted and these results together with the results obtained in control tests in which no stabiliser was present are shown in the following table:

Technical Endrin Sample	Fe Content ppm.	Amount of Stabilizer Added (27% wt. aq. solution)	Stability Days*)
I	<2	0.6	33
I	<2	none	<1
II	20	1.0	19
II	20	none	<1

*) Time at 100°C. when the content of 1,8.9,10,-11,11-hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.-0^{4,10})dodecan-5-one had risen to 3% by weight.

EXAMPLE X.

To a further sample of the technical endrin employed in Example VIII there was added 1% by weight, based upon the endrin, of the sodium salt of N,N-di-2-hydroxyethyl glycine. The stabiliser was added by the method used in Example VIII. The decomposition time of this sample, determined by the method employed in Example VIII, was 41 days.

EXAMPLE XI.

To a solution of endrin in benzene there was added 0.4% by weight, based upon the weight of endrin, of the sodium salt of N,N-di-2-hydroxyethyl glycine. The resulting mixture was diluted with water, the phases were separated, the organic phase filtered through cotton, an additional 0.6% by weight, based upon the endrin, of N,N-di-2-hydroxyethyl glycine was added to the filtrate, and the benzene was removed by evaporation. Upon heating the stabilised endrin at 100° C. there was no observed decomposition after 31 days. Seventy days' heating at 100° C. was required before the content of 1,8,9,10,11,11-hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan-5-one had risen to 3% by weight. The same lot of endrin, without stabiliser, spontaneously decomposed to carbonaceous material within 15 minutes at 100° C.

EXAMPLE XII.

A solution of endrin in benzene was prepared by epoxidation of 1,2,3,4,10,10-hexachloro - 1,4,4*a*,5,8,8*a* - hexahydro - 1,4,5,8-*endo*,*endo*-dimethanonaphthalene in benzene solution using peracetic acid as the epoxidising agent. Two aliquots of the solution thus prepared were taken. To the first aliquot there was added 0.6% by weight, based upon the solids content of the solution, of the sodium salt of di-2-hydroxyethyl glycine. The resulting solution was then diluted with water, the organic phase was separated by centrifuging, benzene was stripped from the solution and the endrin was crystallised from the resulting concentrated solution, the crystals being separated on a basket centrifuge. The crystalline product analysed about 90% by weight 6,7-epoxy-1,2,3,4,10,10 - hexachloro-1,4,4,4*a*,5,6,7,8,8*a*-octahydro - 1,4,5,8-*endo*,*endo* - dimethanonaphthalene.

A second aliquot of the same solution was treated in an identical manner except that addition of the N,N-di-2-hydroxyethyl glycine was omitted.

A portion of the first lot of crystals, containing the stabiliser, was found to contain less than 3% of 1,8,9,10,11,11-hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan - 5-one after seven months' storage at room temperature. A second portion of the same lot of crystals contained less than 3% of 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})-dodecan-5-one after three weeks' storage at 100° C., while a third portion stored at 75° C. was stable, as judged by the same criterion, for 124 days. In none of these portions was there visible evidence of decomposition or loss of biocidal activity within the limits of sensitivity of biological assay. The second lot of crystals, containing no stabiliser, contained 60.7% by weight of 6,7-epoxy-1,2,3,4,10,10-hexachloro - 1,4,4*a*,5,6,7,8,8*a* - octahydro-1,4,5,8 - *endo*,*endo* - dimethanonaphthalene after three weeks' storage at room temperature and spontaneously completely decomposed upon heating for 15 hours at 75° C. or for one hour at 100° C.

EXAMPLE XIII.

To approximately 20% by weight solutions of different lots of technical endrin in benzene there was added guanidine carbonate in the amounts shown in the following table. The benzene was then evaporated from the solutions. The resulting samples of technical endrin containing the guanidine carbonate intimately dispersed throughout were heated

at 100° C. and the content of 1,8,9,10,11,11-hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10}) dodecan-5-one was determined periodically by infrared spectroscopy as a measure of the stability. The results obtained together with the results of control experiments (no stabiliser added) are shown in the following table:

Endrin Sample			Stability	
Designation	Fe content, (parts per million)	Guanidine Carbonate, % wt.	Duration of Heating at 100°C., Days	Content of 1,8,9,10,11-11-Hexachloropentacyclo-(6.2.1.1^{3,6}.0^{2,7}.0^{4,10}) dodecan-5-one at Termination of Heating, % wt.
A	ca. 2	0.1	42	3
A	ca. 2	0.5	73	3
A	ca. 2	1.0	> 100	3
B	20	0.6	23	3
A	ca. 2	none	1	8.8
B	20	none	<1	*)

*) Complete decomposition.

EXAMPLE XIV.

A sample of the technical endrin identified in the preceding sample as Sample A was stabilised by incorporating 1% by weight Na_2CO_3 by the method described in the preceding example. It required 28 days' heating at 100° C. to increase the content of 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan-5-one to 3% by weight, compared to the content of 8.8% that resulted upon heating an unstabilised sample of the same lot of technical endrin for 24 hours.

EXAMPLE XV.

In a typical case in which endrin was stabilised with a nitrite salt according to the invention, there was prepared a solution of endrin in benzene containing approximately 20% by weight of endrin. The solution was washed with water, the phases were separated, and the organic phase was filtered through cotton to remove any remaining traces of water. To this solution there was added 1% by weight of diisopropyl ammonium nitrite, based upon the weight of the endrin contained in the solution. The benzene was then removed by evaporation leaving a solid, mostly crystalline residue consisting of the stabilised technical endrin. A sample of the stabilised endrin was stored at 100° C. in a glass container. The sample was analysed periodically during the storage at 100° C., utilising the absorption spectrum in the infrared to determine the content of the decomposition product 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan-5-one. After 18 days' storage at 100° C. the endrin stabilised by diisopropyl ammonium nitrite was found to contain 3% by weight of this decomposition product.

For purposes of comparison, a second portion of solid technical endrin was prepared by the same method except that the addition of the nitrite salt was omitted. Upon heating at 100° C. the content of the above decomposition product in this unstabilised sample rose to over 70% in 48 hours. Comparison of the two runs shows clearly the improved stabilities that are obtained in accordance with the practice of the invention.

EXAMPLE XVI.

An oil-soluble calcium salt of a formaldehyde-alkyl phenol condensation product produced by condensing para-octyl phenol and formaldehyde in the presence of an aqueous slurry of lime, was dissolved in a light petroleum base lubricating oil. A benzene solution of endrin containing about 20% by weight endrin was washed with water and then dried. To the benzene solution there was added about 0.5% by weight, based upon the weight of endrin, of the calcium phenolate in the form of the solution in mineral oil. The benzene

then was removed by evaporation to leave a solid, mostly crystalline residue consisting of the stabilised technical endrin. A portion of this solid was stored at 100° C. and analysed periodically by means of the infrared absorption to determine the length of time required for the content of the decomposition product, 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$)dodecan-5-one, in the sample to reach 3% by weight.

With the stabilised sample of endrin prepared as above it required 45 days' heating at 100° C. until the content of the decomposition product increased to 3%. A second sample, prepared in the identical manner, but with 1% by weight of stabiliser, required 57 days' heating at 100° C. for the content of the decomposition product to rise to 3% by weight. When the experiments were repeated, but without adding any stabiliser, the content of the decomposition product rose to over 72% upon heating for 48 hours at 100° C.

EXAMPLE XVII.

To a sample of technical endrin there was added about 2% by weight of epichlorohydrin. The epichlorohydrin was incorporated by dissolving the technical endrin in acetone, adding the epichlorohydrin to the acetone solution and then evaporating the acetone. A sample of the resulting solid stabilised endrin was placed in a 22 × 175 millimetres glass test tube and the test tube was suspended in a constant temperature bath maintained at 75° C. To a second test tube suspended in the bath there was added a sample of solid endrin from the same lot which had been treated identically except that addition of the epichlorohydrin was omitted. With this particular preparation of technical endrin decomposition was evidenced by a rapid rise in the temperature of the sample upon or after heating to the bath temperature. Stability was measured by observing the time that elapsed between placing the sample in the bath and the onset of this rise in temperature. For the control sample 3 hours 45 minutes elapsed. The stabilised sample remained 12 hours 20 minutes under the conditions of this accelerated test. In terms of time, therefore, the incorporation of the epichlorohydrin increased the stability of the technical endrin by 229%.

EXAMPLE XVIII.

A solution of technical endrin in benzene, containing about 20% by weight of technical endrin, was washed by shaking with water and the separated organic phase then was filtered through cotton to remove remaining traces of water. To a portion of the filtered solution there was added 0.6% by weight of phenyl glycidyl ether, based upon the amount of endrin in the solution. The benzene was then removed by evaporation to obtain solid (crystalline) technical endrin stabilised by the phenyl glycidyl ether intimately mixed therewith.

A portion of the stabilised endrin was stored in a glass container at 100° C. The sample was analysed periodically during the time of storage at 100° C., utilising the absorption spectrum in the infrared to determine the content of the decomposition product, 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$)dodecan-5-one in the sample.

After 14 days' storage at 100° C. the endrin stabilised by phenyl glycidyl ether was found to contain 3% by weight of this decomposition product.

For the purposes of comparison, a second portion of solid technical endrin was prepared by the same method except that the addition of the phenyl glycidyl ether was omitted. Upon heating at 100° C. the content of the above decomposition product in this sample without stabiliser rose to over 70% in 48 hours.

EXAMPLE XIX.

The experiment described in the preceding example was repeated substituting allyl glycidyl ether for the phenyl glycidyl ether. Upon heating the stabilised endrin at 100° C. the content of 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$) dodecan - 5-one rose to 3% after 5 days' heating, compared to the more than 70% content produced by 48 hours' heating of the endrin without stabiliser.

EXAMPLE XX.

The method of incorporation illustrated in the preceding two examples was employed with epichlorohydrin as the stabilising agent, using a further sample of the same technical endrin that was used in these examples. Upon heating at 100° C. it required 6 days for the content of 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$)dodecan - 5 - one to increase to 3% by weight, compared to the content of more than 70% that resulted upon heating a control sample of the unstabilised endrin at 100° C. for 48 hours.

What we claim is:—

1. A composition comprising an epoxy and halogen - substituted octahydro - *endo,endo*-dimethanonaphthalene compound as herein before defined and, as stabiliser therefor, a minor proportion of an acid binding agent and/or an iron complex forming agent.

2. A composition as claimed in claim 1, wherein said compound is 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a* - octahydro - 1,4,5,8 - *endo,endo* - dimethanonaphthalene.

3. A composition as claimed in claim 1 or 2, wherein the stabiliser is present in an amount of from 0.05 to 25% by weight.

4. A composition as claimed in any one of the preceding claims, wherein the acid binding agent is a hydroxide or basic acting salt of an alkali metal or a hydroxide, oxide or basic acting salt of an alkaline earth metal.

then was removed by evaporation to leave a solid, mostly crystalline residue consisting of the stabilised technical endrin. A portion of this solid was stored at 100° C. and analysed periodically by means of the infrared absorption to determine the length of time required for the content of the decomposition product, 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.$1^{3,6}$.$0^{2,7}$.$0^{4,10}$)dodecan-5-one, in the sample to reach 3% by weight.

With the stabilised sample of endrin prepared as above it required 45 days' heating at 100° C. until the content of the decomposition product increased to 3%. A second sample, prepared in the identical manner, but with 1% by weight of stabiliser, required 57 days' heating at 100° C. for the content of the decomposition product to rise to 3% by weight. When the experiments were repeated, but without adding any stabiliser, the content of the decomposition product rose to over 72% upon heating for 48 hours at 100° C.

EXAMPLE XVII.

To a sample of technical endrin there was added about 2% by weight of epichlorohydrin. The epichlorohydrin was incorporated by dissolving the technical endrin in acetone, adding the epichlorohydrin to the acetone solution and then evaporating the acetone. A sample of the resulting solid stabilised endrin was placed in a 22 × 175 millimetres glass test tube and the test tube was suspended in a constant temperature bath maintained at 75° C. To a second test tube suspended in the bath there was added a sample of solid endrin from the same lot which had been treated identically except that addition of the epichlorohydrin was omitted. With this particular preparation of technical endrin decomposition was evidenced by a rapid rise in the temperature of the sample upon or after heating to the bath temperature. Stability was measured by observing the time that elapsed between placing the sample in the bath and the onset of this rise in temperature. For the control sample 3 hours 45 minutes elapsed. The stabilised sample remained 12 hours 20 minutes under the conditions of this accelerated test. In terms of time, therefore, the incorporation of the epichlorohydrin increased the stability of the technical endrin by 229%.

EXAMPLE XVIII.

A solution of technical endrin in benzene, containing about 20% by weight of technical endrin, was washed by shaking with water and the separated organic phase then was filtered through cotton to remove remaining traces of water. To a portion of the filtered solution there was added 0.6% by weight of phenyl glycidyl ether, based upon the amount of endrin in the solution. The benzene was then removed by evaporation to obtain solid (crystalline) technical endrin stabilised by the phenyl glycidyl ether intimately mixed therewith.

A portion of the stabilised endrin was stored in a glass container at 100° C. The sample was analysed periodically during the time of storage at 100° C., utilising the absorption spectrum in the infrared to determine the content of the decomposition product, 1,8,9, 10,11,11 - hexachloropentacyclo(6.2.1.$1^{3,6}$. $0^{2,7}$.$0^{4,10}$)dodecan-5-one in the sample.

After 14 days' storage at 100° C. the endrin stabilised by phenyl glycidyl ether was found to contain 3% by weight of this decomposition product.

For the purposes of comparison, a second portion of solid technical endrin was prepared by the same method except that the addition of the phenyl glycidyl ether was omitted. Upon heating at 100° C. the content of the above decomposition product in this sample without stabiliser rose to over 70% in 48 hours.

EXAMPLE XIX.

The experiment described in the preceding example was repeated substituting allyl glycidyl ether for the phenyl glycidyl ether. Upon heating the stabilised endrin at 100° C. the content of 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10}) dodecan - 5-one rose to 3% after 5 days' heating, compared to the more than 70% content produced by 48 hours' heating of the endrin without stabiliser.

EXAMPLE XX.

The method of incorporation illustrated in the preceding two examples was employed with epichlorohydrin as the stabilising agent, using a further sample of the same technical endrin that was used in these examples. Upon heating at 100° C. it required 6 days for the content of 1,8,9,10,11,11 - hexachloropentacyclo(6.2.1.1^{3,6}.0^{2,7}.0^{4,10})dodecan - 5 - one to increase to 3% by weight, compared to the content of more than 70% that resulted upon heating a control sample of the unstabilised endrin at 100° C. for 48 hours.

What we claim is:—

1. A composition comprising an epoxy and halogen - substituted octahydro - *endo,endo*-dimethanonaphthalene compound as herein before defined and, as stabiliser therefor, a minor proportion of an acid binding agent and/or an iron complex forming agent.

2. A composition as claimed in claim 1, wherein said compound is 6,7-epoxy-1,2,3,4, 10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a* - octahydro - 1,4,5,8 - *endo,endo* - dimethanonaphthalene.

3. A composition as claimed in claim 1 or 2, wherein the stabiliser is present in an amount of from 0.05 to 25% by weight.

4. A composition as claimed in any one of the preceding claims, wherein the acid binding agent is a hydroxide or basic acting salt of an alkali metal or a hydroxide, oxide or basic acting salt of an alkaline earth metal.

* C L M S *

5. A composition as claimed in claim 4, wherein the acid binding agent is an alkali metal carbonate or nitrite.

6. A composition as claimed in claim 1, 2 or 3, wherein the acid binding agent is a nitrogenous base.

7. A composition as claimed in claim 6, wherein the nitrogenous base is used in the form of a nitrite salt.

8. A composition as claimed in any one of claims 1, 2 or 3, wherein the acid binding agent is a salt of an aromatic compound having a hydroxyl group and an alkyl group substituted in the nucleus and an alkalinous metal as hereinbefore defined.

9. A composition as claimed in claim 11, wherein the alkyl group contains from 5 to 20 carbon atoms.

10. A composition as claimed in claim 8 or 9, wherein the acid binding agent is an alkalinous metal alkyl phenate.

11. A composition as claimed in claim 8 or 9, wherein the acid binding agent is an alkalinous metal salt of a hydroxy aromatic carboxylic acid.

12. A composition as claimed in claim 8 or 9, wherein the acid binding agent is an alkalinous metal salt of the condensation product of an alkyl phenol and a lower aliphatic aldehyde.

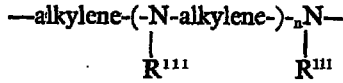
13. A composition as claimed in claim 1, 2 or 3, wherein the acid binding agent is a compound containing an epoxy group substituted on vicinal carbon atoms of a carbon chain.

14. A composition as claimed in claim 13, wherein the epoxy compound is an epihalohydrin, glycidyl ether, phenyl glycidyl ether or allyl glycidyl ether.

15. A composition as claimed in any one of claims 1 to 14, wherein the iron complex forming agent is one which chelates the ferric ion.

16. A composition as claimed in claim 15, wherein the chelating agent is a compound containing at least two functional groups selected from amino, hydroxyl and carboxyl groups, said groups being separated from each other by two or three carbon atoms, including the carbon atom of the carboxyl group when present.

17. A composition as claimed in claim 16, wherein the stabiliser is a compound of the formula $RR^1R^{11}N$, wherein R represents a 2-hydroxyalkyl group, R^1 represents a 1-carboxyalkyl or 1-metalloxyalkyl group, the metal being alkali metal or ammonium, and R^{11} represents a hydrogen atom, or a 2-hydroxyalkyl, 1-carboxyalkyl or 1-metalloxyalkyl group, the metal being alkali metal or ammonium, or a group represented by the formula



wherein alkylene denotes a 1,2-alkylene group, and each R^{111} represents a hydrogen atom, a 2-hydroxyalkyl group or a group represented by R^1 and n is zero or a low integer.

18. A composition as claimed in claim 17, wherein the stabiliser is N,N-dihydroxyethyl glycine or an alkali metal salt thereof.

19. Compositions comprising 6,7-epoxy-1,2,3,4,10,10 - hexachloro - 1,4,4*a*,5,6,7,8,8*a*-octahydro - 1,4,5,8 - *endo*,*endo* - dimethanonaphthalene and a stabiliser substantially as hereinbefore described with reference to the Examples.

20. A method of stabilising epoxy- and halogen - substituted octahydro - dimethanonaphthalene compounds as hereinbefore defined which comprises incorporating at least one stabiliser claimed in any one of claims 1 to 18.

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